CHAPTER 10

Classification of dyeing and printing auxiliaries by function

Terence M Baldwinson

10.1 ELECTROLYTES AND pH CONTROL

The simplest auxiliaries of all are the neutral electrolytes such as sodium chloride and sodium sulphate. These are used in large quantities for dyeing cellulosic materials with direct or reactive dyes and wool with anionic dyes. The major effect of electrolytes on dyes of this type is to increase the degree of aggregation of the dye anions in solution by the common-ion effect, the degree of aggregation varying markedly with dye structure (section 3.1.2). The electrolyte suppresses ionisation of the dye in solution, thereby effectively reducing its solubility in the dyebath and modifying the equilibrium in favour of movement of dye anions from the solution into the fibre. The objective, of course, is to use the optimum amount of salt to give the required rate and degree of exhaustion of the dyebath; too little electrolyte is ineffective whilst too much may aggregate the dye to an extent that may inhibit its diffusion into the fibre, thus giving a tendency to surface coloration only, or even bringing about precipitation. The aggregating effect of electrolytes varies, sodium chloride having a stronger effect than sodium sulphate, but it is generally decreased by raising the temperature.

This effect, which we may term the ‘salting-on’ effect, is the result of interactions between electrolyte and dye. However, there may also be interactions between electrolyte and fibre, giving rise to a positive levelling action as electrolyte anions compete with dye anions for the cationic sites in the fibre. Ionic surfactants (Table 8.1) can of course be regarded as electrolytes, although by hydrophobic interactions they tend to form micelles in concentrated solution and hence may be referred to as colloidal electrolytes. In some respects their levelling action is analogous to that of simple inorganic electrolytes – that is, ionic hydrophobes compete with dye ions of similar charge for sites of opposite charge in the fibre.

Electrolytes are used to promote the exhaustion of direct or reactive dyes on cellulosic fibres; they may also be similarly used with vat or sulphur dyes in their leuco forms. In the case of anionic dyes on wool or nylon, however, their role is different as they are used to facilitate levelling rather than exhaustion. In these cases, addition of electrolyte decreases dye uptake due to the competitive absorption of inorganic anions by the fibre and a decrease in ionic attraction between dye and fibre. In most discussions of the effect of electrolyte on dye sorption, attention is given only to the ionic aspects of interaction. In most cases, this does not create a problem and so most adsorption isotherms of water-soluble dyes are interpreted on the basis of Langmuir or Donnan ionic interactions only. There are, however, some observed cases of apparently anomalous behaviour of dyes with respect to electrolytes that cannot be explained by ionic interactions alone.

The fact is, ionic interaction between dyes, fibres and electrolytes is only part of the story. As Yang [1] has pointed out, hydrophobic interactions also need to be taken into consideration. Whilst this has been accepted for many years in relation to dye–fibre interactions, the extension of the concept to interactions involving neutral electrolytes is novel.

Yang quotes as one of several examples the fact that sodium chloride has a stronger effect than sodium sulphate on decreasing the uptake of CI Acid Red 1 by nylon, which cannot be explained on the basis of ionic interaction alone. It can, however, be explained in terms of the effect of the electrolytes on hydrophobic interaction, the same explanation also being applied to other examples. A lyotropic series is used to explain the effectiveness of hydrophobic interactions, which always coexist with ionic interactions. A semi-quantitative representation of the lyotropic series is shown in Figure 10.1. In such a series, neutral ions have little influence on hydrophobic interactions. Kosmotropes increase hydrophobic interaction and therefore tend to increase dye adsorption, whilst chaotropes decrease both hydrophobic interaction and dye adsorption. Thus, in the example quoted above of CI Acid Red 1 on nylon, sodium chloride has a stronger effect on decreasing dye adsorption than the more kosmotropic sodium sulphate. On this basis, Yang has introduced a modified Donnan model that quantitatively predicts the various effects of electrolytes on either decreasing or increasing dye adsorption.

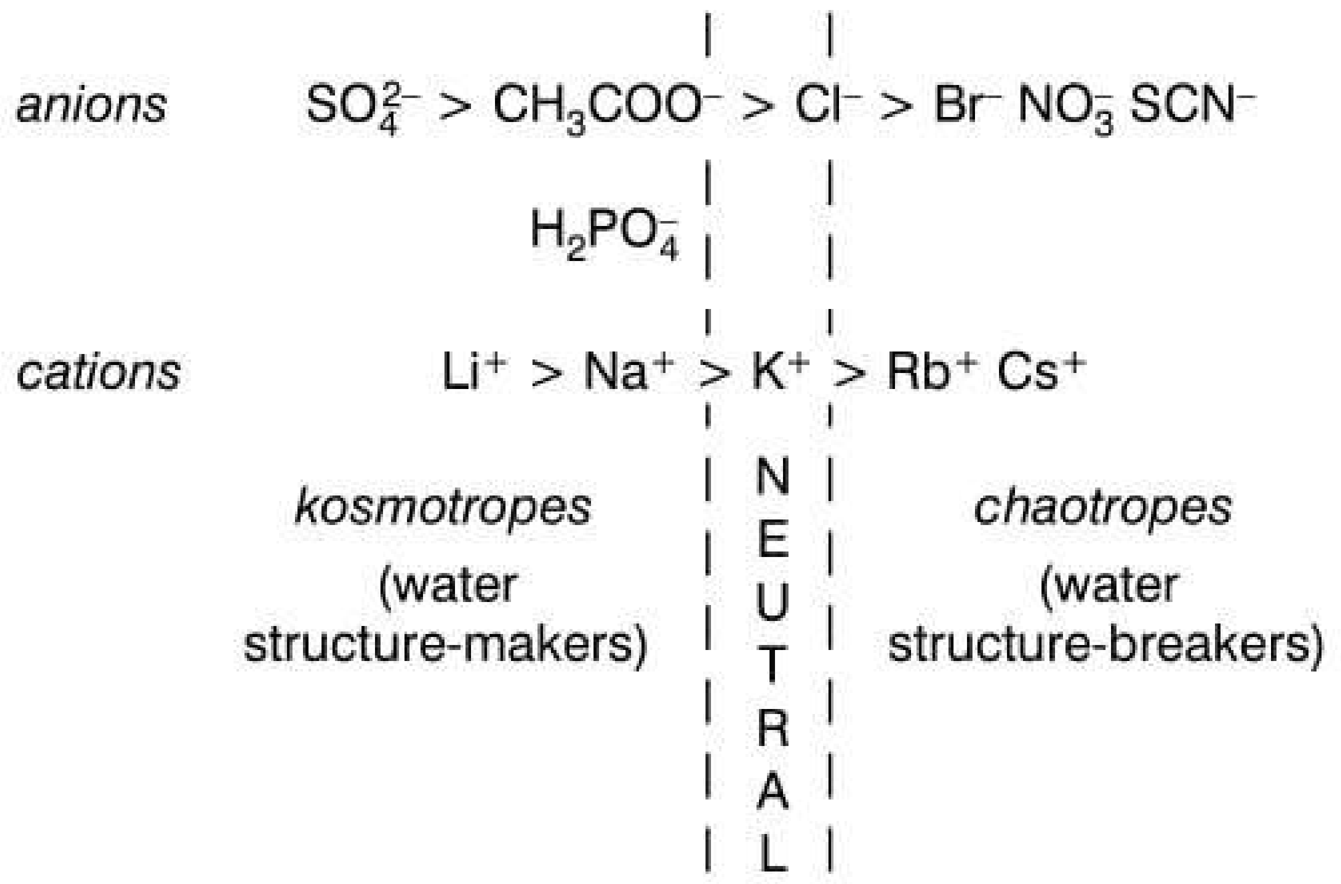
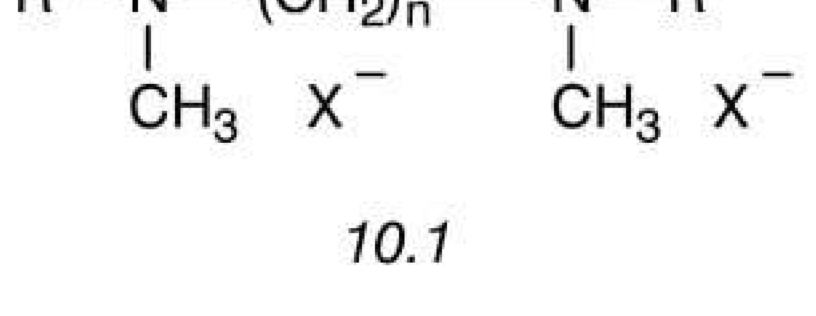


Figure 10.1 Lyotropic series: effectiveness of hydrophobic interactions [1]



$$R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-(CH_2)_n-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-R \quad X^- \quad X^-$$

10.1

n = 3–12
R = n-propyl, n-butyl or benzyl
X = halide, e.g. bromide

Rather more complex compounds that are currently being researched are the bolaform electrolytes [2–4]. Bolaform electrolytes are organic compounds possessing two cationic or two anionic groups linked by a flexible hydrocarbon chain; the terminal groups may be aliphatic or aromatic (e.g. as in 10.1). Their interaction with sulphonated monoazo dyes in the presence of poly(vinylpyrrolidone) as substrate has been studied in detail. However, it remains to be seen what commercial developments take place with these interesting compounds. It seems likely that they would be used in complex formation rather than in the more traditional roles associated with electrolytes in textile processing.

In whatever role electrolytes are used, their effects on the environment need to be considered, particularly when discharged to effluent. High salt loading is undesirable in waste water and sodium sulphate in particular causes corrosion of concrete pipes. It thus makes sense to choose electrolytes carefully and to use the minimum amounts consistent with obtaining the desired effects. Automatic dosing is helpful in this respect. The use of shorter liquor ratios has been promoted on the grounds of economy (less water to heat and less liquor to treat subsequently). However, it should not be overlooked that when dyeing in a short liquor more rinsing baths are required to give the same residual concentration as at a longer liquor ratio. Weible [5] has demonstrated this effect for the washing-off of reactive dyes from fabric having a retention capacity of 4 l/kg using 60 g/l of electrolyte. At a liquor ratio of 20:1, some 12 g/l and 2.4 g/l of electrolyte are found in the first and second rinses respectively. These rise to 30 g/l and 15 g/l when a liquor ratio of 8:1 is used. Equation 10.1 was used by Weible to calculate these concentrations.

$$C_s = \frac{cR}{FV} \text{ (g/l)} \tag{10.1}$$

C_s = concentration in rinsing bath (g/l)
c = concentration in treatment bath (g/l)
FV = liquor ratio (l/kg)
R = retention capacity of goods (l/kg)

More detailed information on attempts to reduce the impact of electrolytes on the environment is given under the individual dye classes discussed in Chapter 12.

The great majority of coloration processes demand some control over the treatment pH, which varies from strongly alkaline in the case of vat, sulphur or reactive dyes, to strongly acidic for levelling acid dyes. The concept of pH is a familiar one; its theoretical derivation can be found in all standard physical chemistry textbooks and has been particularly well explained in relation to coloration processes [6,7] both in theory and in practice. We are concerned here essentially with the chemistry of the products used to control pH and their mode of action. It has been stated [7] that: ‘Unfortunately, pH control appears simple and easy to carry out. Add acid and the pH decreases; add base (alkali) and the pH increases. However, pH is the most difficult control feature in any industry’.

The control of pH in textile coloration processes is ensured by three fundamentally different techniques:

(a) the maintenance of a relatively high degree of acidity or alkalinity
(b) the control of pH within fairly narrow tolerances mainly in the near-neutral region
(c) the gradual shifting of the pH as a dyeing proceeds.

Approach (a) is normally the easiest to control, and is used in the application of levelling acid and 1:1 metal-complex dyes to wool or nylon, and of the reactive, sulphur or vat dyes to cellulosic fibres. The agents traditionally used are the stronger acids and alkalis such as sulphuric, hydrochloric and formic acids, sodium carbonate and sodium hydroxide. In certain operations, particularly fixation in steam (as in printing), steam-volatile acids are replaced with non-volatile products such as citric acid. Use of approach (a) can lead to the misconception already mentioned, that pH is easy to control, particularly as the dye–substrate systems involved are not normally sensitive to minor pH shifts. Nevertheless, strong acids and alkalis can react to produce quite drastic changes in pH; this can occur, for example, when alkali is carried over from wool scouring into initially acidic dyebaths.

Wool and nylon absorb acid from dyebaths, thereby inducing a change in the dyebath pH, but wool will absorb significantly more acid than nylon [8] – a factor to be borne in mind when comparing results on these two fibres, especially in those systems using 'half-milling' acid dyes for which the controlling agent is generally the weaker acetic acid; such systems represent a compromise between approaches (a) and (b) and are moderately sensitive to change in pH. In this area, the organic formic and acetic acids are of interest. Formic, of course, is a stronger acid than acetic. Hence, acetic acid has been traditionally the preferred choice for the adjustment of slightly acidic media, down to about pH 4, whereas formic was the choice below this level. It has been demonstrated, however, that for general purposes formic acid is preferred to acetic acid, particularly on economical and environmental grounds [9]. Formic acid has an extremely low BOD, being biodegraded to carbon dioxide and water. In any case, being a much stronger acid, smaller amounts are needed, thus giving less load for disposal. For example, in order to obtain pH values of 4.5, 4.0 and 3.3, the amount of formic acid 85% needed is, respectively, about 62%, 50% and 12% of that of acetic acid 80%. Other advantages of formic acid are that it has a more powerful neutralising effect than acetic acid and it is less corrosive than mineral acids.

Approach (b) needs greater awareness of the factors that not only determine pH but also help to stabilise it against interference. Most of the dye–fibre systems requiring approach (b) are operated in the near-neutral region (pH 4–9) and are much more sensitive to minor changes in pH. In addition, the pH of the water supply may vary, or drift during heating. Even the pH of pure water changes on heating, from 7.47 at 0 °C to 7.00 at 24 °C and 6.13 at 100 °C, but that of the process water used in dyehouses and printworks can change much more drastically, most commonly showing an increase. Changes in pH on heating may counteract the intended response of process liquors, especially in the central pH range associated with approach (b); even more critical can be the effect of any acids or alkalis carried over from previous processes.

The dye–fibre systems of obvious interest for approach (b) are milling acid and 1:2 metal-complex dyes on wool or nylon, basic dyes on acrylic fibres and disperse dyes on various fibres. With wool and nylon there is often some overlap with approach (c) (section 12.2).

Where control is not too critical, simple electrolytes of weak bases with strong acids (such as ammonium sulphate) or strong bases with weak acids (such as sodium acetate) are often used to produce slightly acidic or slightly alkaline media respectively. Ammonium acetate is also commonly used, producing a less acidic effect than ammonium sulphate. Occasionally acetic acid and sodium carbonate are used, necessitating careful control and monitoring. These simple expedients are not suitable for systems requiring more sensitive control, however, and use of single electrolytes such as ammonium sulphate or sodium acetate more properly belong to control systems based on approach (c). More precise control is achieved by the use of buffering systems. By the use of electrolyte pairs, these systems set the initial pH and exert a protective action that tends to resist changes arising from contaminants entering by way of the substrate or the water supply.

Buffering systems are generally based on combinations of:

- a weak acid together with the salt of this acid formed from a strong base, or
- a weak base together with the salt of this base formed from a strong acid.

The most commonly used example of the first type is acetic acid/sodium acetate, which functions well over the pH range 3.8–5.8. Acetic acid with ammonium acetate is also used although it is less effective, especially in those boiling dyebaths from which ammonia can escape into the atmosphere, thus allowing the pH to fall. Such acetate buffers have the advantage of low cost. Somewhat more expensive are the phosphate buffers, of which the most commonly used is a mixture of sodium dihydrogen orthophosphate (NaH_2PO_4) with disodium hydrogen orthophosphate (Na_2HPO_4). Here, as with most polybasic acid systems, the distinction between the acid and its salt seems blurred at first sight. In fact, sodium dihydrogen phosphate is the 'acting acid' and disodium hydrogen phosphate is its salt. The tribasic orthophosphoric acid and its three salts can be used to produce a series of buffers, each active within a particular pH range:

- orthophosphoric acid and the monosodium salt, main buffering region pH 2.5–3.5
- the mono- and di-sodium salts, main buffering region pH 6–8
- the di- and tri-sodium salts, main buffering region pH 10.5–11.

This can be seen from the titration curve for phosphoric acid [6] shown in Figure 10.2. In practice the mono- and di-sodium salt system is used most extensively, since this covers the pH range over which precise control is most often needed. These phosphate buffers are more resistant than the acetate systems to temperature-induced changes.

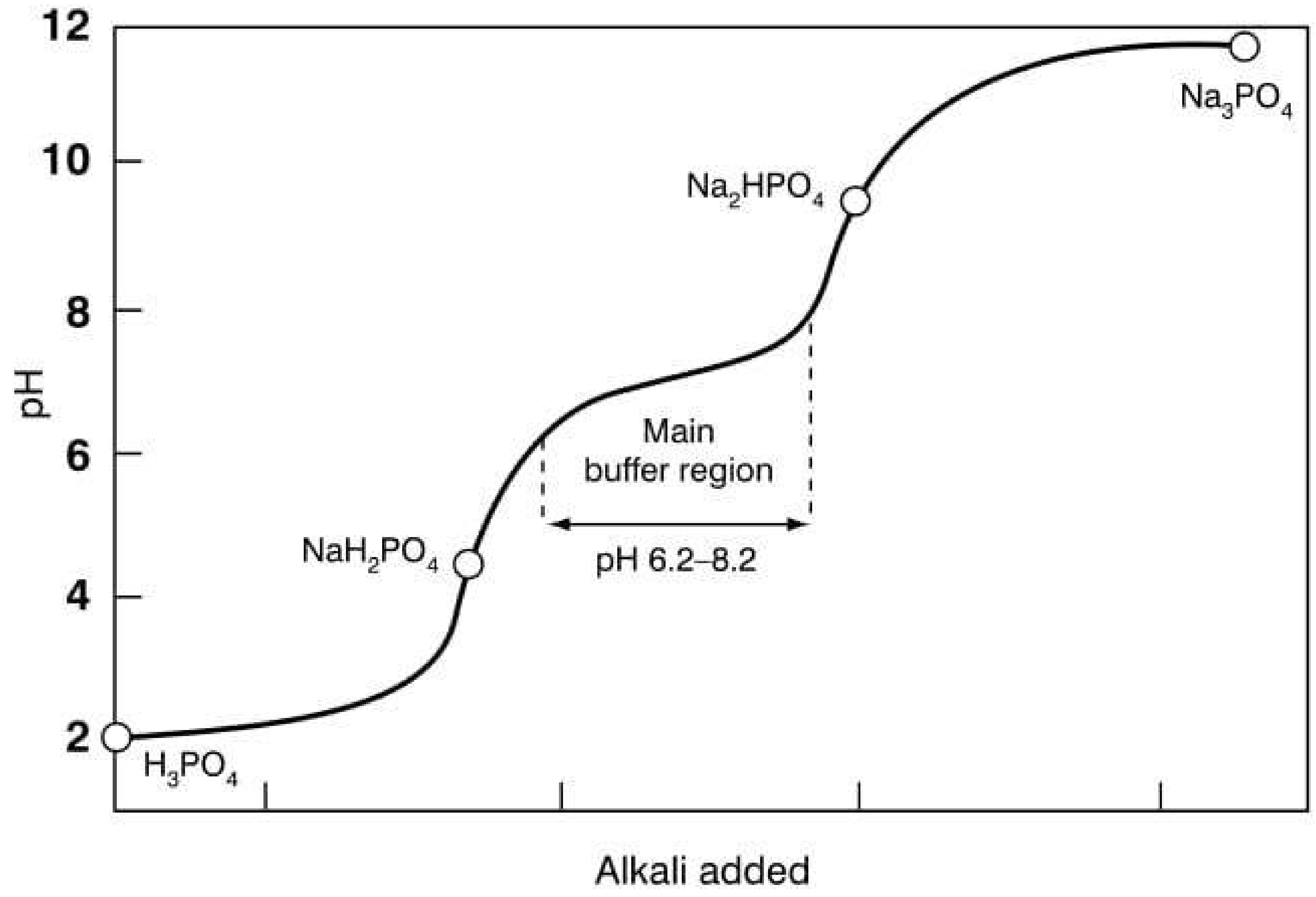


Figure 10.2 Orthophosphate buffer system

The most common buffering system containing a weak base together with its salt formed with a strong acid is ammonia with ammonium sulphate. Some useful buffers are obtained from combinations of unrelated acids or bases with salts. The following combinations find occasional use in textile coloration processes, but the acetates and orthophosphates are most frequently used:

- pyrophosphoric acid ($H_4P_2O_7$) and its salts (pH 3–9)
- orthoboric acid (H_3BO_3), sodium tetraborate (borax $Na_2B_4O_7$) and sodium hydroxide (pH 8.1–10.1)
- citric acid and sodium hydroxide (pH 2.1–6.4)
- sodium carbonate and sodium bicarbonate (pH 9.3–11.3).

The pyrophosphate buffer is of particular technical interest as it can be used over the relatively wide range of pH 3–9. Unlike the orthophosphate titration curve, that for the tetrabasic pyrophosphate system is almost straight [6]. This linearity (Figure 10.3) means that effective buffering action is available across the whole pH range simply by using various pairs of ionised components and varying their proportions; even so, however, it does not seem to be widely used.

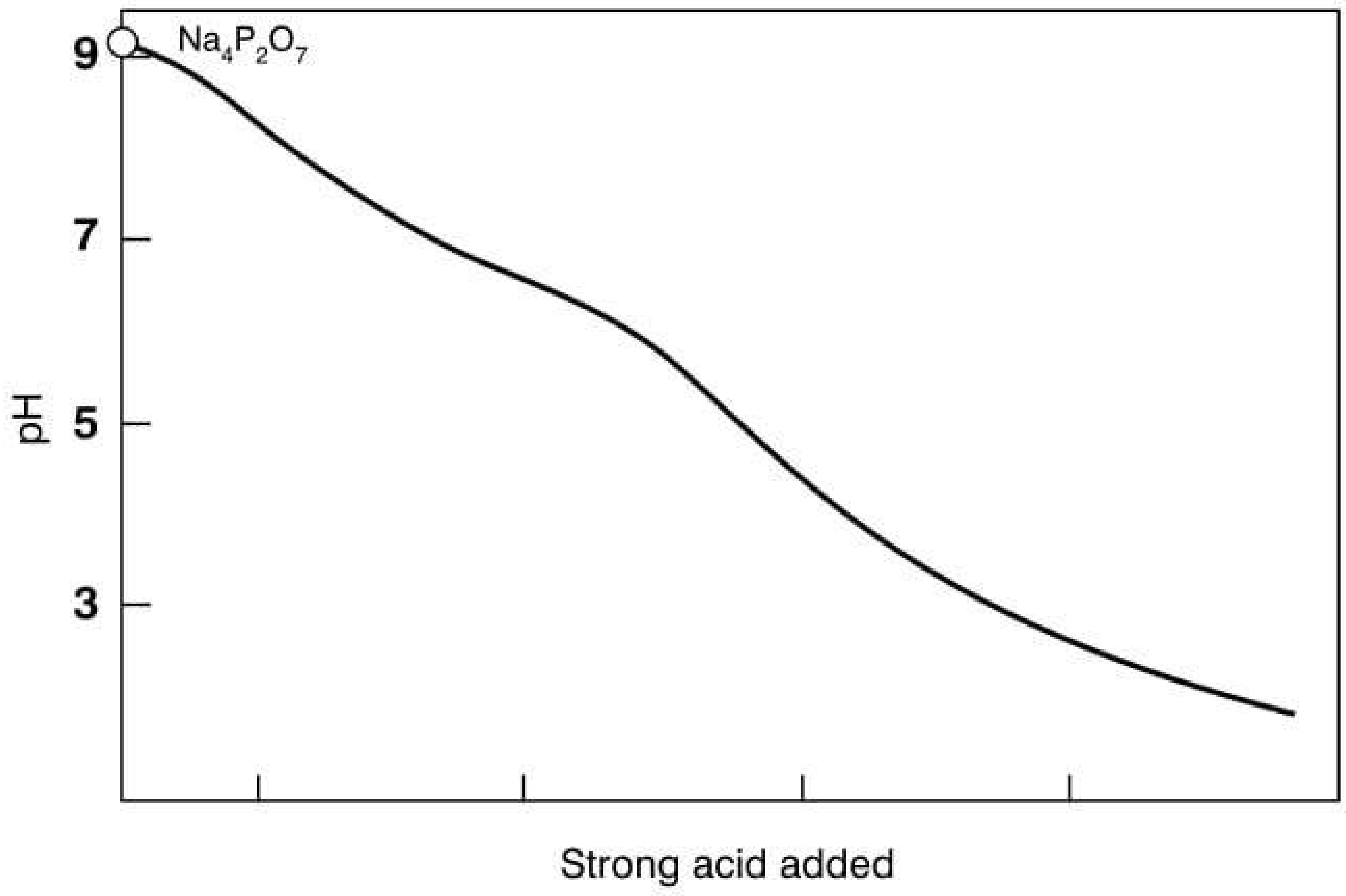


Figure 10.3 Pyrophosphate buffer system

The mechanism of buffering can be described by reference to the acetic acid/sodium acetate system. In aqueous solution sodium acetate can be considered to be practically completely ionised (Scheme 10.1), the equilibrium being wholly to the right-hand side. Since acetic acid is a weak acid it is only slightly ionised, and the equilibrium represented by Scheme 10.2 lies mainly to the left-hand side. This low degree of ionisation is even further suppressed in the presence of sodium acetate as a result of the common ion (in this case acetate) effect operating through the law of mass action. The undissociated acetic acid is, in effect, a ‘bank’ of hydrogen and acetate ions that can be brought into play as a neutralising mechanism when either acidic or alkaline chemicals enter the system (either by deliberate addition or adventitiously). If a small amount of an acidic solute is added to the mixture, the added hydrogen ions combine with acetate ions to form undissociated acetic acid, which has only a minimal effect on the pH of the system. If an alkaline solute is added to the buffer, the added hydroxide ions react with the bank of hydrogen ions to form undissociated water and so again the ionic balance and hence the pH remain essentially the same. The mechanisms of other buffering systems are similar: buffering action is increased by adding more of the components, keeping their proportions constant.

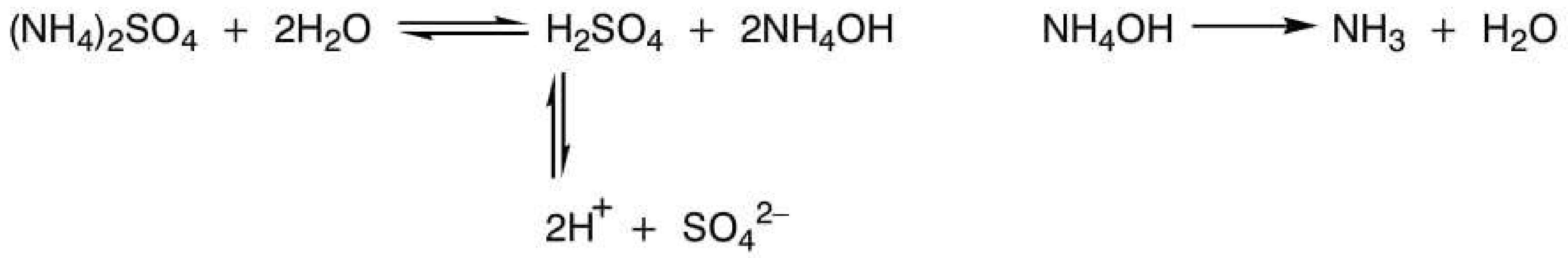
$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$$

Scheme 10.1

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

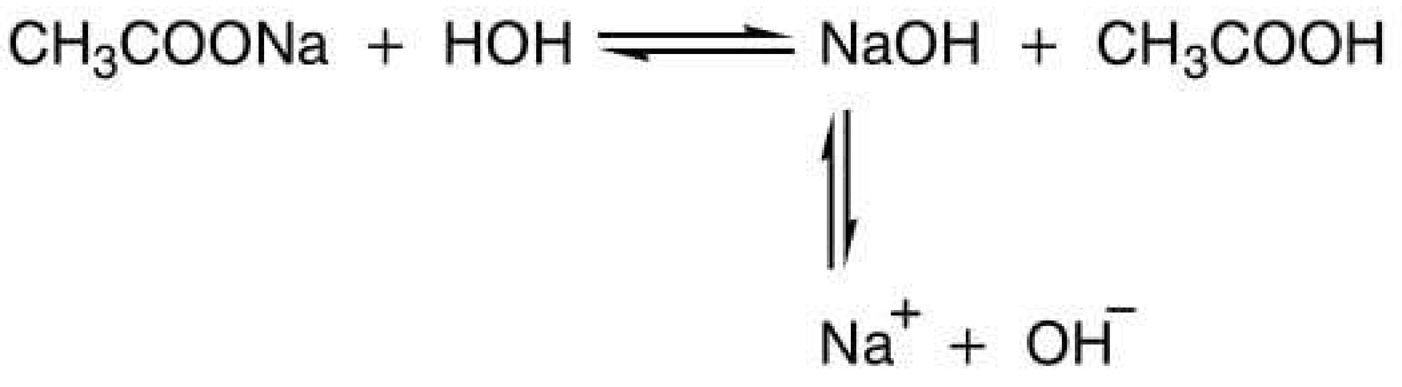
Scheme 10.2

Approach (c) for pH control involves a deliberate shift of pH during the processing cycle, in a consistent direction rather than randomly. Systems of this type are particularly useful for non-migrating anionic dyes on wool or nylon and have long been known in this connection. More recently, similar systems have been adopted for reactive dyes on cellulosic fibres. The simplest and most widely used of these systems consist of the salts of strong acids with weak bases or of strong bases with weak acids, examples being ammonium sulphate and sodium acetate respectively. Ammonium sulphate, for instance, dissociates in aqueous media to yield the dominant strong-acid species of sulphuric acid, so lowering the pH (Scheme 10.3) at a rate that increases with temperature, especially when the ammonia formed can be released from an open dyebath. Ammonium acetate functions in the same way but does not yield as great a pH shift. Similarly, a solution of sodium acetate tends to produce the dominant strong-alkali species of sodium hydroxide (Scheme 10.4), thus increasing the pH.



$$\begin{array}{l} (NH_4)_2SO_4 + 2H_2O \rightleftharpoons H_2SO_4 + 2NH_4OH \qquad NH_4OH \longrightarrow NH_3 + H_2O \\ \qquad\qquad\qquad\qquad\qquad\quad \Big\updownarrow \\ \qquad\qquad\qquad\qquad\qquad\quad 2H^+ + SO_4^{2-} \end{array}$$

Scheme 10.3



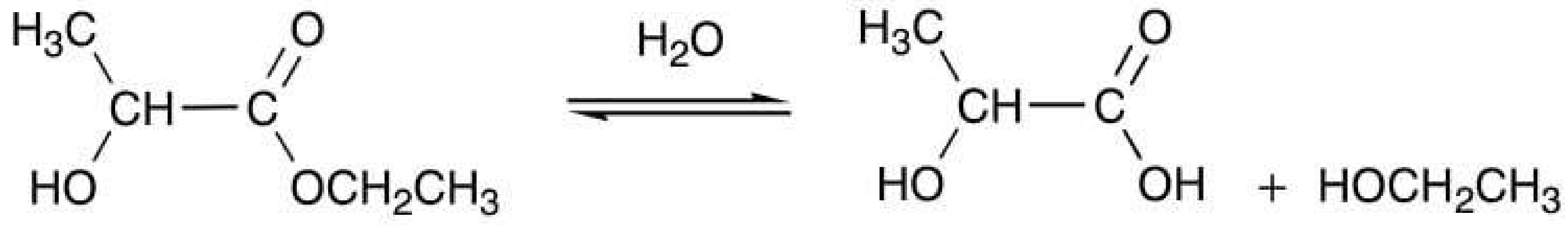
$$\begin{array}{l} CH_3COONa + HOH \rightleftharpoons NaOH + CH_3COOH \\ \qquad\qquad\qquad\qquad\qquad\quad \Big\updownarrow \\ \qquad\qquad\qquad\qquad\qquad\quad Na^+ + OH^- \end{array}$$

Scheme 10.4

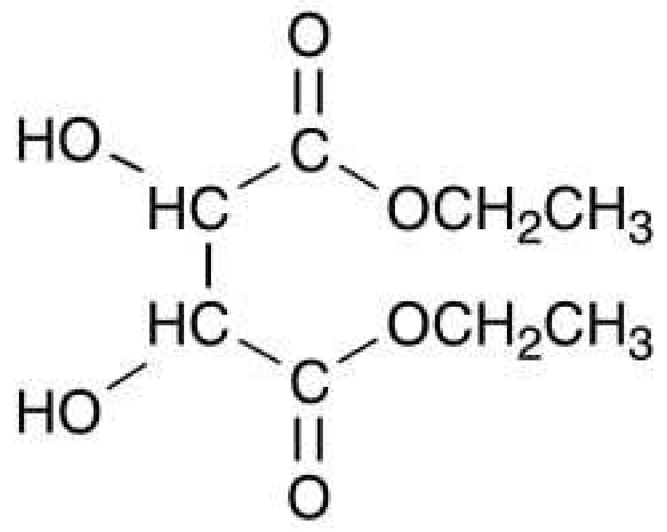
Acetic acid (b.p. 118 °C) is not boiled off from open dyebaths as readily as ammonia but is rapidly flashed off in steam or dry heat processes, thus developing the maximum degree of alkalinity under these conditions. The sodium salts of less volatile acids, such as sodium citrate, can be used to develop a lower degree of alkalinity.

If the process demands a gradual shift from about pH 9 to a slightly acidic pH, ammonium sulphate together with ammonia can be used. This gives a safer, more uniform development of acidity than can be achieved by making additions of acid to an alkaline bath, although the degree of acidity developed will clearly depend on the ease with which ammonia can escape from the system. In enclosed or partially enclosed machines this system does not function so efficiently [10–12].

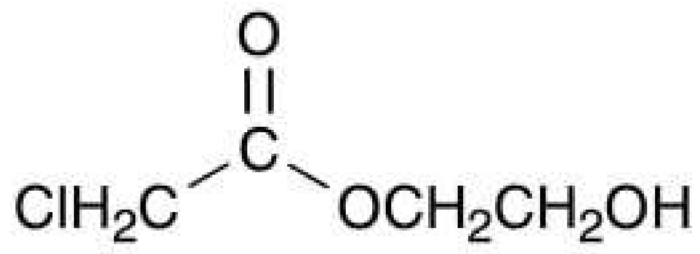
Another method of obtaining a pH shift in the direction of acidity is to use an organic ester that hydrolyses to the alcohol and acid under the conditions of processing. Ethyl lactate (Scheme 10.5) and diethyl tartrate (10.2) have been recommended for applying milling and chrome dyes to wool [13]. 2-Hydroxyethyl chloroacetate (10.3) and γ-butyrolactone (10.4), which hydrolyses during processing to give 4-hydroxybutyric acid (Scheme 10.6), have also been recommended. Such hydrolysable esters may be used alone, beginning at a near-neutral pH, but more likely in conjunction with an alkali to give a higher starting pH. Thus γ-butyrolactone and sodium tetraborate (borax), giving a pH shift from about 8 to 5.6, have been recommended for the dyeing of wool [14], as has 2-hydroxyethyl chloroacetate with sodium hydroxide for the dyeing of nylon [15]. Such hydrolysable esters are sometimes sold under proprietary trade names. The disadvantages of hydrolysable esters have been their higher cost, a limited pH range and, where the dyebath is to be reused, the need for increasing quantities of ester to overcome the buffering effect caused by the accumulation of salts [7,16]. Interest in these systems has declined due to environmental pressures on the one hand and the increased availability and sophistication of automatic dosing and monitoring systems on the other.



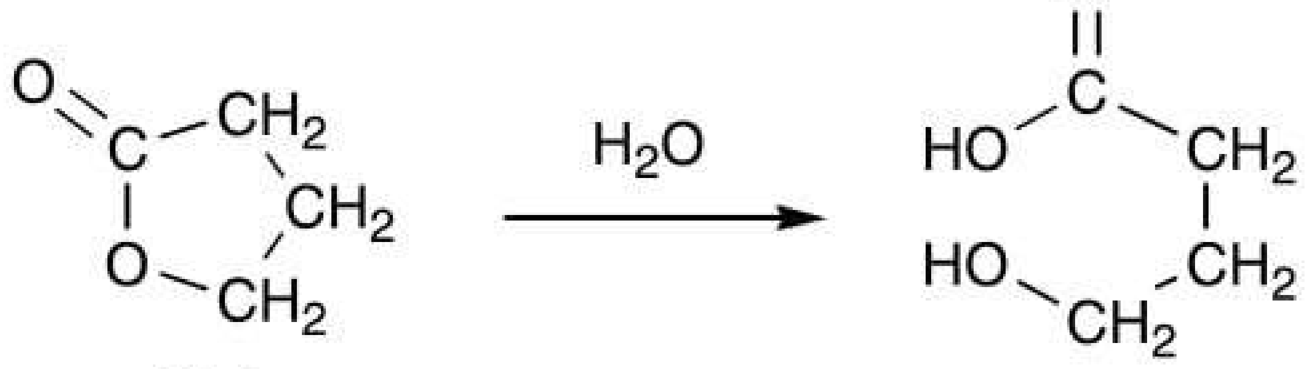
Scheme 10.5



10.2



10.3



10.4

Scheme 10.6

The advantages of automatic metering and monitoring devices were well described by Mosimann [17] and have recently been re-emphasised [9]. Such devices are clearly of great value in environmental terms since they are crucial in ensuring that the minimum quantity of agent is used, thus reducing the effluent load to a minimum. The use of strong acids and bases for control of pH-shift systems is obviously fraught with difficulties where the operation is carried out manually. If a sophisticated automatic monitoring and dosing system is used, however, the use of such compounds has certain very worthwhile advantages:

(a) The adjusting chemicals are the cheapest available;
(b) The entire range of pH values can be controlled by using just two chemicals;
(c) Since a buffering system is not built up in the bath, the pH can be shifted in any direction to any degree, easily and with the minimum addition of chemicals;
(d) As a result of (c), any variation in the intrinsic pH of the substrate or water supply can be easily neutralised;
(e) Exhausted dyebaths can often be reused as there is no build-up of buffering agent; and
(f) There are no environmental problems.

It should be noted that automatic dosing and monitoring of dyes and chemicals can be used generally and is not restricted to pH control.

10.2 SEQUESTERING AGENTS

The tendency of soaps and other carboxylates to form insoluble complexes with calcium and magnesium ions in hard water is mentioned in sections 9.4 and 9.8.2. Apart from decreasing the efficiency of the anionic surfactant, deposition of such insoluble complexes on the textile substrate can cause problems in subsequent processing and particularly in coloration. Even trace amounts of certain transition-metal or alkaline-earth elements may cause processing difficulties. The formation of 'iron spots', particularly in bleaching, is well known: multivalent transition-metal cations catalyse the decomposition of hydrogen peroxide (although divalent calcium and magnesium ions have a stabilising effect) and localised staining or tendering of the fibre may occur. In coloration trace-metal ions can react with certain dyes, giving rise to precipitation, discoloration, unlevel dyeing and reduced fastness.

The processing water is the most obvious source of such extraneous metal ions, but other potential sources should not be overlooked. For example, trace metals may be dissolved from the surfaces of machinery and fittings. The substrate may already contain such metals, as may also any chemicals or dyes used. Hence these problems cannot always be avoided simply by ensuring the supply of suitable water – indeed, the overzealous treatment of water can actually lead to the presence of troublesome aluminium ions that were not originally present! Such problems can be solved using chemicals that react preferentially with the metal ions, effectively preventing them from interfering with the mainstream reaction or process. Such chemicals are aptly known as sequestering agents. Other terms frequently used in the literature include the derivative 'sequestrants' and 'complexing agents', although complexing does cover a wider field than just metal–ion chelation with which we are concerned here.

Sequestering agents work by a mechanism of complex formation, often in the form of chelation. A chelating agent contains substituents suitably located to form one or more chelate rings by electron donation to the metal ion (section 5.2), the resulting complex remaining soluble and innocuous under the conditions of processing. The most useful donating atoms are nitrogen, as found in amines or substituted amines, and oxygen in the form of carboxyl, phosphate or ionised hydroxy groups. As in the formation of dye–metal chelates (such as chrome mordant and metal-complex dyes), at least two electron-donating atoms in the sequestering agent structure must be arranged so that a stable ring can be formed with the metal ion, the highest stability resulting from five- and six-membered rings.

A great many chemicals exhibit sequestering capability but not all are of commercial value in textile processing. Earlier literature [18,19] mentioned three main types:

- aminopolycarboxylates
- phosphates, mainly inorganic
- hydroxycarboxylates.

However, environmental awareness, in addition to commercial and technical exploitation, has resulted in considerable activity in this area, leading to a greatly expanded range of products in recent years, as well as some conflicting statements with regard to their environmental properties. The scheme of classification adopted here is as follows:

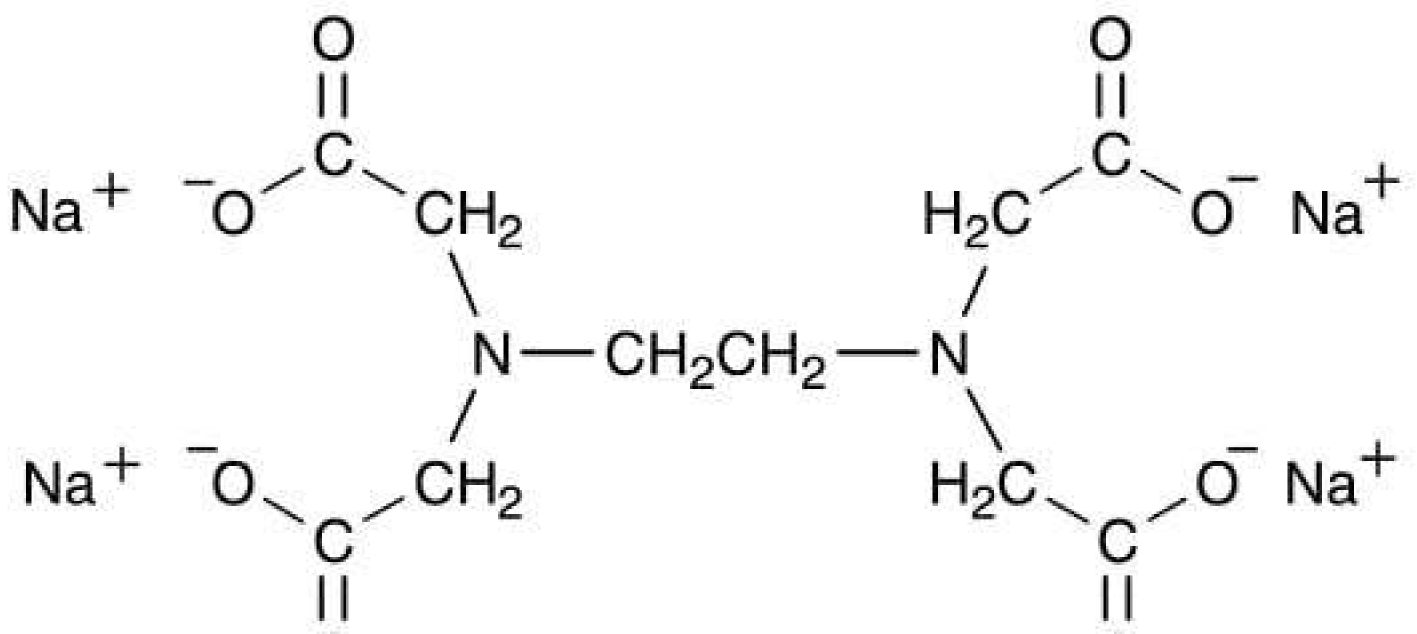
- aminopolycarboxylates and their analogues, e.g. hydroxyaminocarboxylates
- phosphates and phosphonates
- hydroxycarboxylates
- polyacrylic acids and derivatives.

10.2.1 Aminopolycarboxylates and their analogues

These are powerful chelating agents, having good environmental properties [20]. Important members include:

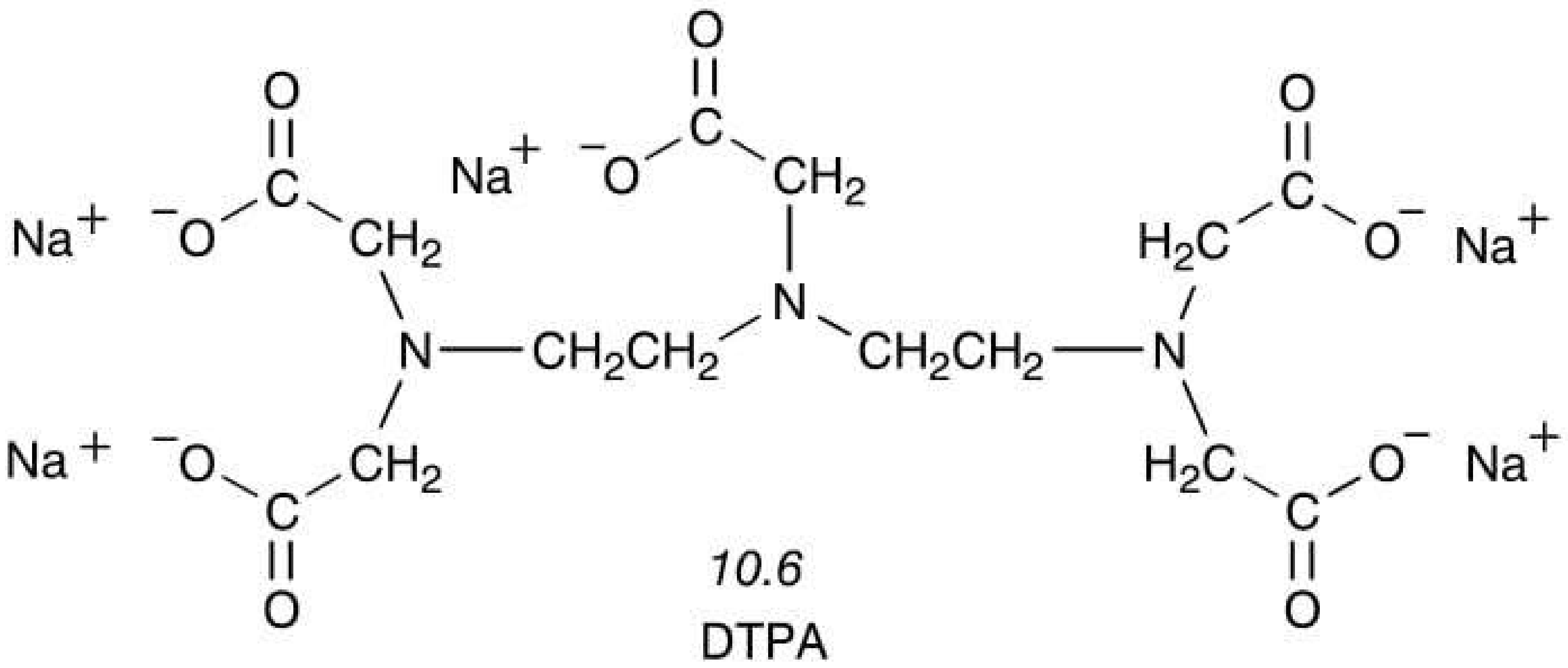
– ethylenediaminetetra-acetic acid	EDTA	(10.5)
– diethylenetriaminepenta-acetic acid	DTPA	(10.6)
– nitrilotriacetic acid	NTA	(10.7)

These products are sold as free acids or sodium salts. Analogues of these aminopolycarboxylic acids include the hydroxyaminocarboxylic acids. These structures are derived



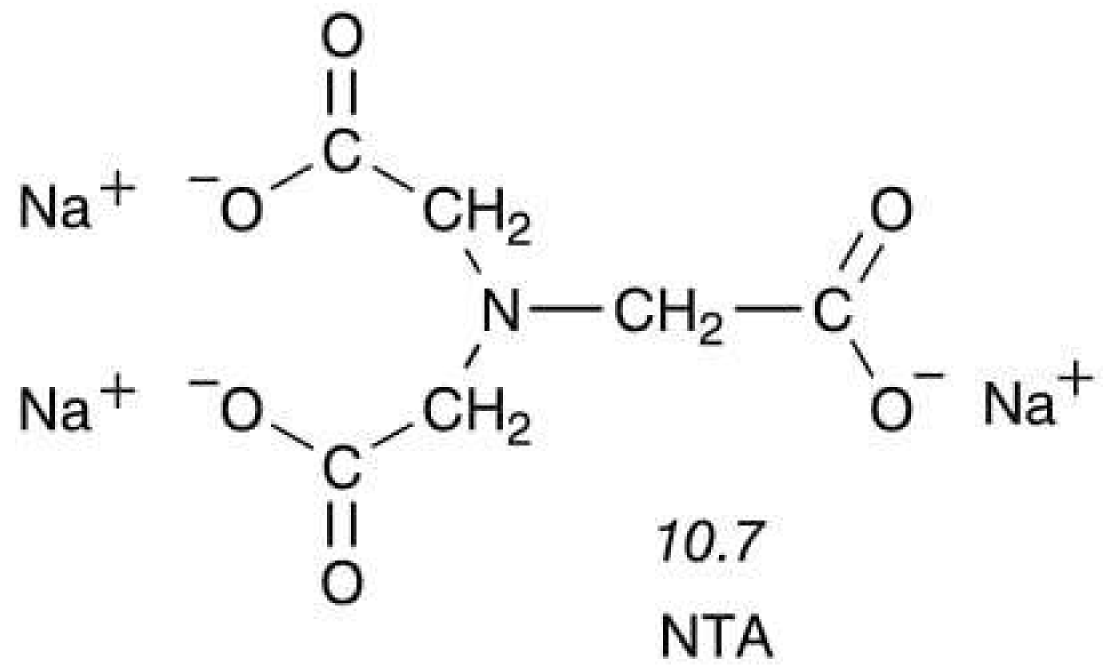
10.5

EDTA



10.6

DTPA

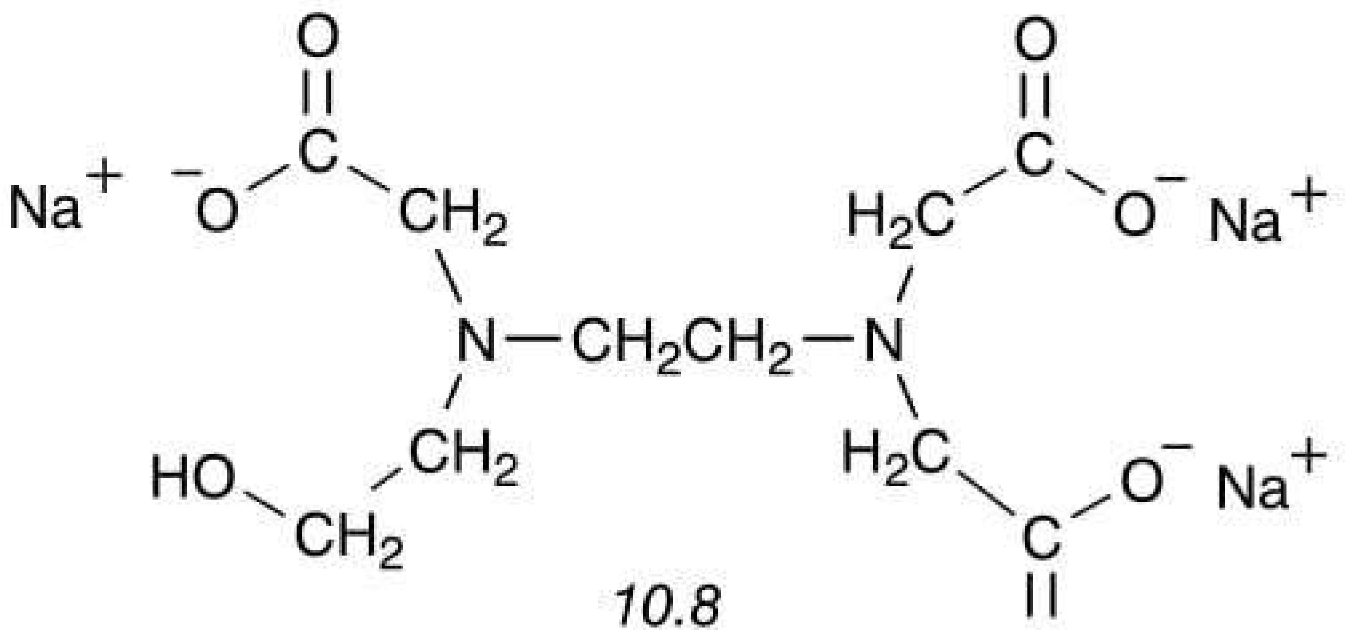


10.7
NTA

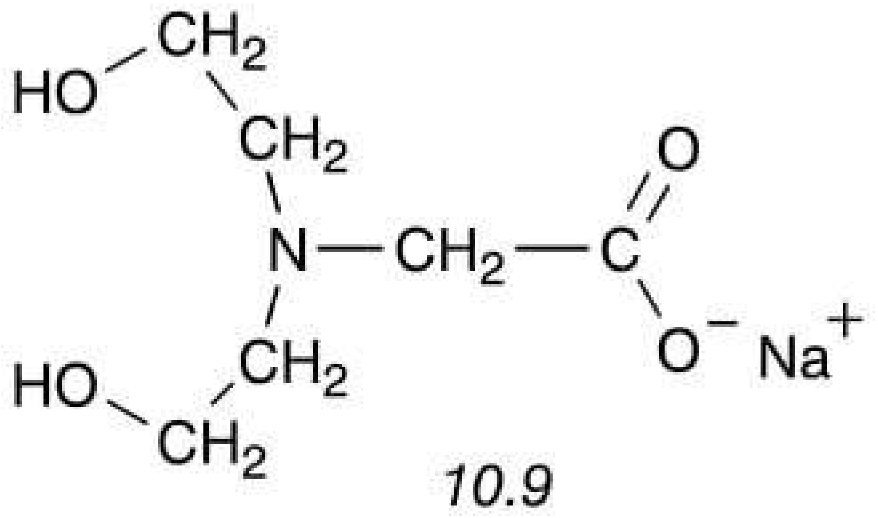
by replacing one or more carboxymethyl groups of the aminopolycarboxylate by a hydroxyethyl group. Examples include:

N-(hydroxyethyl)ethylenediaminetriacetic acid HEDTA (10.8)
in which one of the carboxymethyl groups of EDTA has been replaced by a hydroxyethyl group

N,*N*-bis(hydroxyethyl)glycine DEG (10.9)
in which two of the carboxymethyl groups of NTA have been replaced by hydroxyethyl groups.



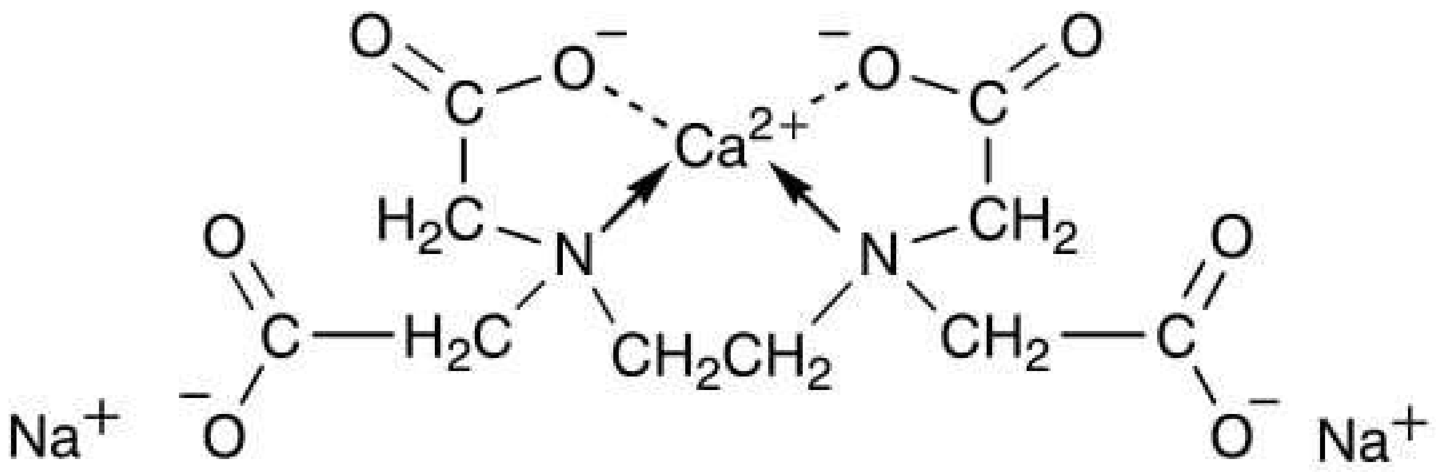
10.8
HEDTA



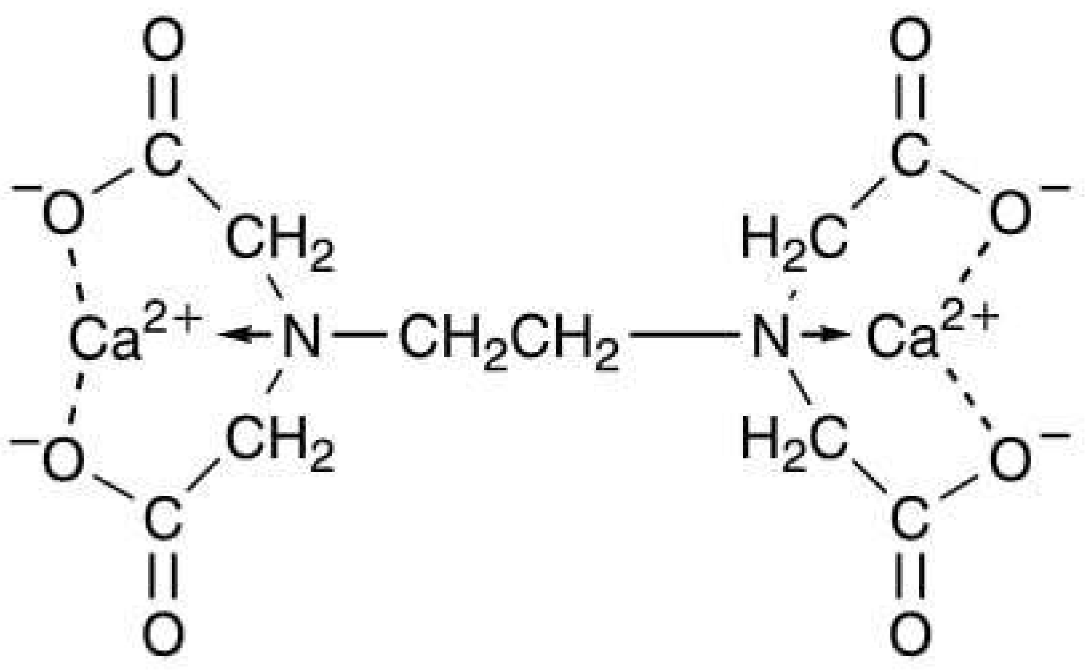
10.9
DEG

These compounds are not persistent in the environment, NTA degrading slightly more quickly than EDTA, DTPA or HEDTA [20].

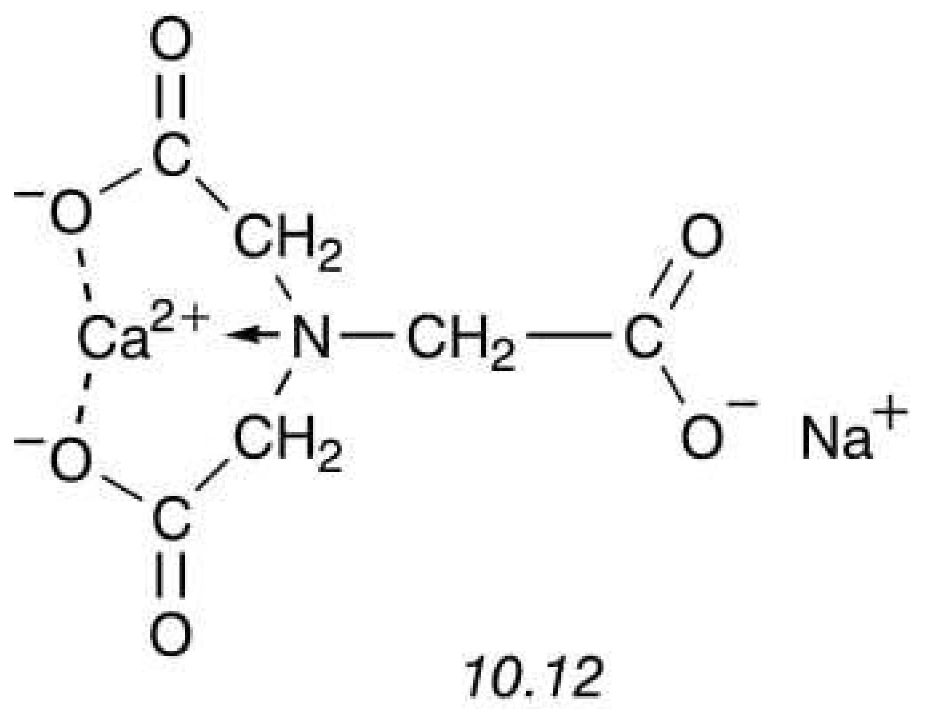
These aminopolycarboxylates act as sequestering agents by forming complexes in which each metal ion is chelated into one or more five-membered rings. It is often assumed that one molecule of sequestering agent interacts with one metal ion and for many practical purposes this is a valid assumption. The nature of the complexes actually formed, however, may depend on other factors such as the pH of the medium. It is difficult to represent such structures in detail, particularly as water of solvation is usually involved. It is convenient to adopt a simplified representation, omitting the water of solvation, as for the EDTA–calcium complex shown in structure 10.10, in which the arrows represent coordination bonds and the calcium ion is held by three five-membered rings. At pH values below 11 the structure tends to be more like that shown in 10.11, which also resembles the complex formed with NTA (10.12).



10.10

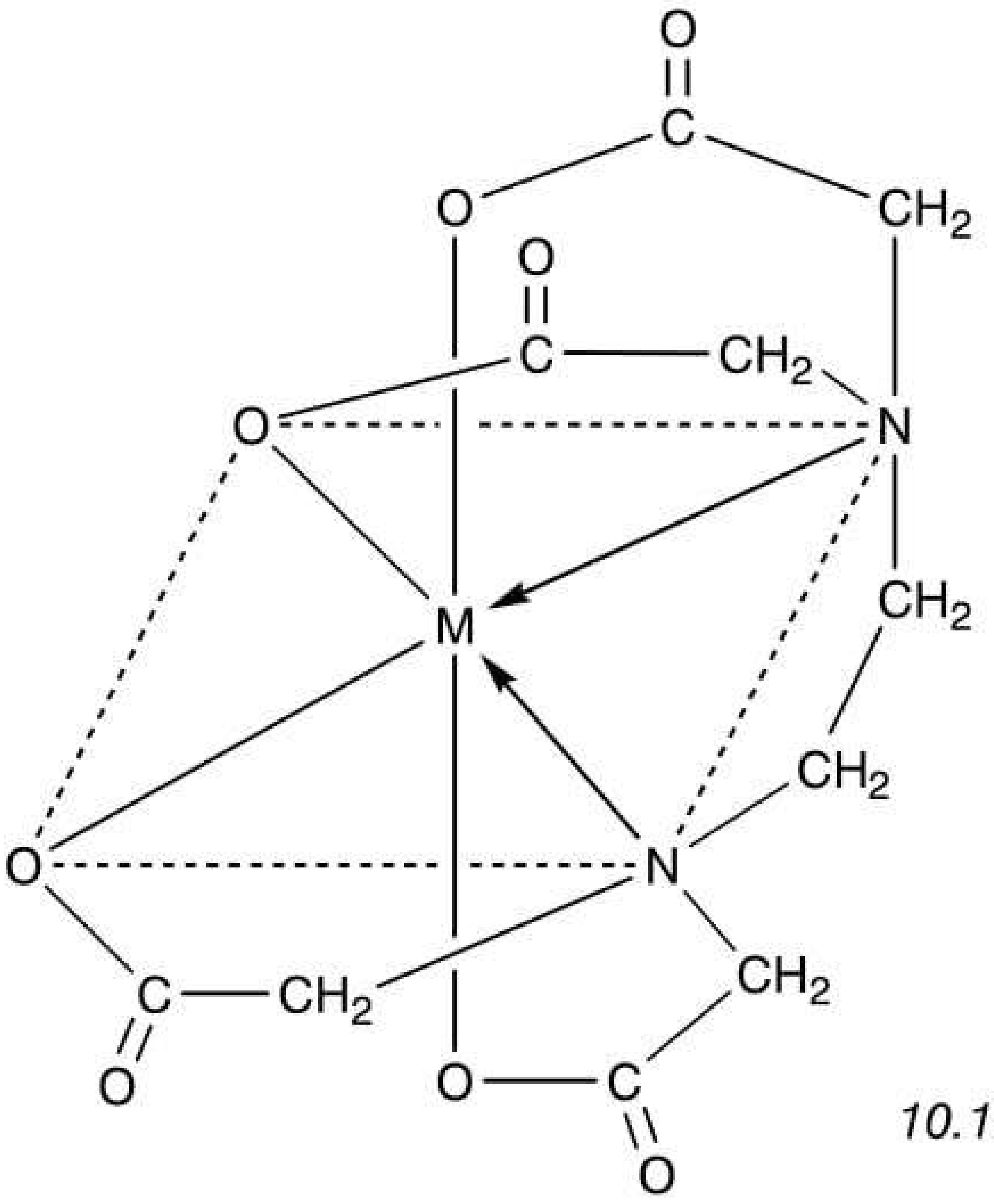


10.11



10.12

A more elaborate representation of an EDTA-metal complex (10.13), which gives some indication of the three-dimensional aspects of the structure, shows a complex of five five-membered rings [18]. A similar representation of a DTPA-metal complex shows a system of eight five-membered rings.

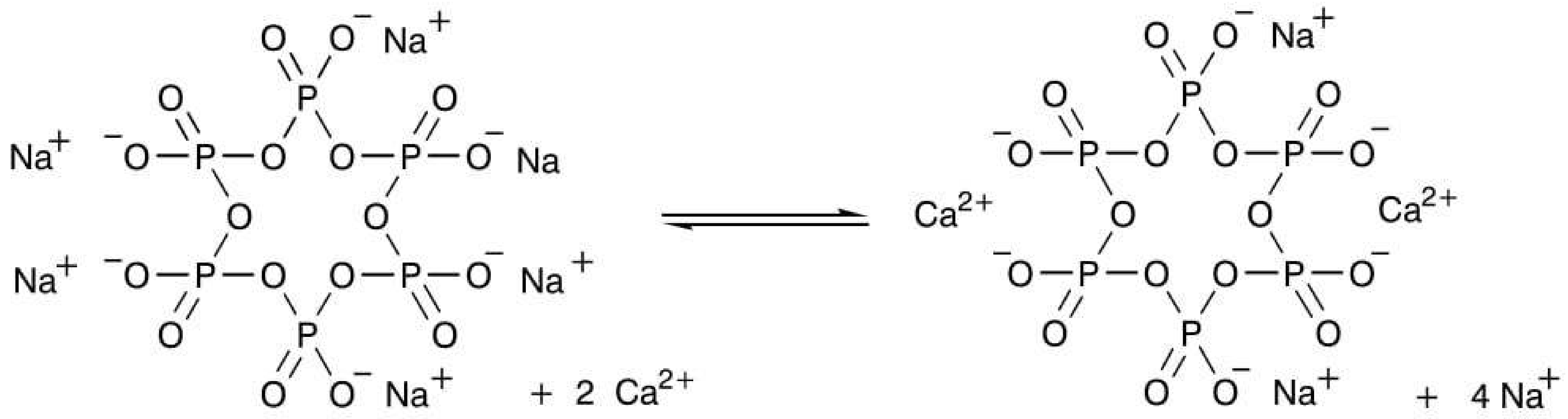


10.13

10.2.2 Phosphates and phosphonates

Various polyphosphates are effective sequestering agents under appropriate conditions. The best known of these is sodium hexametaphosphate (10.14), the cyclic hexamer of sodium orthophosphate. Further examples are the cyclic trimer sodium trimetaphosphate (10.15), as well as the dimeric pyrophosphate (10.16), the trimeric tripolyphosphate (10.17) and other linear polyphosphates (10.18). All of these polyanions function by withdrawing the troublesome metal cation into an innocuous and water-soluble complex anion by a process of ion exchange as shown in Scheme 10.7 for sodium hexametaphosphate. Hence these compounds are sometimes referred to as ion-exchange agents.

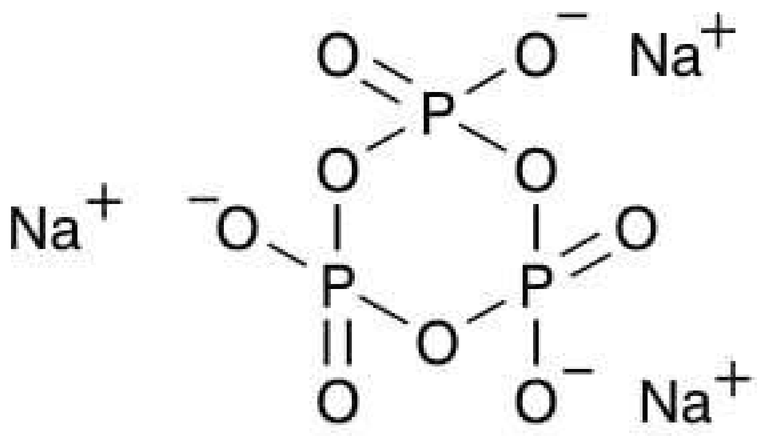
The disadvantage of the polyphosphates is that at the temperatures (100 °C or higher) used in many textile processes they can be hydrolysed into simpler phosphates that cannot retain the metal atom in the sequestered form. For example, dicalcium disodium hexametaphosphate hydrolyses on prolonged boiling to yield the insoluble calcium orthophosphate. This is one of the main reasons why polyphosphate sequestrants are used much less extensively than the more versatile and stable aminopolycarboxylates.



10.14

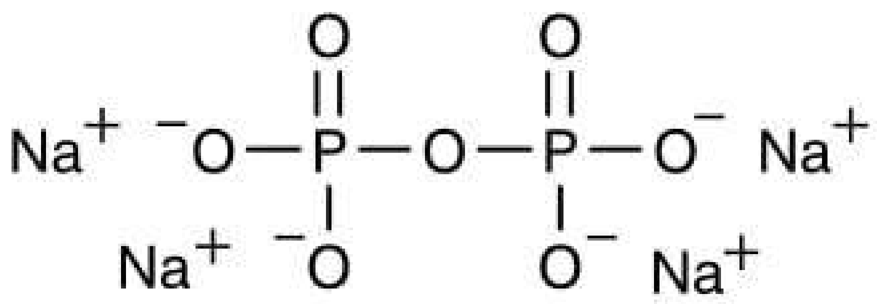
Sodium hexametaphosphate

Scheme 10.7



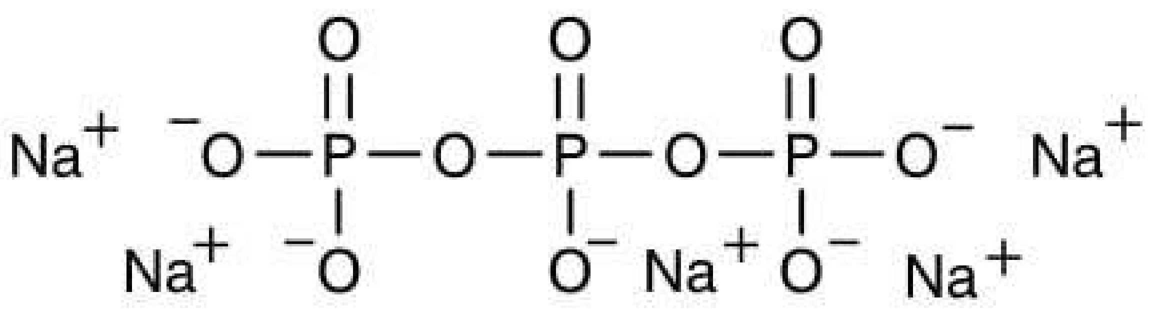
10.15

Sodium trimetaphosphate



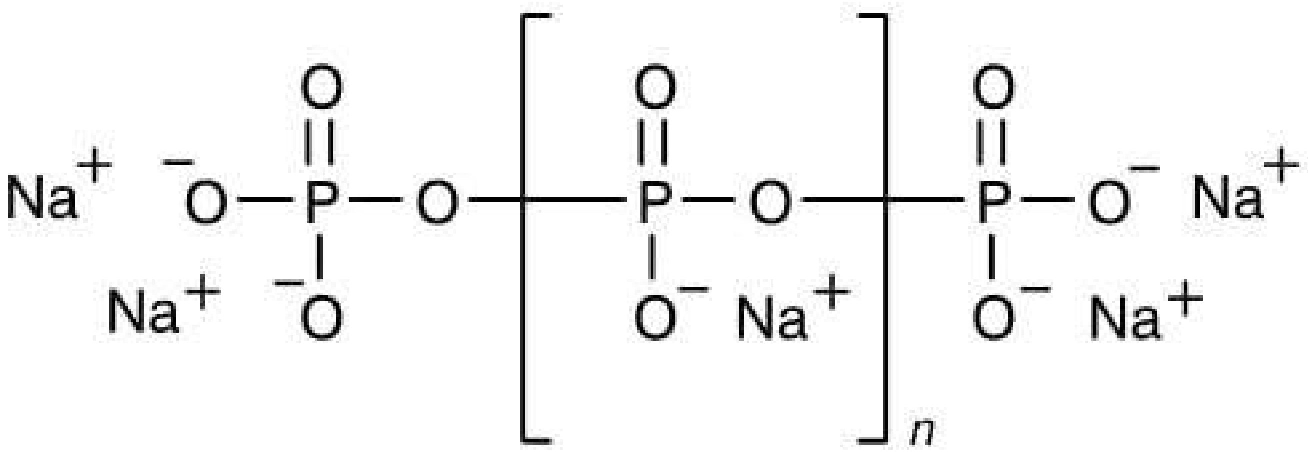
10.16

Sodium pyrophosphate



10.17

Sodium tripolyphosphate



10.18

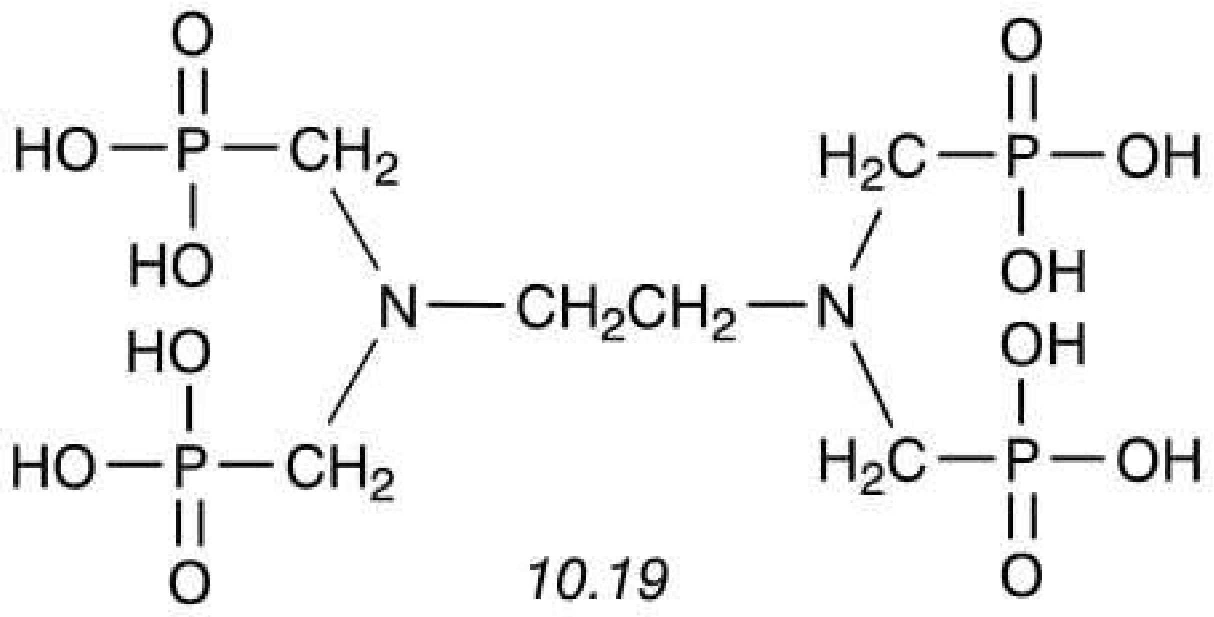
Sodium polyphosphate

A structural compromise between these two types of compound can also give products with sequestering properties, although they are phosphonates rather than phosphates, since they contain C–P rather than C–O–P linkages. Examples of these aminopolyphosphonates are:

– ethylenediaminetetramethylphosphonic acid	EDTMP	(10.19)
– diethylenetriaminepentamethylphosphonic acid	DETMP	(10.20)
– nitrilotrimethylphosphonic acid	ATMP	(10.21)
– hydroxyethylethylenediaminetrimethylphosphonic acid	HEDTMP	(10.22)
– hexamethylenediaminetetramethylphosphonic acid	HMDTMP	(10.23)

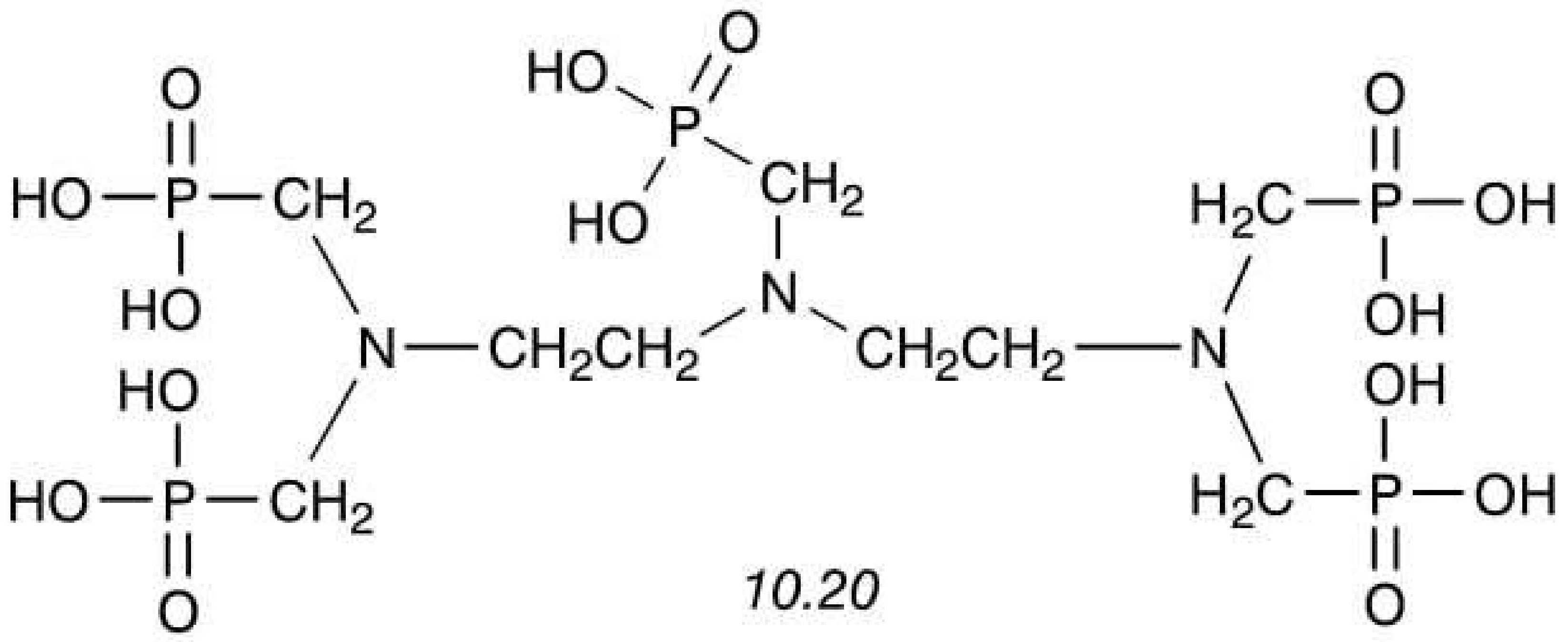
Two sequestrants of the phosphonate class unrelated to aminopolycarboxylic acids are:

1-hydroxyethane-l,1-diphosphonic acid	HEDP	(10.24)
2-phosphonobutane-1,2,4-tricarboxylic acid	PBTC	(10.25)



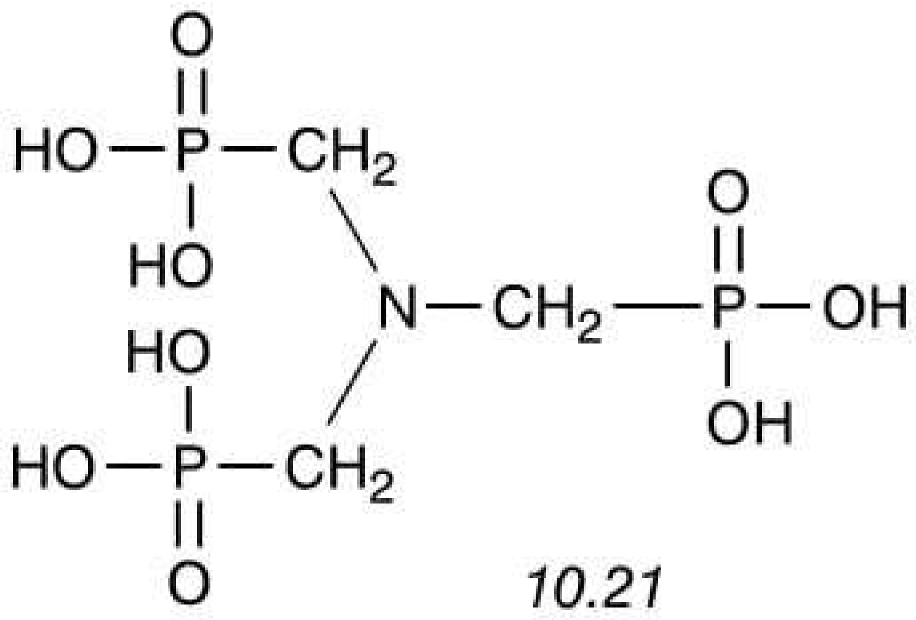
10.19

EDTMP



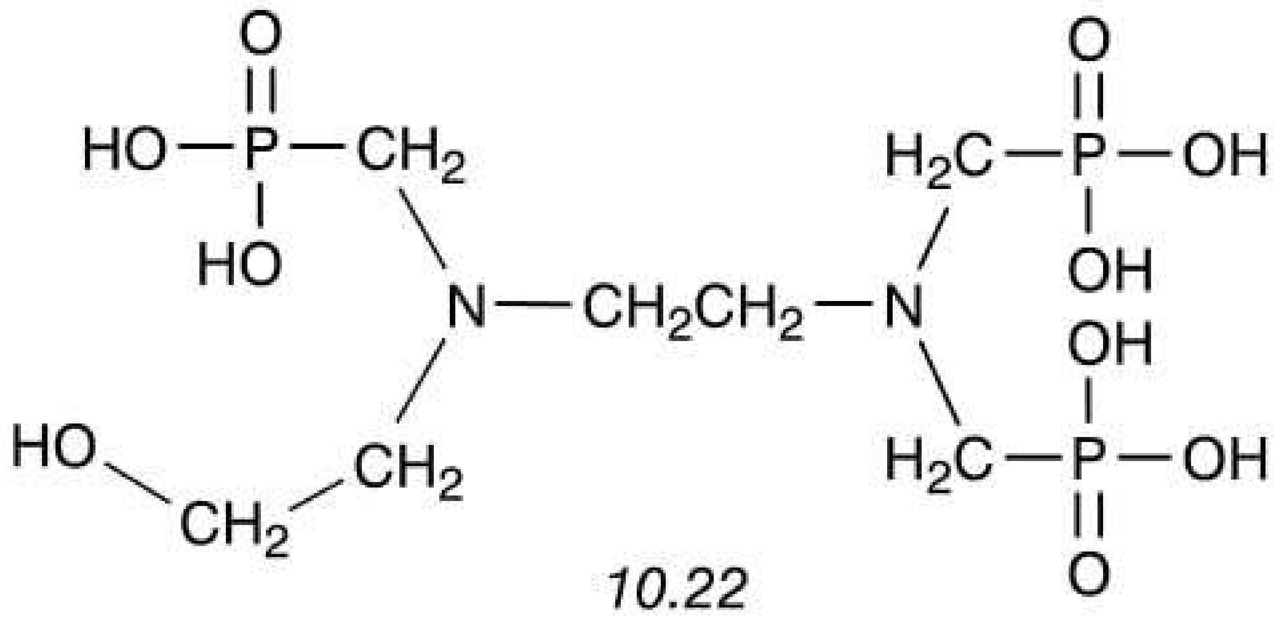
10.20

DETMP



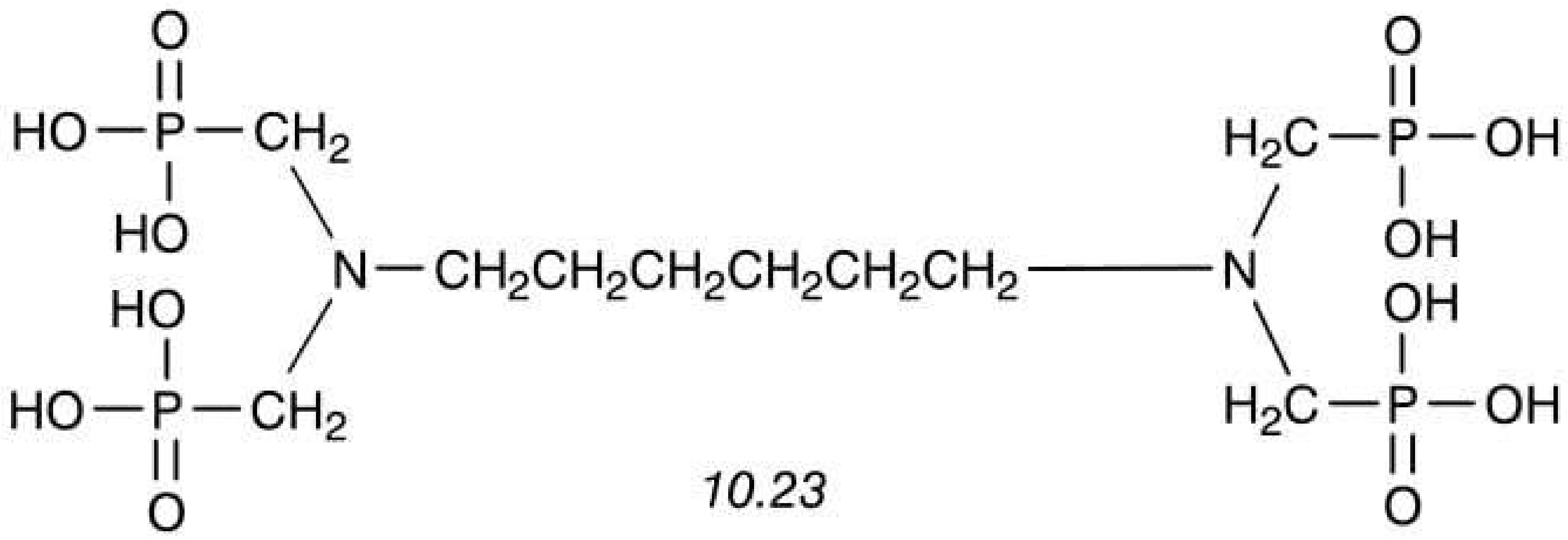
10.21

ATMP



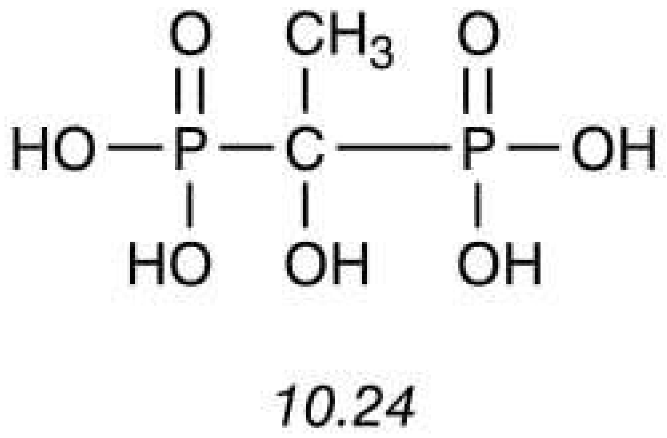
10.22

HEDTMP



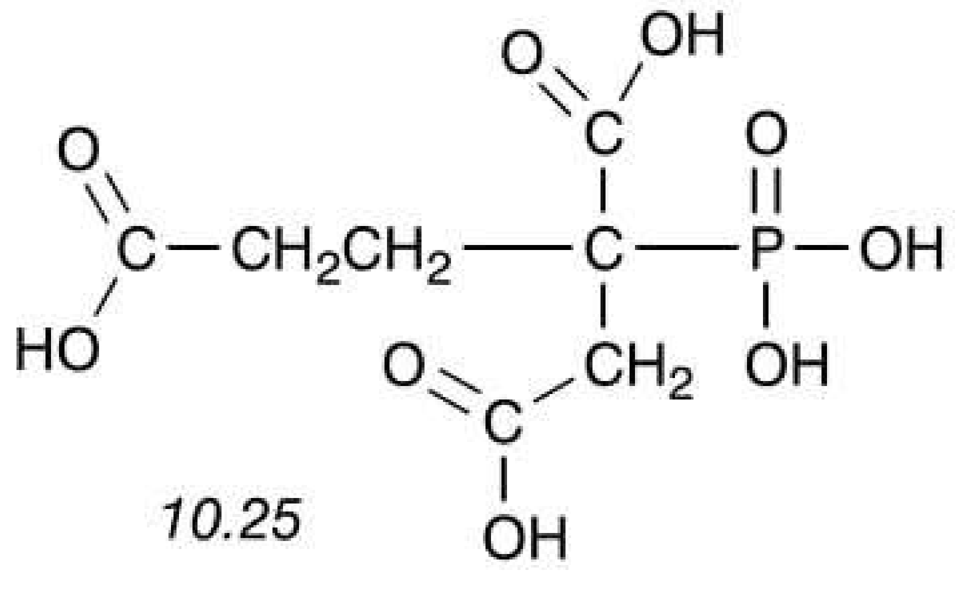
10.23

HMDTMP



10.24

HEDP



10.25

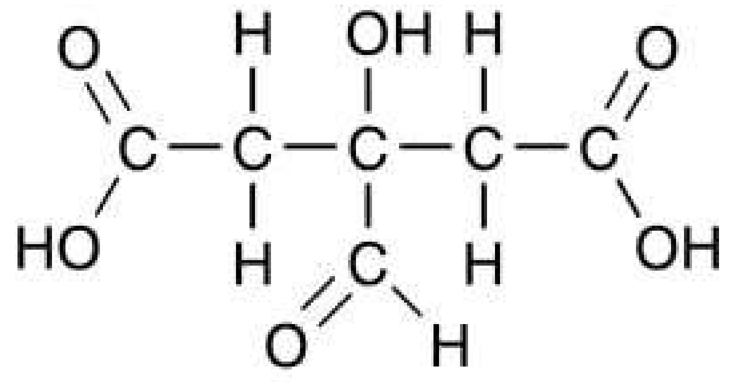
PBTC

The consumption of these phosphonates in textile processing is small in relation to that of the aminopolycarboxylates; they are mainly used in detergent formulations [21,22] as sodium, potassium, ammonium or alkanolamine salts.

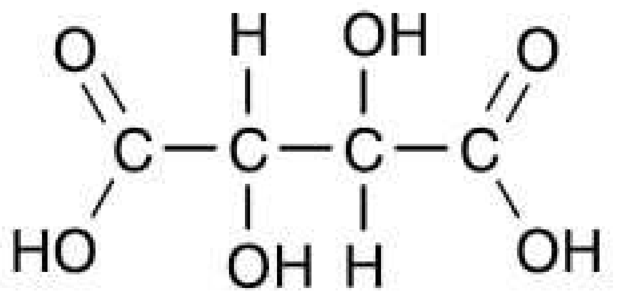
Environmentally, phosphates generally have been a sensitive issue, not least because they can cause eutrophication of watercourses, and the situation is still not resolved completely. No aerobic or anaerobic bacterium has been found to date that will biodegrade aminopolyphosphonates under the treatment conditions used today, yet these products are not biologically persistent. They are partially eliminated photolytically, partially absorbed in sediment or eliminated by precipitation [23,24]. They show 50–80% elimination in the Zahn–Wellens test. They show low aquatic toxicity and are non-toxic to humans, animals and plants. Detailed ecological properties are listed by Schöberl and Huber [25]. Held [26] has investigated the ecological behaviour of sequestering agents based on phosphonic acids in detail, concluding that although they contain phosphorus they do show ecological advantages compared with other types and thus their use is justified.

10.2.3 Hydroxycarboxylates

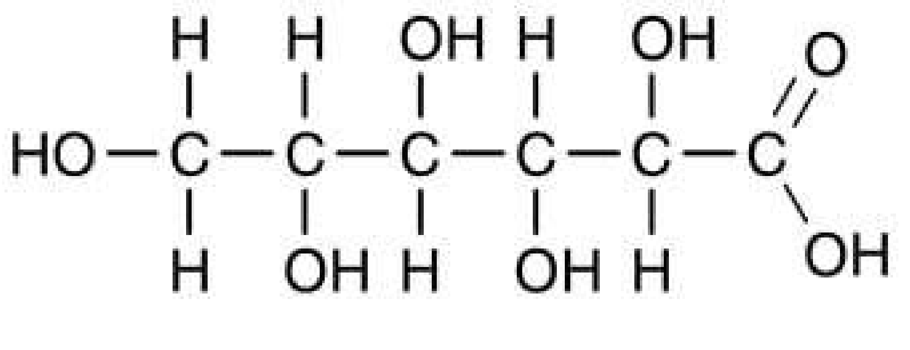
The hydroxycarboxylic acids provide a range of sequestering agents of which the best known are citric (10.26), tartaric (10.27) and gluconic (10.28) acids. The toxic oxalic acid (10.29) is now rarely used. However, these acids are much less important as sequestering agents for textile processes than either the aminopolycarboxylates or the polyphosphates. Hydroxycarboxylates are easily biodegraded but do have a high COD. It has been pointed out [20] that glucoheptanoic acid (2,3,4,5,6,7-hexahydroxyheptanoic acid; 10.30) is also used in the USA, on the grounds that this compound is less prone to browning at high temperatures although it possesses no other advantages, having less binding power as well as being more expensive than other hydroxycarboxylic acids.



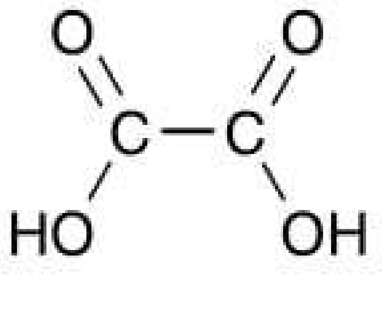
10.26
Citric acid



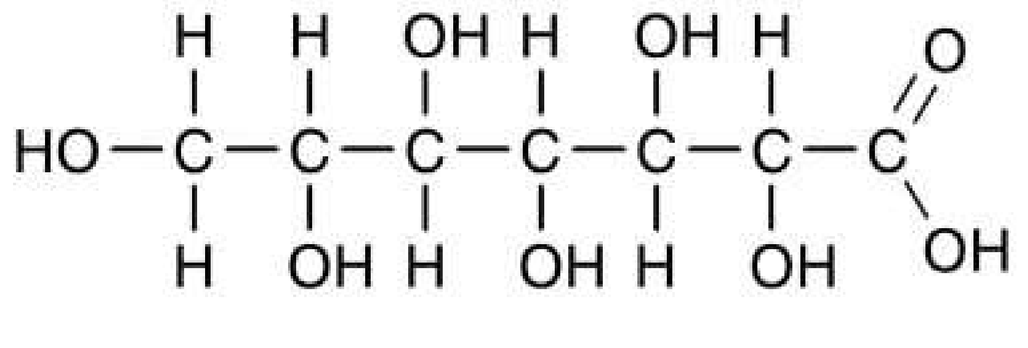
10.27
Tartaric acid



10.28
Gluconic acid



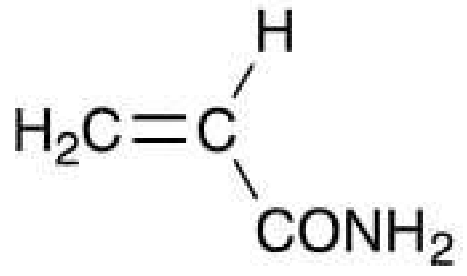
10.29
Oxalic acid



10.30

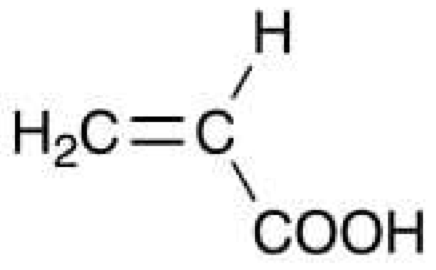
10.2.4 Polyacrylic acids and their derivatives

Recent research has led to some more complex sequestering agents, particularly the polymeric carboxylic acids referred to as polycarboxylates. These are, in effect, polyelectrolytes and as such have close similarities to the products described later as dispersing and solubilising agents (section 10.6), thickening agents or migration inhibitors (section 10.8). Common monomers used in the production of these compounds, either as homopolymers or as copolymers with each other, include acrylamide (10.31) and various unsaturated acids (10.32–10.34). The common and essential feature of these monomers is the carbon–carbon double bond.



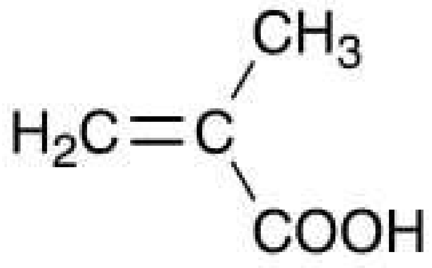
10.31

Acrylamide



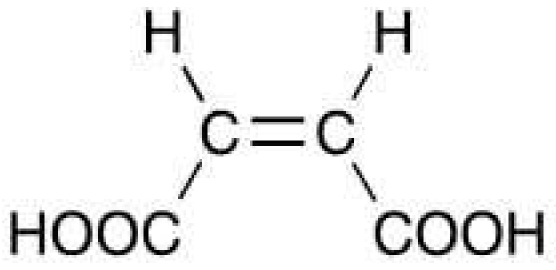
10.32

Acrylic acid



10.33

Methacrylic acid

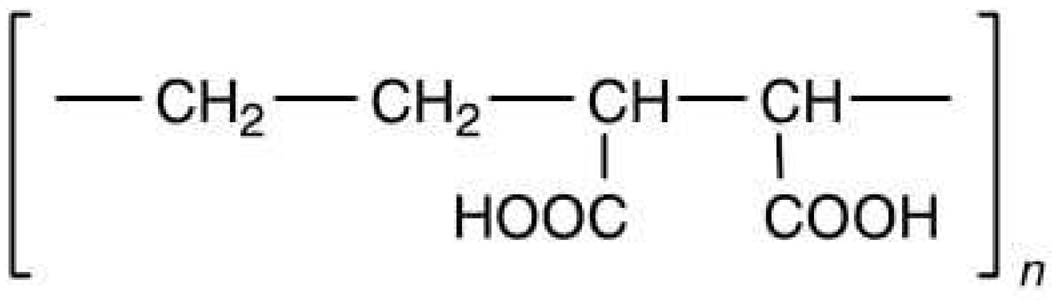


10.34

Maleic acid

Polymers which have been suggested for use as sequestering agents [23,27] include:

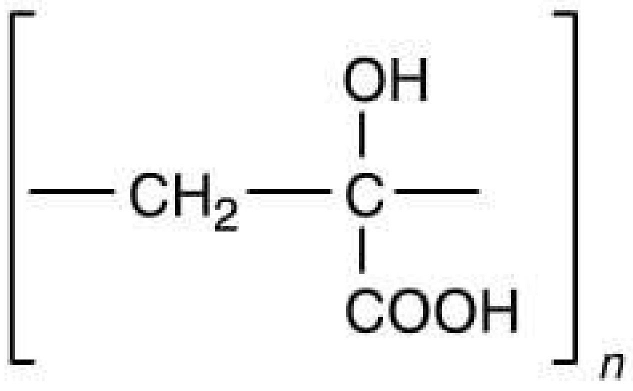
- poly(butadiene-1,2-dicarboxylic acid) EMA (10.35)
  which is an ethylene–maleic acid copolymer
- poly(α-hydroxyacrylic acid) PHAS (10.36)
- poly(3-hydroxymethylhexatriene-1,3,5-tricarboxylic acid) (10.37)
  which is a copolymer of acrylic acid with hydroxymethacrylic acid
- poly(3-formylhexatriene-1,3,5-tricarboxylic acid) (10.38)
  which is a copolymer of acrylic acid with 2-formylacrylic acid.



$$\left[-CH_2-CH_2-\underset{HOOC}{\underset{|}{CH}}-\underset{COOH}{\underset{|}{CH}}-\right]_n$$

10.35

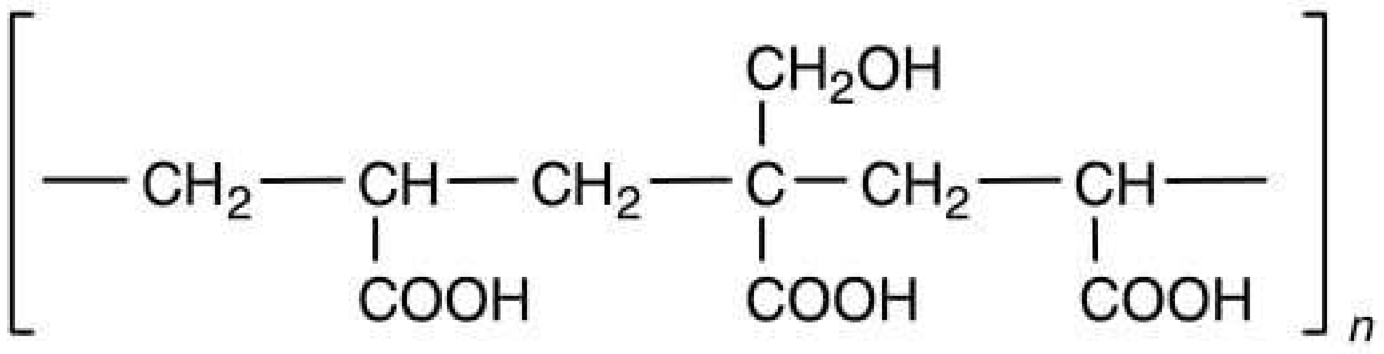
EMA



$$\left[-CH_2-\overset{OH}{\overset{|}{\underset{COOH}{\underset{|}{C}}}}-\right]_n$$

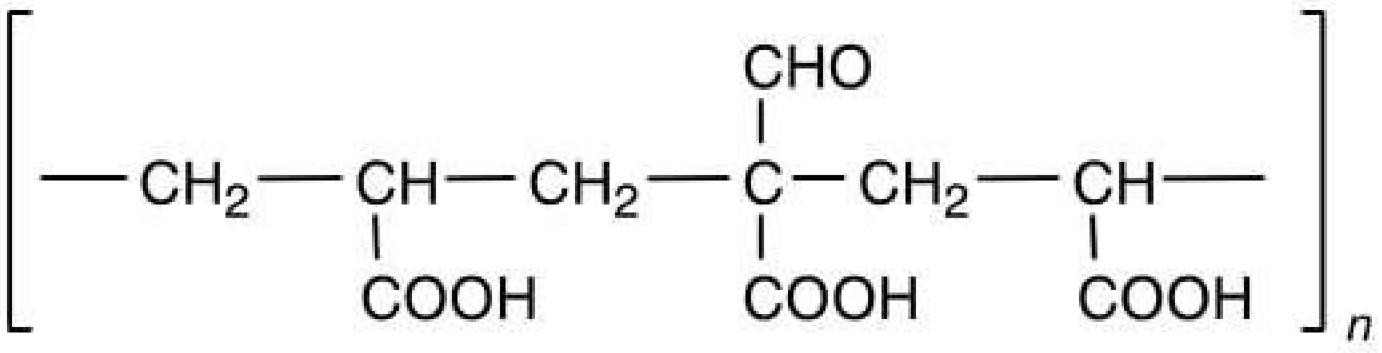
10.36

PHAS



$$\left[-CH_2-\underset{COOH}{\underset{|}{CH}}-CH_2-\overset{CH_2OH}{\overset{|}{\underset{COOH}{\underset{|}{C}}}}-CH_2-\underset{COOH}{\underset{|}{CH}}-\right]_n$$

10.37



$$\left[-CH_2-\underset{COOH}{\underset{|}{CH}}-CH_2-\overset{CHO}{\overset{|}{\underset{COOH}{\underset{|}{C}}}}-CH_2-\underset{COOH}{\underset{|}{CH}}-\right]_n$$

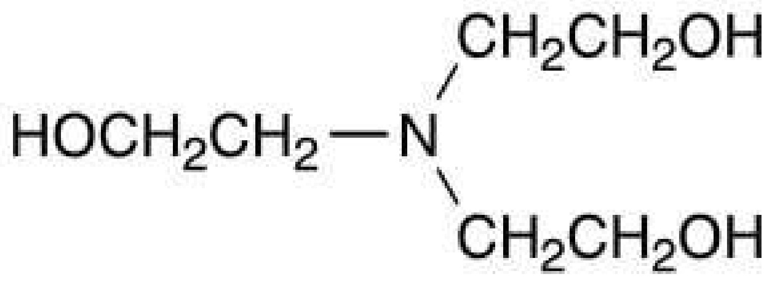
10.38

These agents are generally described as ion-exchange reagents rather than complex-forming chemicals. They tend to operate by sequestering the metal by an ion-exchange mechanism and as a result of their polyelectrolytic character they keep the complex dispersed. Oligomers with a molecular mass of 1200–8000 (i.e. relatively low) are said to give optimum sequestering power. Polymers of high molecular mass (i.e. $M_r = 10^6$–10^7) are useful as flocculating agents or migration inhibitors.

Although these acrylic oligomers and polymers show little decomposition in effluent treatment, they pose no significant threat to the environment since they can be removed easily by adsorption on activated sludge or by precipitation as an insoluble calcium complex [23]. Exhaustive tests have not revealed any adverse environmental influence. Their aquatic toxicity is negligible and toxicity to warm-blooded mammals is slight. Mutagenic, carcinogenic or teratogenic effects have not been found so far.

A further development [27] is the formation of so-called sugar–acrylate copolymers in which acrylic acid is copolymerised with glucose or other saccharides. Unlike other sequestering agents these polymers are said to be readily biodegradable, this being the main reason for their development.

An unusual type of sequestering agent is triethanolamine (10.39). This compound is cheap and exclusively useful for complexing iron(III) in strongly alkaline solutions, e.g. up to 18% sodium hydroxide. It does in fact remain active as a complexing agent even in more strongly alkaline solutions although solubility can be a problem.



10.39

Triethanolamine

10.2.5 The action of sequestering agents

Sequestering agents are often used rather indiscriminately, in amounts far in excess of the stoichiometric quantities required by the particular set of conditions. Instructions often simply state 'add 0.5–1.0 g/l of a suitable sequestering agent such as EDTA'. Whilst this is convenient for most purposes, it is worth bearing in mind that the action of sequestering agents is governed by physico-chemical factors that, among other things, determine a hierarchy of efficacy. When the type and concentration of trace-metal ions to be sequestered is known, a more discriminatory approach can be adopted regarding the choice of agent. In some cases, including the treatment of water, this more precise specification of type and quantity can be important.

Little more need be said here about the simple ion-exchange reactions such as that between sodium hexametaphosphate and calcium ions (Scheme 10.7). It is useful, however, to consider in more detail those reactions involving chelation (Scheme 10.8). This is a reversible reaction, the equilibrium being dependent on the process pH and the concentrations of the reacting species (Equation 10.2). While chelated complexes are less stable at higher temperatures, this effect can be ignored in practice. The factors involved have been discussed in some considerable detail by Engbers and Dierkes [20,23].

$$\text{Sequestering agent (SA)} + \text{Metal ion (MI)} \rightleftharpoons \text{Chelated complex (CC)}$$

Scheme 10.8

$$K_s = \frac{[CC]}{[SA][MI]} \tag{10.2}$$

The stability of the complex is generally expressed in terms of its stability constant, which is the logarithm of the equilibrium constant (K_s in Equation 10.2) of the reaction in Scheme 10.8. A high stability constant indicates a powerful sequestering effect. For example, amongst the aminopolycarboxylates the stability constant for a given metal ion generally increases in the order: NTA < HEDTA < EDTA < DTPA. Metals can also be listed in order of increasing stability constant: $Mg^{2+} < Ca^{2+} < Mn^{2+} < Al^{3+} < Zn^{2+} < Co^{3+} < Pb^{2+} < Cu^{2+} < Ni^{3+} < Fe^{3+}$. The stability constants at 25 °C for six metals with four different aminopolycarboxylates are shown in Figure 10.4.

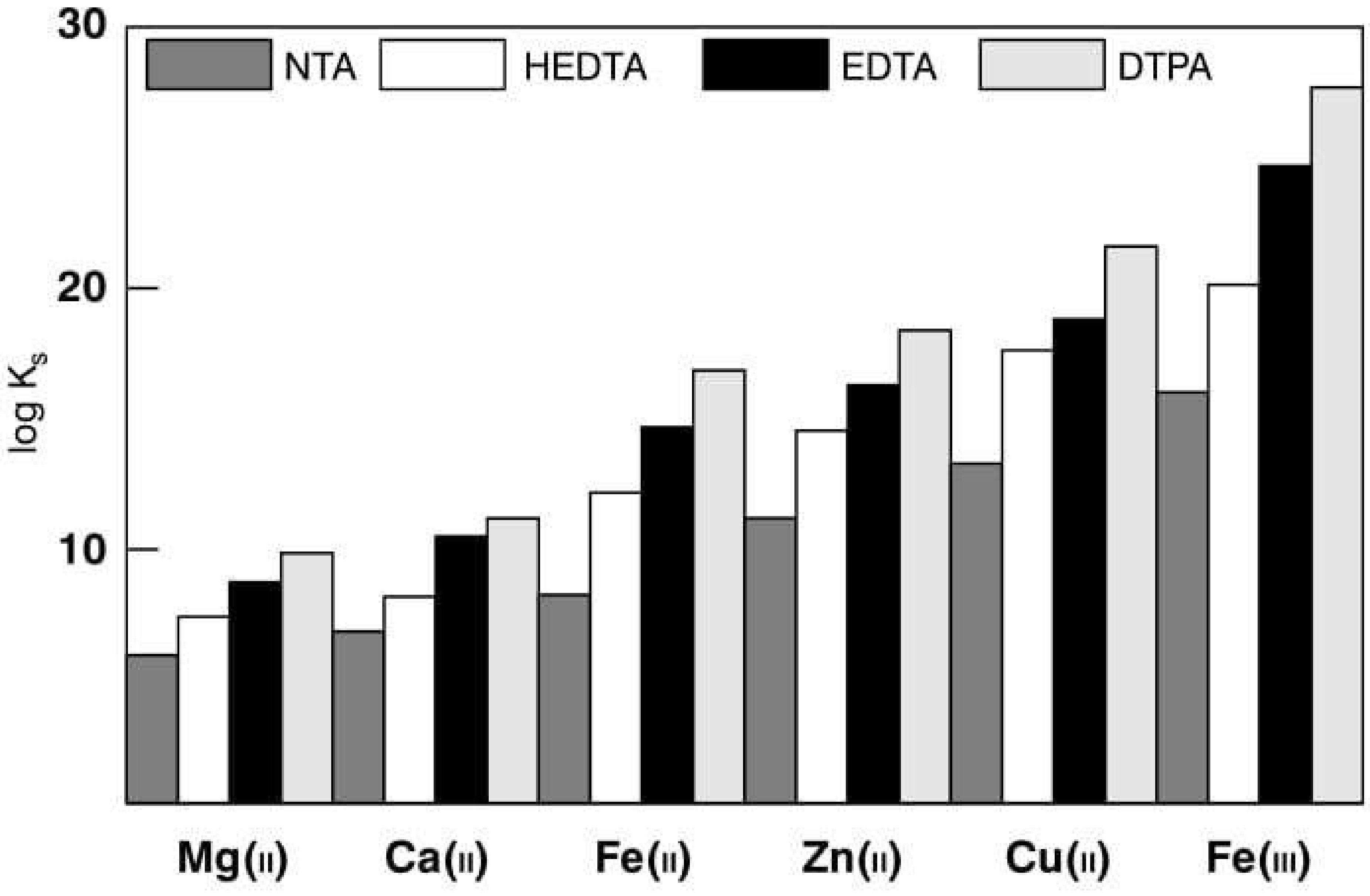


Figure 10.4 Stability constants of aminopolycarboxylate chelates [20]

Thus for the series of sequestering agents and metal ions mentioned, the magnesium–NTA complex has the lowest stability and iron(III)–DTPA the highest. This scale of values effectively constitutes a displacement series. This means, in general, that in any system containing more than one metal it is the metal forming the most stable complex (that is, the complex having the highest stability constant) that chelates preferentially. When these ions have been completely chelated, any remaining sequestering agent then begins to sequester the metal that forms the complex having the next highest stability constant. Similarly if iron(III) enters a system in which, for example, calcium is already chelated, the iron will displace the calcium since the iron complex has the higher stability constant. The calcium will only remain chelated if sufficient sequestering agent is present to sequester both iron and calcium.

Adding protons or hydroxide ions to the system will influence the position of the chelation equilibrium. The stability constant of a complex is thus influenced by the pH of the system and pH is an important consideration in the choice of sequestering agents. Figure 10.5 provides a very good illustration of the high sensitivity of the conditional stability constant (K_c) to the pH of the system, using the same four aminopolycarboxylates in the presence of iron(II) and iron(III). The pH-related stability constant is known as the conditional stability constant, log K_c. The effects of pH on the conditional stability constants of the same four aminopolycarboxylates with other metal ions are shown in Figures 10.6 to 10.9.

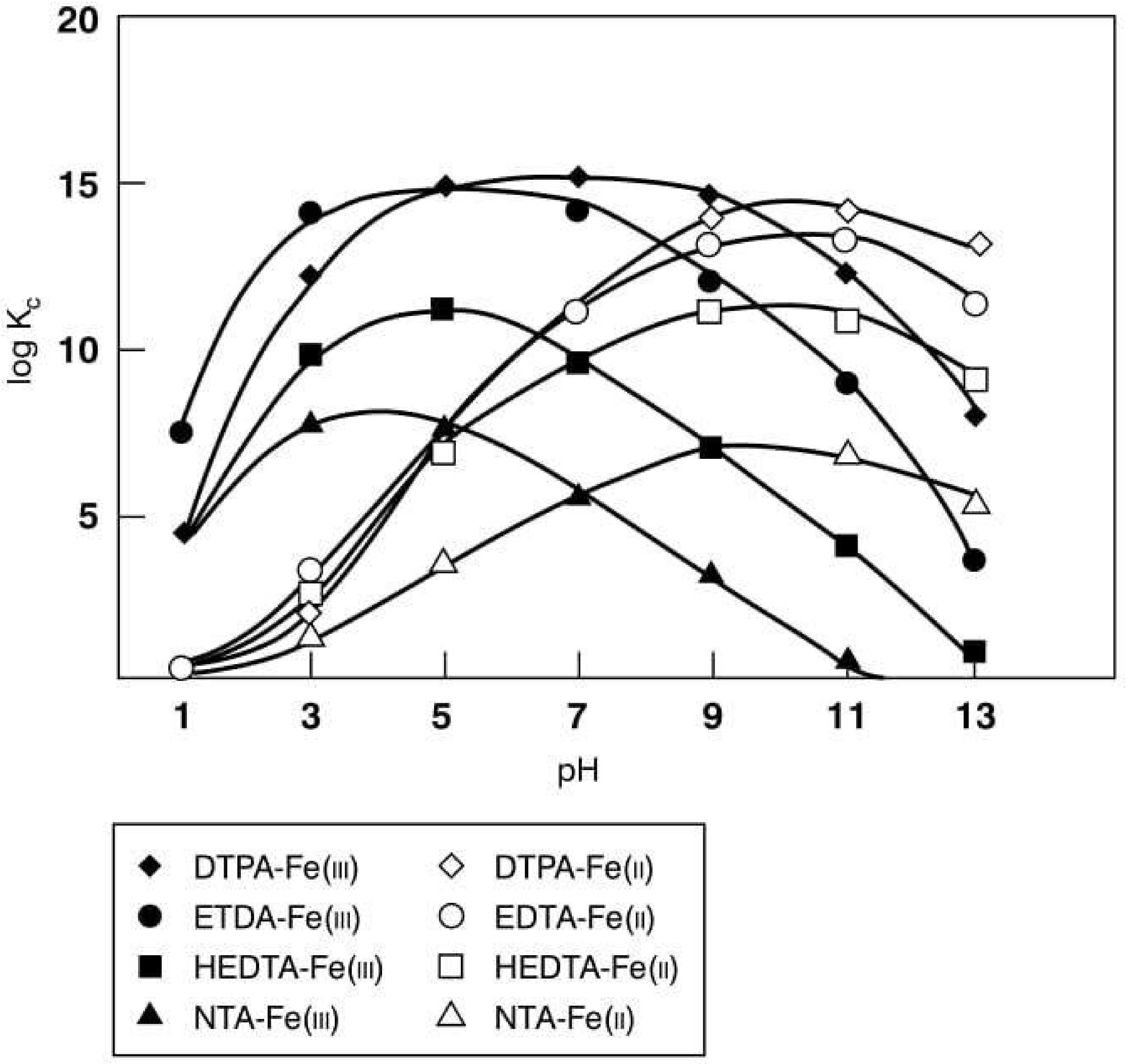


Figure 10.5 Effect of pH on the conditional stability constants at 25 °C of Fe(III) and Fe(II) chelates of aminopolycarboxylic acids [20]

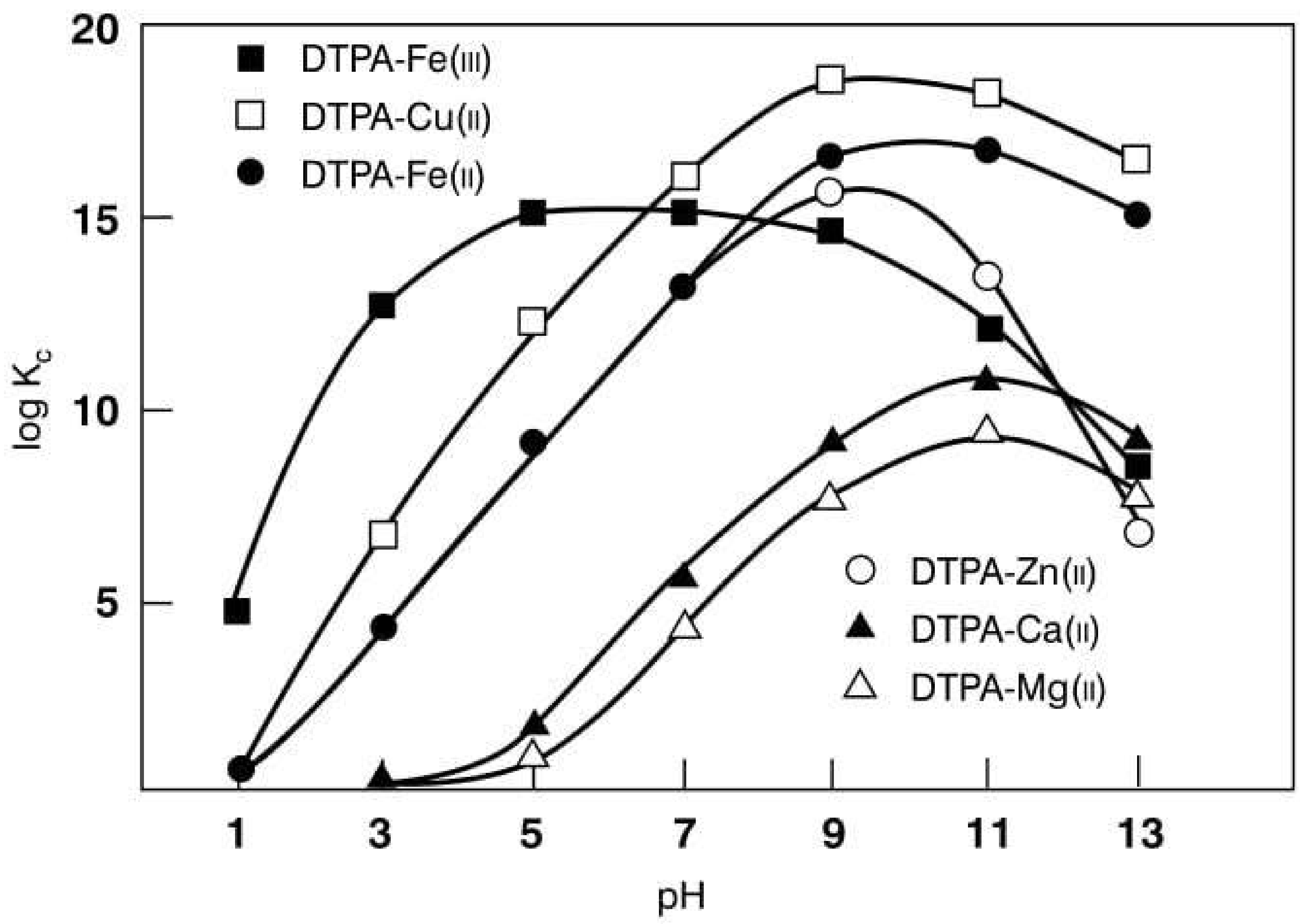


Figure 10.6 Effect of pH on the conditional stability constants at 25 °C of metal chelates of DTPA [20]

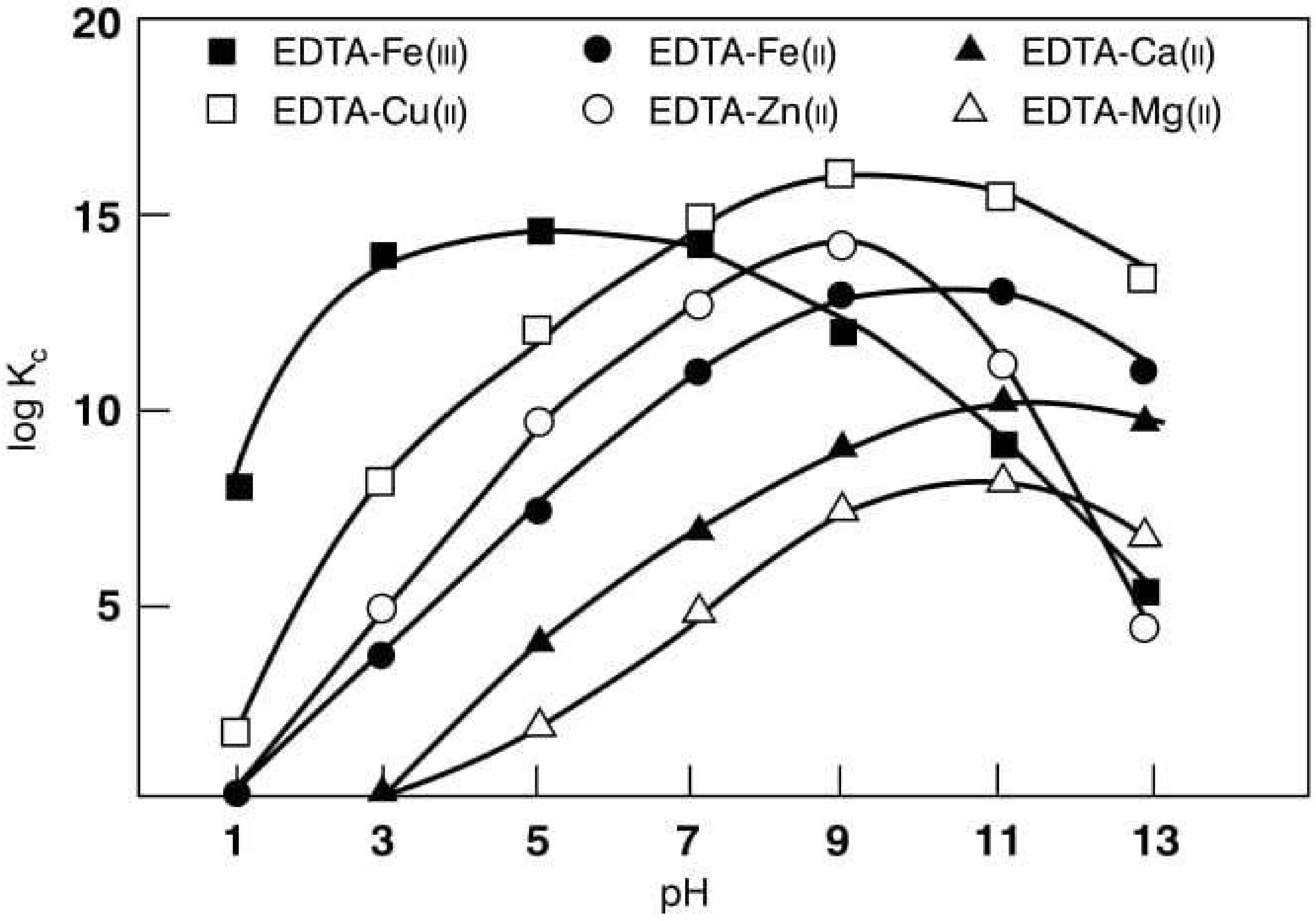


Figure 10.7 Effect of pH on the conditional stability constants at 25 °C of metal chelates of EDTA [20]

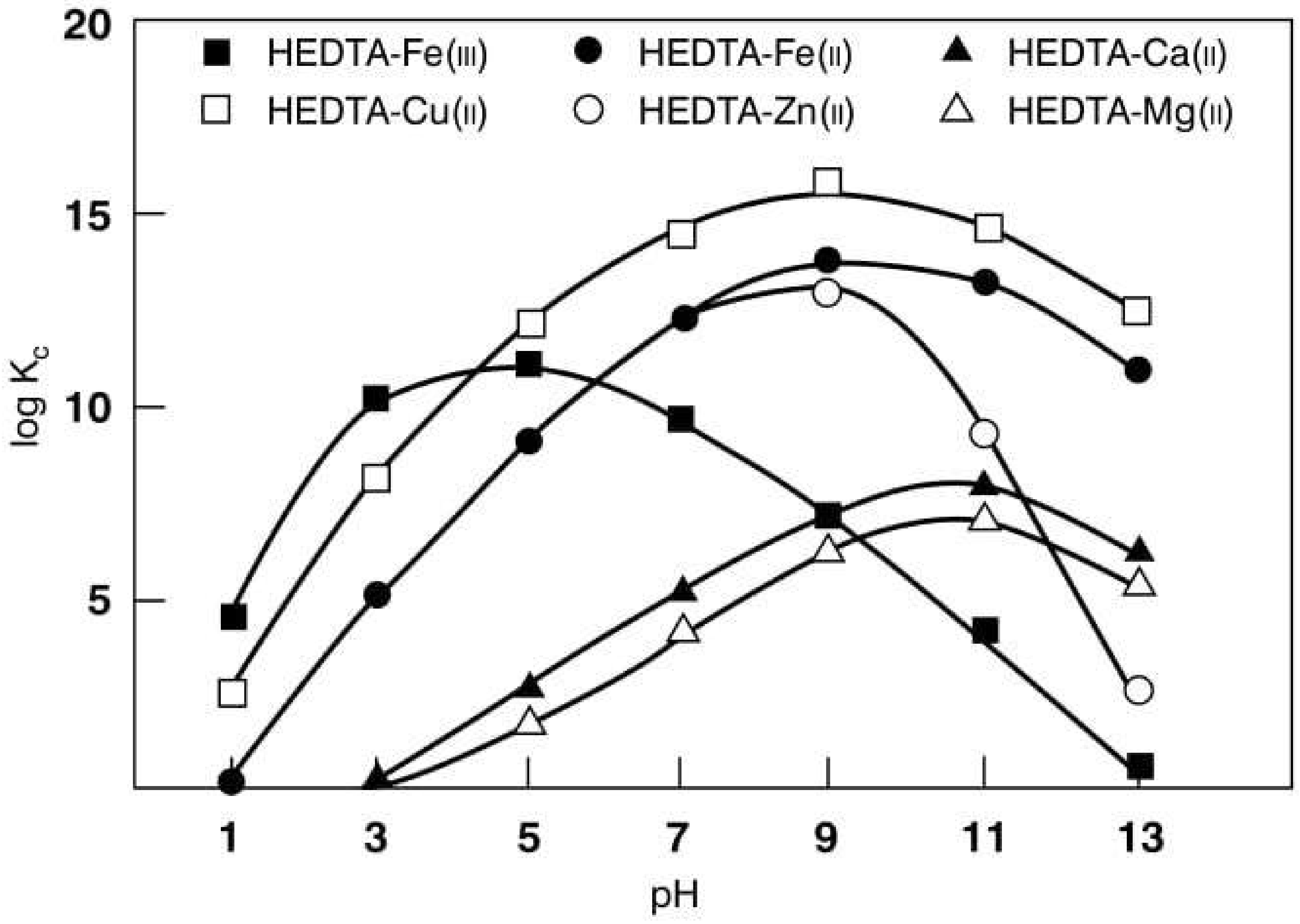


Figure 10.8 Effect of pH on the conditional stability constants at 25 °C of metal chelates of HEDTA [20]

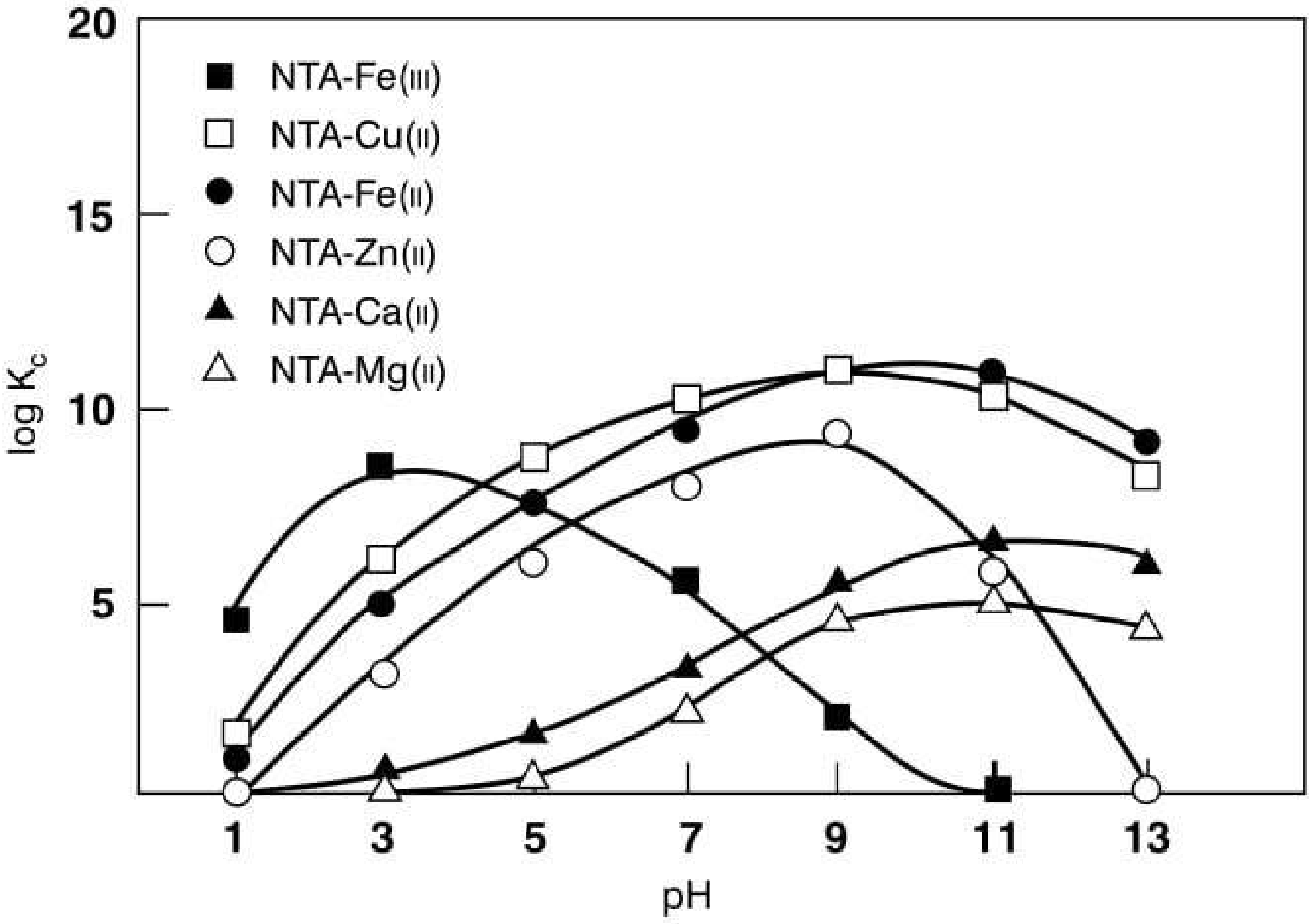


Figure 10.9 Effect of pH on the conditional stability constants at 25 °C of metal chelates of NTA [20]

It should not be overlooked that stability constants can be affected significantly by the presence of electrolytes. For example, the stability constant of the Ca–EDTA complex changes from 12 in distilled water to 10.5 in 0.1N KCl and to 8.5 in 1.0N KCl. The inorganic polyphosphates tend to be most efficient under slightly acidic conditions whilst the aminopolycarboxylates generally work best under neutral or alkaline conditions, although they still show some usefulness, and are used, at pH values of around 4.5. Generalisations like these can be misleading, however, since efficiency varies from one metal ion to another at different pH values for each sequestering agent. The phosphates are good sequestrants for magnesium and calcium but are considerably less effective for trivalent cations, which can be successfully sequestered with NTA, EDTA and DTPA up to about pH 9. At higher pH values iron(III) tends to be precipitated from these complexes. It was mainly for this reason that the hydroxyaminocarboxylates were developed, this basically being their main use. For example, HEDTA will sequester iron(III) ions at pH 9 and DEG works well at pH 12. Although effective with most metal ions, DEG will not sequester calcium or magnesium, and HEDTA is also not as efficacious with these hard water ions as are the aminopolycarboxylates. At pH values above 12 iron(III) can be sequestered with triethanolamine (10.39), either alone or together with EDTA.

Most divalent and trivalent ions, with the exception of the alkaline-earth metals, are effectively chelated by the hydroxycarboxylates citric and tartaric acid, and citric acid will also sequester iron in the presence of ammonia. Another hydroxycarboxylate, gluconic acid, is especially useful in caustic soda solution and as a general-purpose sequestering agent.

Clearly, the efficiency of sequestering action must be optimised for a specific set of conditions. Thought needs to be given especially to the pH of the system and to whether broad-spectrum or specific sequestering is required. The extent of knowledge of the trace-metal ions present will determine whether a precise addition or an arbitrary excess of agent is appropriate. Finally, in some circumstances problems can arise from the use of certain sequestering agents that can remove the coordinated metal from a dye chromogen with subsequent changes in shade or fastness properties. Metal-complex acid dyes and mordanted dyes are obviously vulnerable, but also many direct and reactive dyes contain coordinated copper atoms.

10.2.6 The uses of sequestering agents

Notwithstanding the comments made above in relation to the need to adopt a more or less sophisticated approach to the selection and use of sequestering agents to target known contamination by trace metals, an attempt will now be made to provide general recommendations [28]. This approach will also indicate the wide range of uses for these agents in textile wet processing.

Sized warp yarns sometimes contain metal salts or complexes (e.g. copper or zinc compounds) as fungicides or bactericides and these can interfere with enzyme action in subsequent desizing. Phosphonates such as ATMP, DETMP, EDTMP and PBTC are suitable for use here, sequestering the heavy metals at pH 6.8–7.0, the effectiveness of each agent being dependent on the type of enzyme and the metal ions present. The use of the phosphonates HEDP or PBTC helps to reduce cellulose damage to a minimum in oxidative desizing with persulphate.

In the kier boiling of cotton, the action of sodium hydroxide can be intensified by the use

of sequestering agents. The phosphonates EDTMP, HEDP and PBTC have been recommended. In practice, however, the tendency is to use synergistic mixtures, such as:
– phosphonate and gluconate
– phosphonate and triethanolamine
– aminopolycarboxylate and gluconate or triethanolamine.

Polycarboxylates may also be added to increase dispersing power and so reduce the possibility of incrustations. Fine-tuning will again depend on the process details, the machine type and the degree of scouring necessary.

Phosphonates are useful additions in acidification treatments after alkaline processing to assist in the removal of metal compounds that have limited solubility in alkali.

Under the strongly alkaline conditions of mercerising, addition of either gluconate or triethanolamine with a little HEDP is useful. The presence of a polycarboxylate helps to prevent precipitation on machine components.

Certain transition-metal salts catalyse redox reactions, leading to uneven treatment and perhaps damage to the substrate. Sequestering agents are therefore employed to complex these metal ions and so to inhibit their catalytic activity. In reductive bleaching with dithionite, PBTC acts as a stabiliser at pH 5.5–6.5 and EDTA also gives good results. At higher pH values, aminopolyphosphonates (e.g. EDTMP) and aminopolycarboxylates are useful. Only triethanolamine is effective at pH 13. For oxidative bleaching with hypochlorite or chlorite, the amine oxides of ATMP and PBTC may be used. Aminopolycarboxylates are less suitable, whilst the amine oxide of NTA is unsuitable.

In the stabilisation of peroxide with silicate, the use of a polycarboxylate, perhaps in combination with a polyphosphonate such as DETMP (or PBTC in a lesser amount) helps amongst other things in preventing fibre damage and incrustations on fabric or machine. Conversely, aminopolyphosphonates such as EDTMP or DETMP may themselves be suitable as stabilisers in the absence of silicate. Combinations of sequestering agents may also be used to obtain a synergistic effect, the following mixtures having been suggested for use with silicates:
– DETMP, HEDP and either gluconate or triethanolamine
– DETMP, DTPA and gluconate.

Polycarboxylates may also be added to help prevent incrustations. It should be borne in mind, however, that magnesium is an essential component in most cases of stabilisation in peroxide systems, so any mixture of sequestrants should have minimum binding effect on this metal ion.

In the pretreatment and dyeing of synthetic fibres, the aminopolyphosphonates can assist in the removal of oligomers.

Some dyes contain a coordinated transition metal as an essential part of their chromogenic structure and this must be left undisturbed by any sequestrant used to complex extraneous metal ions in the system. Hence a balance of properties is needed, phosphates and hydroxycarboxylates being useful. It is claimed that polycarboxylates can be molecularly engineered to give the required balance of properties.

Wool is exceptionally prone to absorb metal ions, particularly in the weathered tips of the fibres, leading to shade differences on subsequent dyeing, especially if chelatable dyes are used. Hence sequestering agents can be essential additions to scouring, rinsing and dyeing baths in order to remove this absorbed metal. However, it is difficult to say which sequestrant or mixture of sequestrants gives the best results. Careful laboratory tests need to be carried out beforehand, taking into account the chemical structure of the dyes to be used, the type of metal ions involved, the pH value of the dyebath and the type and concentration of electrolyte present.

In many dyeing and printing operations, livelier, more intense colours can be obtained with better reproducibility and perhaps better fastness to rubbing by careful choice of sequestering agent for use in the coloration process. The addition of triethanolamine with vat dyes can be beneficial in helping to prevent unnecessary loss of reducing agent or over-oxidation. Triethanolamine together with EDTMP or HEDP can be used where the concentration of alkali is less than 10 g/l NaOH (or 22 ml/l caustic soda liquor 38°Bé). Bronzing of sulphur dyeings can often be prevented using triethanolamine with polyphosphate, polyphosphonate or polycarboxylate. Azoic combinations can be very sensitive to metal contamination. EDTA, or perhaps combinations of polyphosphate, polyphosphonate or polycarboxylate, can help in the solubilisation of naphtholates and in the stabilisation of their colloidal solutions, whilst EDTA, for example, can assist in protecting solutions of diazonium salts from metal-induced catalytic decomposition.

Polyphosphates, or in lower amounts the very effective polyphosphonates, are helpful in applications of fluorescent brightening agents. Sequestering agents can be useful additions in the afterwashing of dyeings and prints, for example polyphosphates, polyphosphonates or polycarboxylates such as, amongst others, a polyacrylate of molecular mass 3000–4000 or an acrylic–maleic acid copolymer. In the soaping of vat or azoic dyeings, recrystallisation is accelerated and rubbing fastness improved by the use of sequestering agents, examples being mixtures of polyphosphonates and polycarboxylates, such as HEDP and an acrylic–maleic acid copolymer.

The sugar–acrylate polymers [27] are recommended for applications similar to those mentioned above for polycarboxylate polymers and copolymers.

10.3 MACROMOLECULAR COMPLEXING AGENTS

Macromolecular complexing agents have featured a good deal in recent research. Although they do not yet appear to have attained any significant commercial use, they possess interesting properties, not least their environmental advantages, that offer potential for future exploitation.

The term macromolecule includes all large molecules, including textile fibres and polymers. The polyelectrolytes used as dispersing agents (section 10.6) or as thickening agents and migration inhibitors (section 10.8) are examples of linear macromolecules. Cyclic macromolecules are also known. An important feature of such macromolecules often responsible for their functioning as auxiliaries is their ability to form complexes, particularly with dyes or fibrous polymer segments. In the case of linear macromolecules, the complexes are generally formed by multipoint attachment with the smaller entity situated alongside the macromolecule. Cyclic macromolecules, on the other hand, may exhibit the interesting property of complexing another compound within its centre, the macromolecule completely surrounding the complexed entity. Thus such agents have some functional similarity with sequestering and chelating agents. However, whereas sequestering and chelating agents are generally used to complex simple metal ions, the macrocyclic complexing agents are usually engineered to complex with bigger molecules such as dyes, polymer segments or surfactants and do not act as simple metal-sequestering agents. It is these properties that have stimulated much research into the possible uses of macrocyclic complexing agents as auxiliaries in coloration processes or as agents for helping to clean up textile wastes. It is particularly interesting that certain macrocyclic agents can be obtained from natural replenishable sources. Four types of macrocyclic complexing agents are considered here:

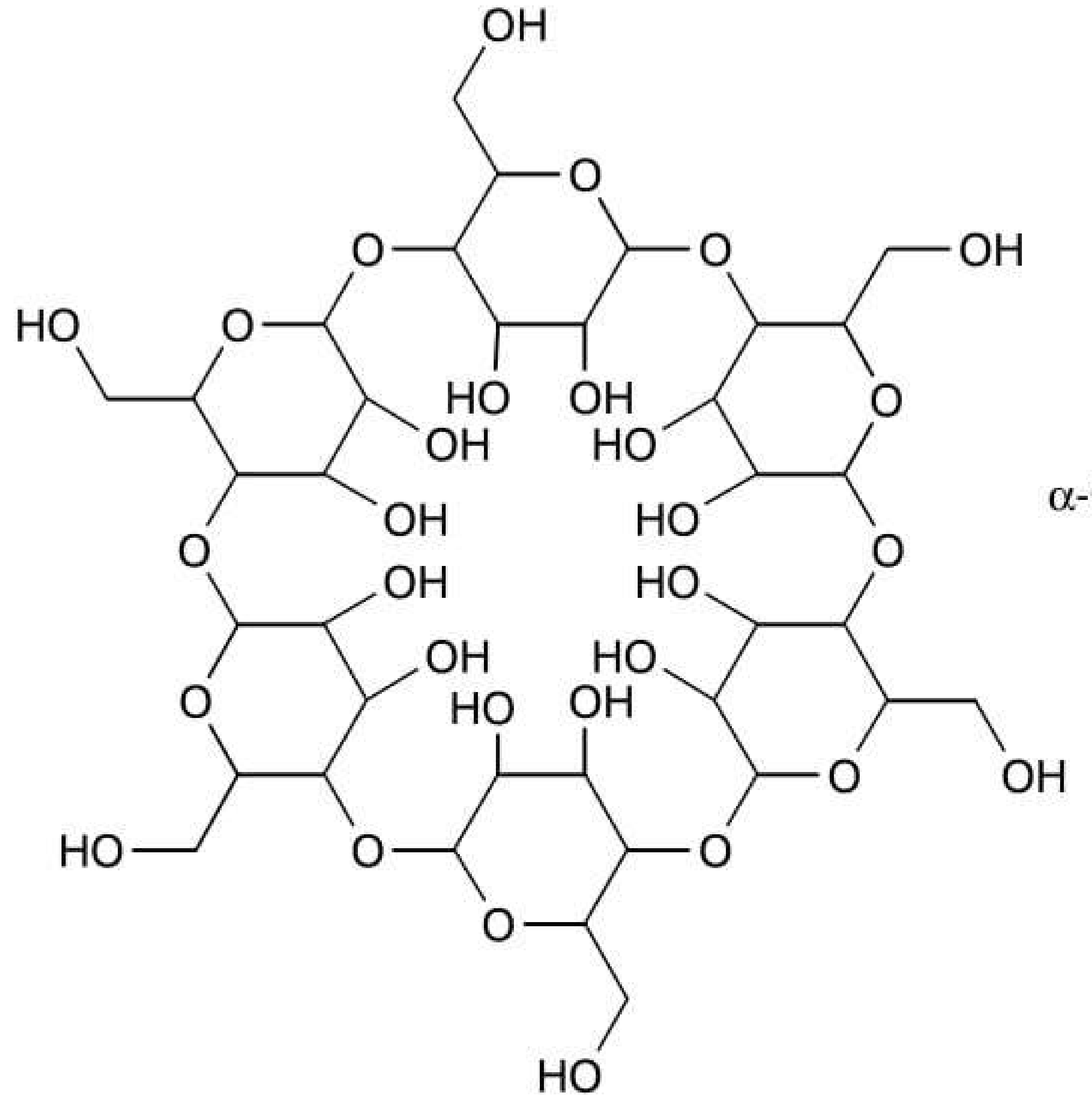
- cyclodextrins
- cucurbituril
- crown ethers
- liposomes such as phosphatidylcholine derivatives.

The discussion, however, is relatively brief in view of the fact that little commercial development seems to have taken place so far.

10.3.1 Cyclodextrins

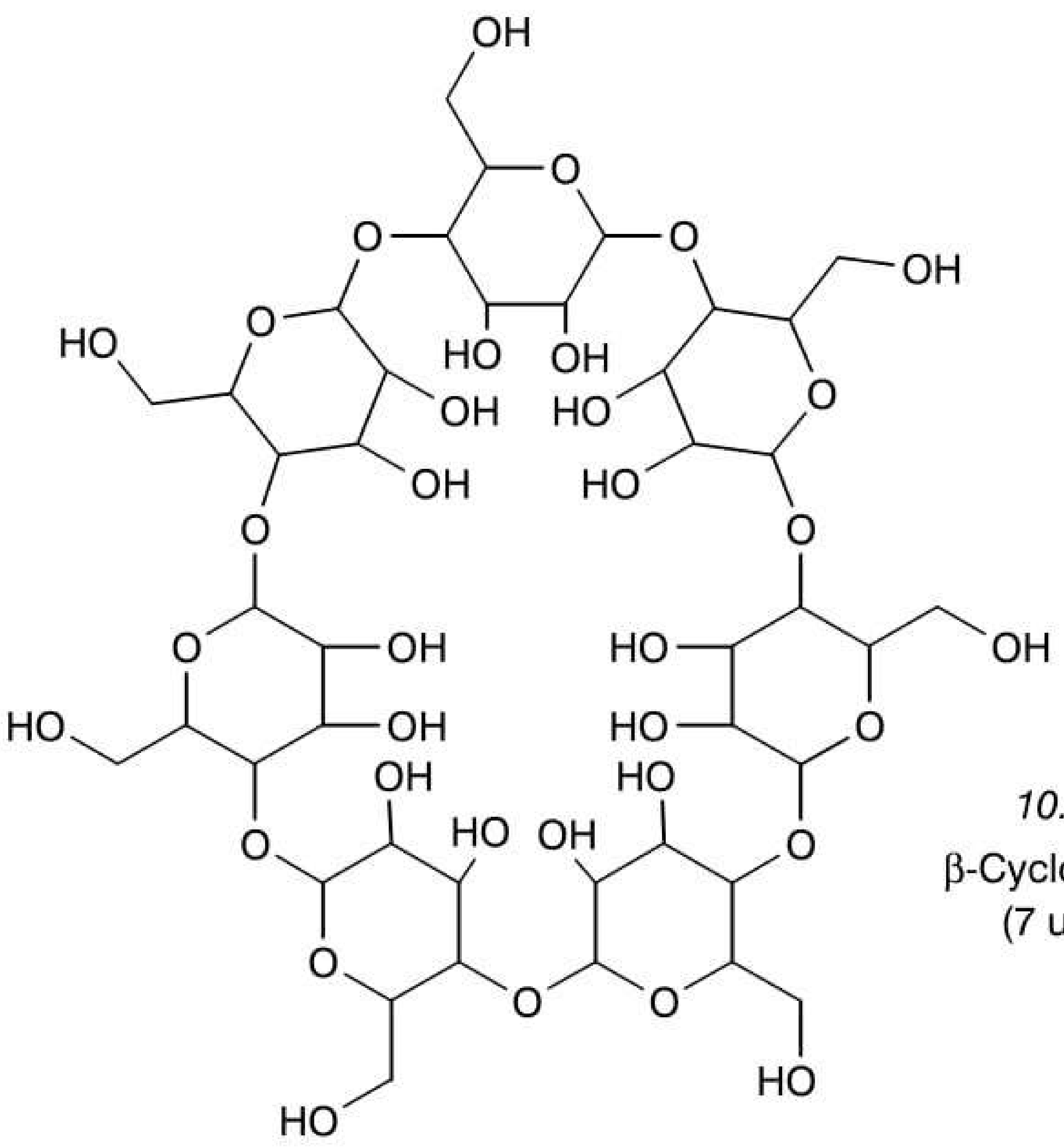
Cyclodextrins are obtained by enzymatic depolymerisation and extraction from starch. They comprise rings of D-glucose units and α-, β-, or γ-cyclodextrin can be obtained [29], depending on whether 6, 7 or 8 glucose units are present in the ring (10.40). The dimensions of the outer and inner surfaces increase as the number of glucose units increases (Figure 10.10). The important characteristic feature of these cylindrical structures that influences their properties lies in the different nature of their surfaces, the outer being essentially hydrophilic whilst the inner is essentially hydrophobic [29–31]. Thus the outer surface confers aqueous solubility whilst the inner surface is capable of attracting suitably configured hydrophobic moieties into the cavity, thus forming a complex, sometimes referred to as an inclusion complex. Obviously, the size of the hydrophobic moiety to be complexed must be such that it can fit into the cavity of the cyclodextrin used (i.e. α, β or γ).

In addition, the versatility of cyclodextrin macromolecules as a group is enhanced by the fact that derivatives of cyclodextrins can be prepared [32]. This is achieved, for example, by

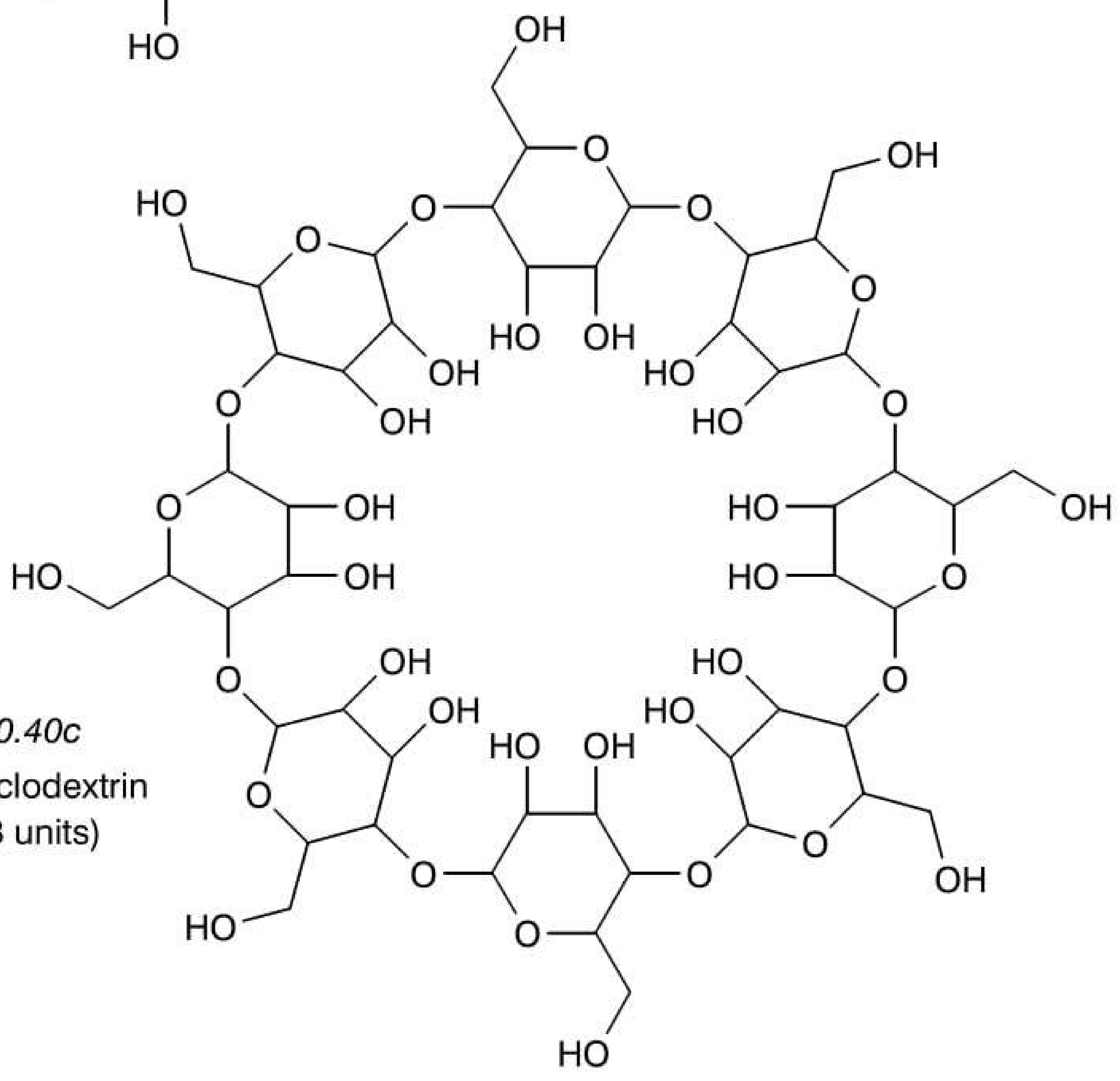


10.40a

α-Cyclodextrin (6 units)



10.40b
β-Cyclodextrin
(7 units)



10.40c
γ-Cyclodextrin
(8 units)

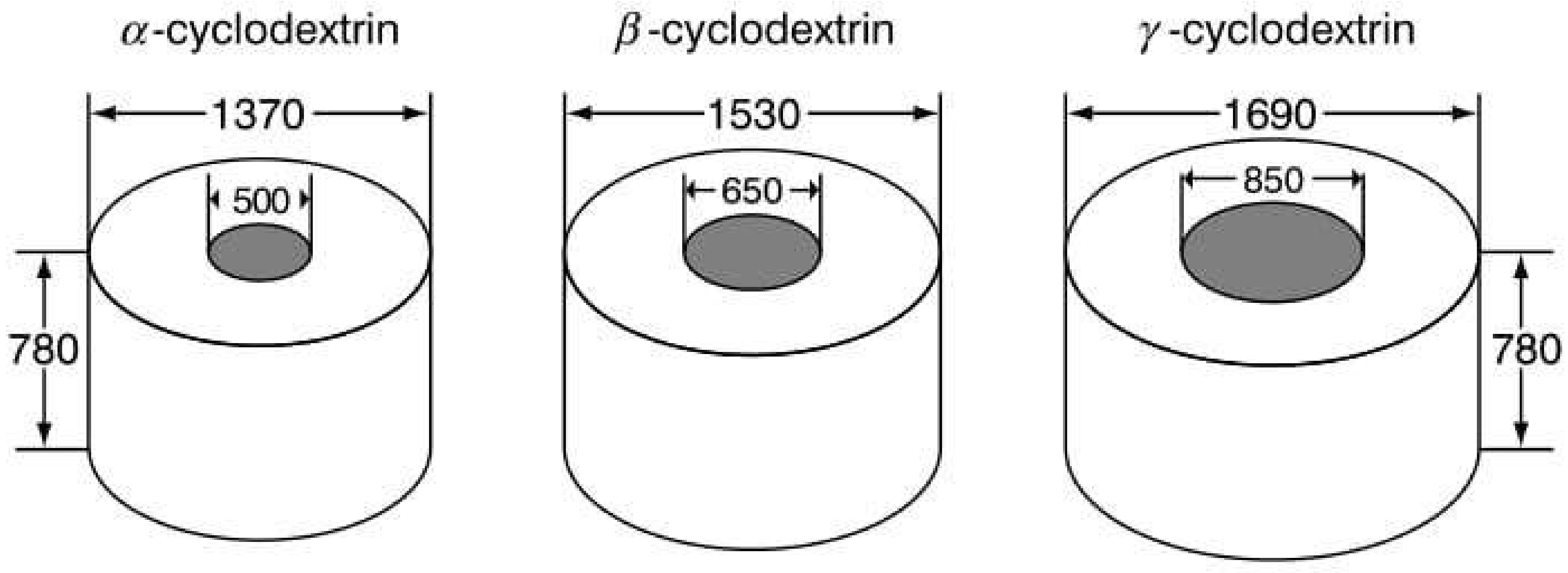
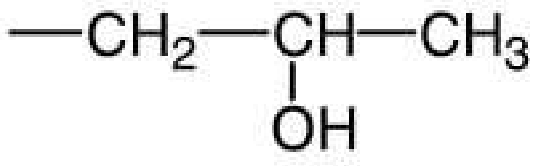
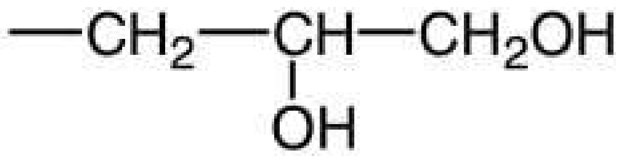
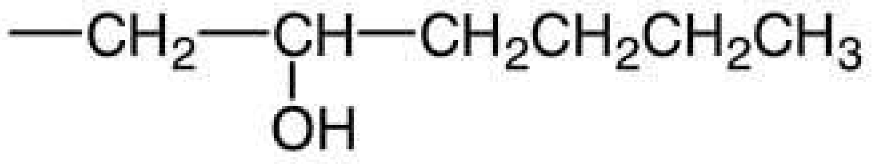
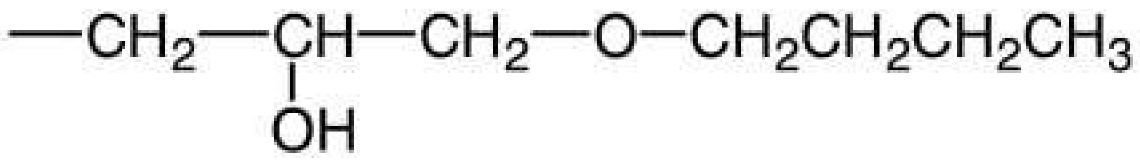
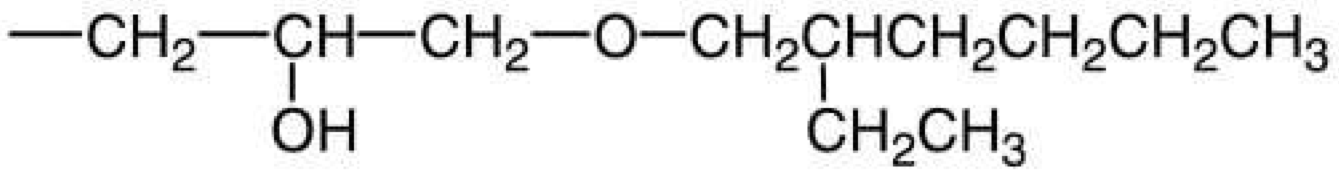
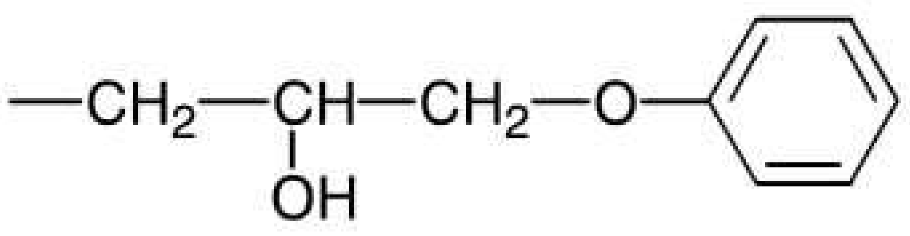
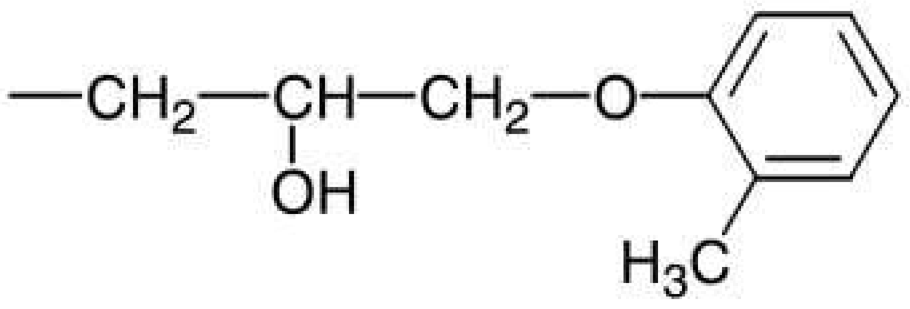
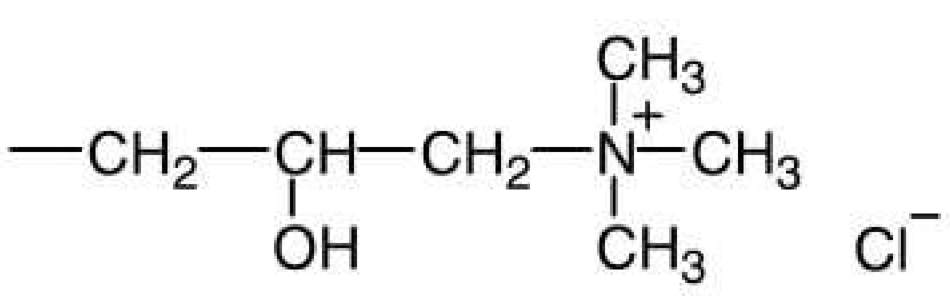
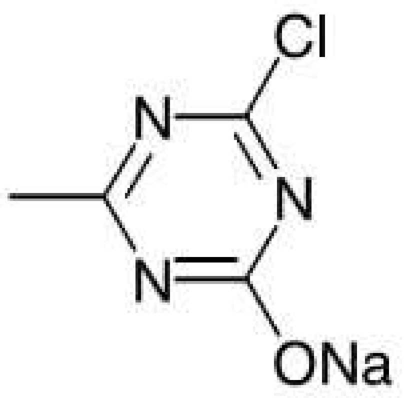
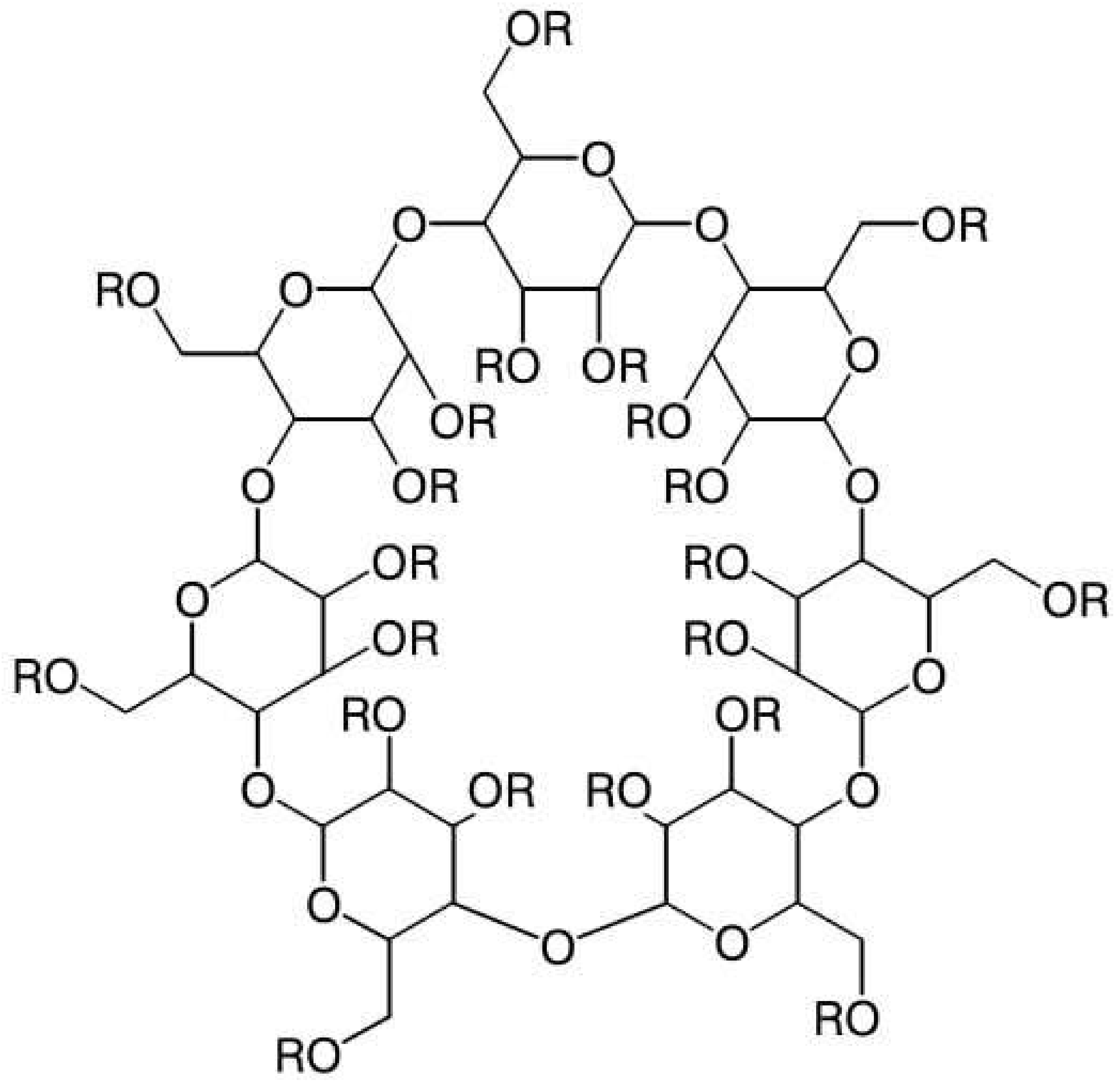


Figure 10.10 Dimensions of cyclodextrins [29]

substituting to various degrees the hydrogen atoms of the hydroxy groups (Table 10.1). Introduction of a hydroxypropyltrimethylammonium chloride grouping gives a cationic derivative, whilst the monochlorotriazinyl substituent gives rise to a derivative that is analogous to a reactive dye. This cyclodextrin derivative, therefore, is capable of reacting with fibrous macromolecules that contain nucleophilic groups.

Table 10.1 Typical derivatives of β-cyclodextrin [32]

R Group	
$-H$	β-cyclodextrin
 $-CH_2-\underset{OH}{CH}-CH_3$	2-hydroxypropyl
 $-CH_2-\underset{OH}{CH}-CH_2OH$	2,3-dihydroxypropyl (glyceryl)
 $-CH_2-\underset{OH}{CH}-CH_2CH_2CH_2CH_3$	2-hydroxyhexyl
 $-CH_2-\underset{OH}{CH}-CH_2-O-CH_2CH_2CH_2CH_3$	*n*-butylglyceryl
 $-CH_2-\underset{OH}{CH}-CH_2-O-CH_2\underset{CH_2CH_3}{CH}CH_2CH_2CH_2CH_3$	2-ethylhexylglyceryl
	phenylglyceryl
	*o*-tolylglyceryl
$-CH_2-COONa$	sodium carboxymethyl
 $-CH_2-\underset{OH}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3 \quad Cl^-$	2-hydroxypropyltrimethylammonium
	monochlorotriazinyl



Once complex formation has taken place, the physico-chemical nature of both the cyclodextrin and the complexed substance is changed. For example, complexing diminishes the vapour pressure of volatile compounds and increases the stability of compounds that are sensitive to light or air [32]. The aqueous solubility of some sparingly soluble compounds can be increased by complexing, this being attributable to the influence of the hydrophilic exterior of the cyclodextrin. Complexing with cyclodextrin can also increase the hydrolytic stability of some compounds, including dyes [29]. The functionality of cyclodextrin complexes, like that of metal-sequestrant complexes, is governed to a large extent by the stability constant of the complex and this is markedly influenced by stereochemical factors.

Cyclodextrins have ecologically advantageous properties. Not only are they produced from natural and replenishable sources, they are biodegradable, non-toxic and possess no allergenic potential [32,33]. They are commercially available in bulk quantities at an optional degree of purity and have been used for many years in pharmaceuticals.

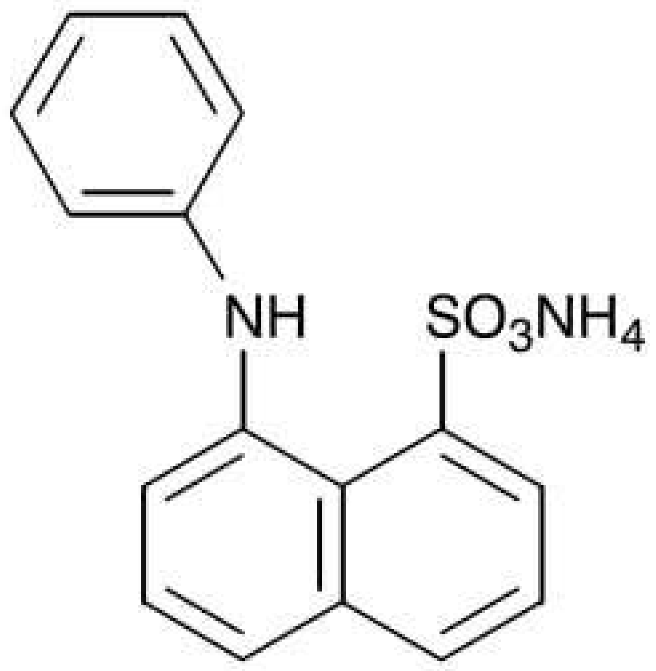
The general uses of cyclodextrins (i.e. non-textile as well as textile) have been reviewed [30]. Research into possible textile applications has been ongoing since the 1950s and has covered many aspects, from preparation of substrates through coloration processes to finishing, as well as effluent treatment. A brief review of more recent textile-related research is given here to demonstrate the wide range of potential applications of these interesting products.

Substrate preparation

It has been claimed that complexes of β-cyclodextrin with anionic surfactants, notably higher fatty alcohol ethoxylates, improve scouring efficiency on cotton and wool in laboratory-scale processing [34]. Residual surfactants carried over from preparation can have undesirable effects in subsequent processing. When cyclodextrins complex with surfactants, their surface activity is reduced. Hence cyclodextrins are potentially useful for the removal of residual amounts of surfactants from substrates [35]. The use of α- and β-cyclodextrins has been studied in this context with one cationic, one anionic and four nonionic agents. α-Cyclodextrin tended to form weaker complexes than β-cyclodextrin. Methylated β-cyclodextrin was especially useful. The hollow interior of a β-cyclodextrin molecule is capable of the optimum accommodation of a benzene ring and is thus particularly good for complexing ethoxylated phenols.

Acid dyes

The formation of complexes of the fluorescent tracer dye ammonium 1-phenylaminonaphthalene-8-sulphonate (10.41) with cyclodextrins has been investigated with favourable results, especially in environmental studies [33]. The ability of this dye to complex with cyclodextrins has been exploited mainly as an analytical tool in the study of cyclodextrin applications, since its fluorescence is easily measured. The interaction of α-, β- and γ-cyclodextrins with azo acid dyes containing alkyl chains of different lengths has been reported [36,37]. The formation and isolation of solid complexes between β-cyclodextrin and CI Acid Red 42, CI Acid Blue 40 or Erionyl Bordeaux 5BLF (Ciba) have been reported [29].



10.41

Basic dyes

The structure and formation constants of α-, β- and γ-cyclodextrin complexes with azoniabetaine dyes have been studied, the formation constants decreasing in the order: β-CD > γ-CD > α-CD [31]. Complexes of methylene blue (CI Basic Blue 9) with cyclodextrins have been examined, β-cyclodextrin giving the highest stability constant. This was indicative of almost ideal fitting of the dye molecule into the cyclodextrin cavity [38]. Complexing with cyclodextrins increased the fluorescence intensity of the dye, this effect also being highest with β-cyclodextrin.

Direct dyes

The application to cotton of CI Direct Orange 46, Red 81 and Blue 71 at 90 °C in the presence of a cyclodextrin, sodium chloride and borax (to give pH 9) gave results that varied with the dye and auxiliary combination present [39]. The formation and isolation of solid complexes between β-cyclodextrin and CI Direct Orange 40, Orange 46, Blue 86 or Green 26 and between γ-cyclodextrin and Green 26 have been reported [29]. The complexes of β-cyclodextrin with Orange 46 or Green 26 were evaluated for the dyeing of cotton with them in the presence of electrolyte at 90 °C. Greater amounts of the complexes were needed to obtain depths matching those obtained conventionally using the uncomplexed dyes. It is not clear whether complexing with the cyclodextrin interferes with the capability of the dye to interact with the fibre in the usual way. The stability of these complexes does not appear to be high.

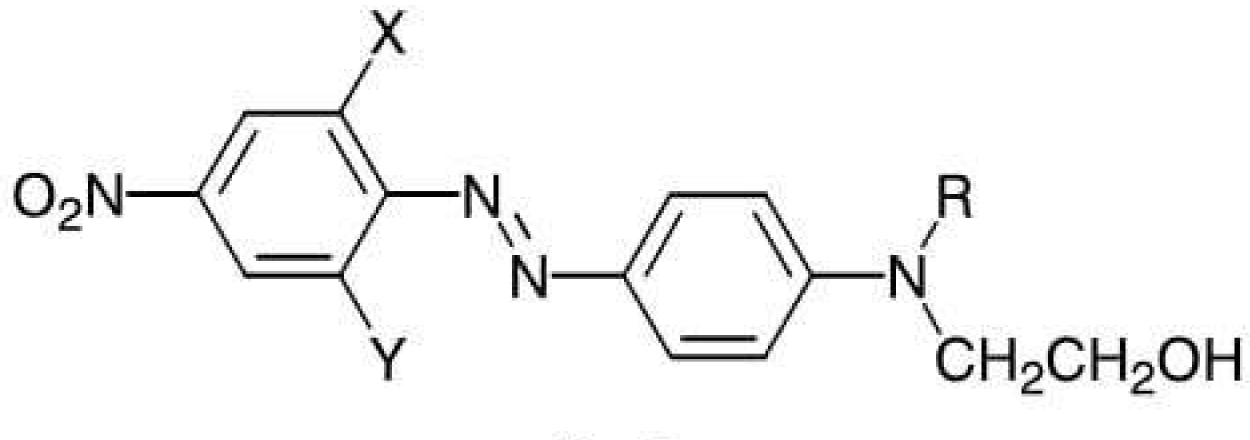
Disperse dyes

Detailed dyeing studies have been carried out using complexes formed between disperse dyes (Table 10.2) and cyclodextrins. One study [40,41] evaluated the complexing and subsequent dyeing properties of five related disperse dyes (10.42) on polyester. The results indicated that dyes which have no *ortho* substituents in the diazo component formed 1:1-complexes with α-, β- and γ-cyclodextrins. Dyes having electron-withdrawing groups in both of these *ortho* positions formed 1:1-complexes with β-cyclodextrin and 2:2-complexes with γ-cyclodextrin. Dyes 3 to 5 have a substituted diazo grouping that is larger than the cavity of α-cyclodextrin and so they are unable to form complexes with this macrocyclic molecule. It was suggested that such complexing could be used as a retarding mechanism in dyeing with disperse dyes, although these studies were restricted to a maximum temperature of 90 °C.

Table 10.2 Dyes used in complexing with cyclodextrins [40,41]

Dye	X	Y	R	MSCS
1	H	H	CH_2CH_3	4.35
2	H	H	CH_2CH_2OH	4.35
3	Cl	Cl	CH_3	7.29
4	Cl	Cl	CH_2CH_2OH	7.29
5	NO_2	Br	CH_2CH_2OH	8.21

MSCS maximum size of cross-section of the substituted ring in the diazo component



10.42

Buschmann *et al.* [29,42] have studied the formation and isolation of solid complexes between disperse dyes and cyclodextrins. Disperse dyes free from their usual diluents, such as dispersing agents, were used. Complexes were formed as listed in Table 10.3. CI Disperse Blue 79 did not form complexes with either β- or γ-cyclodextrin. The complexes with CI Disperse Orange 11, Orange 29, Red 82, Violet 1, Blue 165, Resolin Red FRL or Resolin Yellow 5GL were studied in the dyeing of polyester at 130 °C. An important aspect of these dyeings was that they were carried out using only the dye–cyclodextrin complex in water, without the addition of dispersing or levelling agents. Good level dyeings of high exhaustion were obtained, even though complexing with cyclodextrins increases the aqueous solubility of disperse dyes. Thus particularly important advantages are claimed for this process over the traditional method of dyeing with disperse dyes: the fact that no dispersing or levelling agents are needed coupled with higher exhaustion leads to much less pollution of the effluent.

Table 10.3 Formation of complexes between cyclodextrins and disperse dyes [42]

With β-cyclodextrin:	CI Disperse Yellow 3
	CI Disperse Yellow 42
	CI Disperse Orange 11
	CI Disperse Orange 29
	CI Disperse Violet 1
	CI Disperse Violet 31
	CI Disperse Blue 56
	CI Disperse Blue 165
	Resolin Red FRL (DyStar)
	Resolin Yellow 5GL (DyStar)
With γ-cyclodextrin:	CI Disperse Orange 11
	CI Disperse Orange 29
	CI Disperse Red 82
	CI Disperse Violet 1
	CI Disperse Blue 56
	CI Disperse Blue 165
	Resolin Red FRL (DyStar)
	Resolin Yellow 5GL (DyStar)

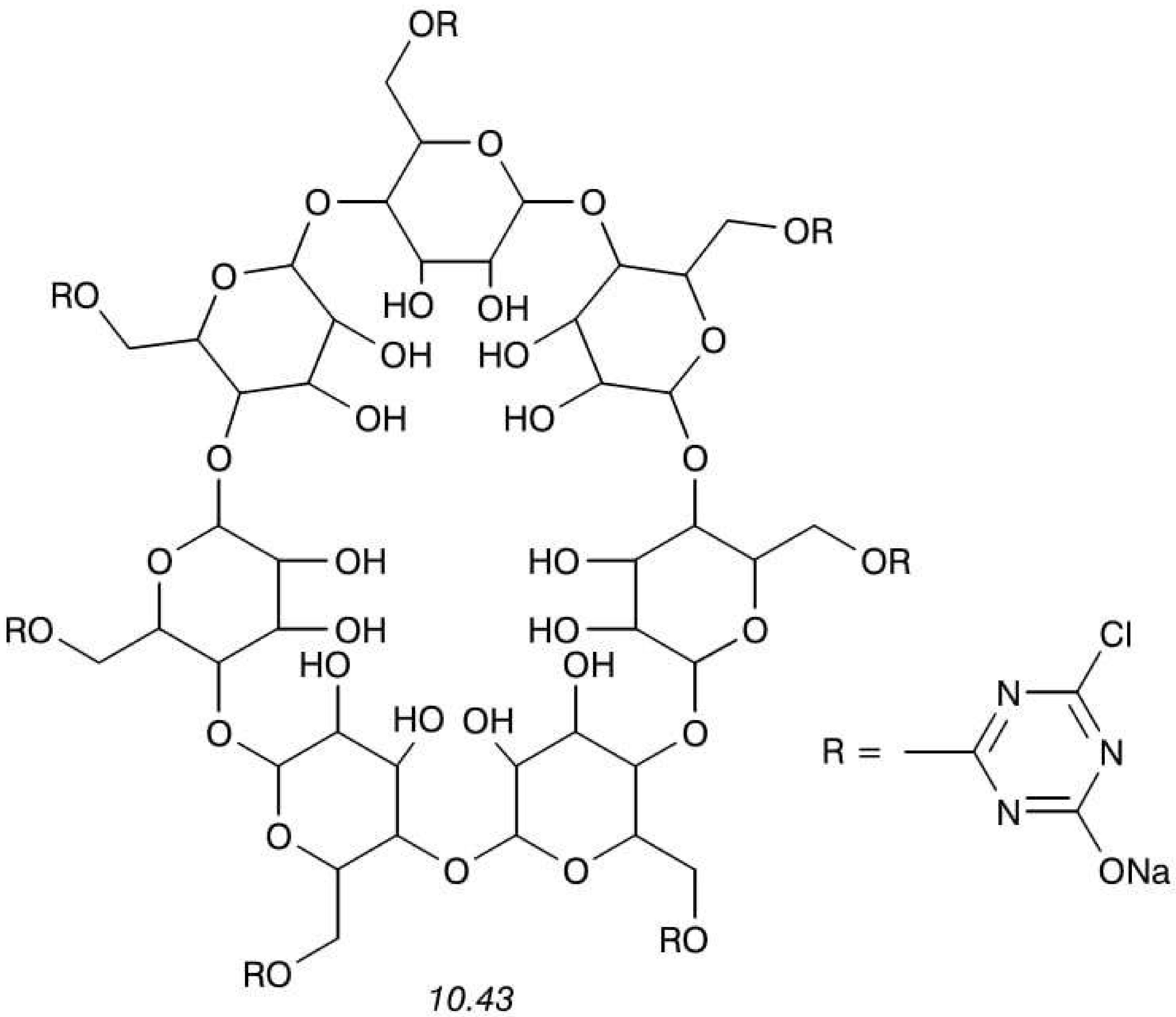
Reactive dyes

The formation and isolation of solid complexes between cyclodextrins and reactive dyes have been reported, but no dyeing results were presented [29]. Complexes were formed between β-cyclodextrin and CI Reactive Orange 16, Violet 5, Blue 38 or Blue 114 and between γ-cyclodextrin and CI Reactive Blue 38 or Blue 114.

The use of β-cyclodextrin and its fibre-reactive heptasubstituted monochlorotriazine derivative (10.43) has been studied in an effort to minimise the amount of the environmentally undesirable hygroscopic agent urea that is necessary when printing with reactive dyes [43]. Although this detailed research covered many variables as regards print paste additives, it involved only one reactive dye. It was found that the 300 g/kg urea normally used could be reduced to 75 g/kg when 40 g/kg of the reactive cyclodextrin derivative was used or to zero when 80 g/kg of the cyclodextrin was used, comparable results being obtained in all cases. Such cyclodextrins may function in several possible ways. The exterior hydrophilic surface of the cyclodextrin may enhance dye solubility in the same way as traditional hygroscopic agents and the hydrophobic cavity may assist this by complexing with the dye. The reactive cyclodextrin derivative may first react with the fibre and then attract further dye through its ability to absorb dye into its hydrophobic cavity.

Finishing

It has been demonstrated [32,44] that the various β-cyclodextrin derivatives shown in Table 10.1 can be applied to the surface of appropriate fibres by dyeing methods traditionally used



10.43

for those fibres. When the agent has become attached to the fibre surface, the cavity of the cyclodextrin derivative is still available for the accommodation of appropriate hydrophobic guest compounds. Such guest chemicals may be, for example, perfumed, bactericidal, waterproofing or stain-resist agents. Thus the concept offers a versatile potential for the development of special finishing effects.

The mechanisms by which certain β-cyclodextrin derivatives can become successfully attached to respective fibres are analogous to those operating between dyes and fibres. The monochlorotriazine derivative can be applied to cellulosic fibres either:

– by padding and fixing for 5 minutes in saturated steam at 100 °C or 3 minutes contact heat at 150 °C
– or by printing followed by drying for 2 minutes at 100 °C and steaming in saturated steam for 8 minutes at 100 °C.

The protective action of the alginate thickening agent in the print paste is believed to play a significant part in the success of this printing method. Application of the reactive β-cyclodextrin by an exhaust method, as used for hot-dyeing monochlorotriazine reactive dyes, was unsuccessful. This is probably because the cyclodextrin derivative, although a monochlorotriazine, does not possess the structural features, such as a planar molecule and a conjugated system of double bonds, that play an important role in the substantivity of reactive dyes for cellulosic fibres. Nor was padding followed by a cold (15 h at 25 °C) or hot (4 h at 80 °C) batching treatment successful. Several derivatives with hydrophilic (2,3-dihydroxypropyl or 2-hydroxypropyl) or lipophilic (*n*-butylglyceryl, 2-ethylhexylglyceryl or *o*-tolylglyceryl) substituents showed evidence of fixation to polyester by exhaust application at 130 °C. The anionic sodium carboxymethyl derivative could be fixed to nylon and the cationic 2-hydroxypropyltrimethylammonium derivative became fixed to an acrylic fibre by exhaust application at atmospheric pressure and 95–98 °C.

Effluent treatment

Since cyclodextrins form complexes with various other substances, including many dyes and surfactants, it is clear that they could be useful in effluent treatment. They are potentially suitable for the reduction or removal of polluting substances either by immobilisation or by solubilisation and extraction and thus can accelerate detoxification [30].

Summary

Cyclodextrins, discovered as long ago as 1930, have been the subject of much research since the 1950s, covering the whole field from textile preparation to effluent treatment. Their capability to form complexes with surfactants, dyes and segments of fibrous polymers is now well-established, yet little or no commercial exploitation appears to have grown out of their research and environmental potential. Most of the work has been done with β-cyclodextrin and its derivatives, followed by γ-cyclodextrin. The cavity of α–cyclodextrin appears to be too small for it to be widely used in textile applications. Thus there are limits to complex-forming capability depending on the molecular size and nature of the cyclodextrin in relation to the molecular size, nature and configuration of potential guest compounds.

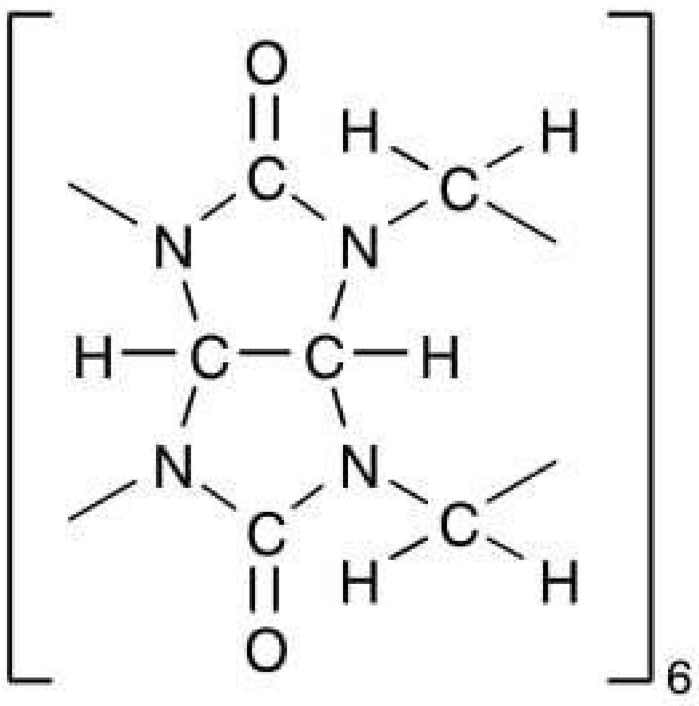
Much of this research has been carried out with single guest compounds. Evidently, the behaviour of these systems is highly specific, leading to a need for considerable fine-tuning in extending the concept to more heterogeneous commercial conditions. For example, there have been few investigations of cyclodextrins with typical trichromatic mixtures of dyes, in which the compatible behaviour of all the components may be difficult to resolve. This is implicit in the work of Yun *et al.* [45], who studied the compatibility of β-cyclodextrin with 27 water-soluble dyes. They demonstrated marked specificity in cyclodextrin–dye interactions and found that this was influenced by electrolytes and surfactants, as well as by pH. Complexing with β-cyclodextrin protected some dyes from the effects of salts and acids; this could be desirable or problematic, depending on requirements. It was also found that β-cyclodextrin improved the levelling of certain acid dyes [45].

Further problems may arise from the possible effects of residual cyclodextrins on subsequent processes. For example, as described above, a cyclodextrin can be used to remove residual surfactants from a fabric after scouring, yet it is possible that any residual cyclodextrin could itself interfere with subsequent coloration or finishing processes to the same extent as the surfactants that have been eliminated.

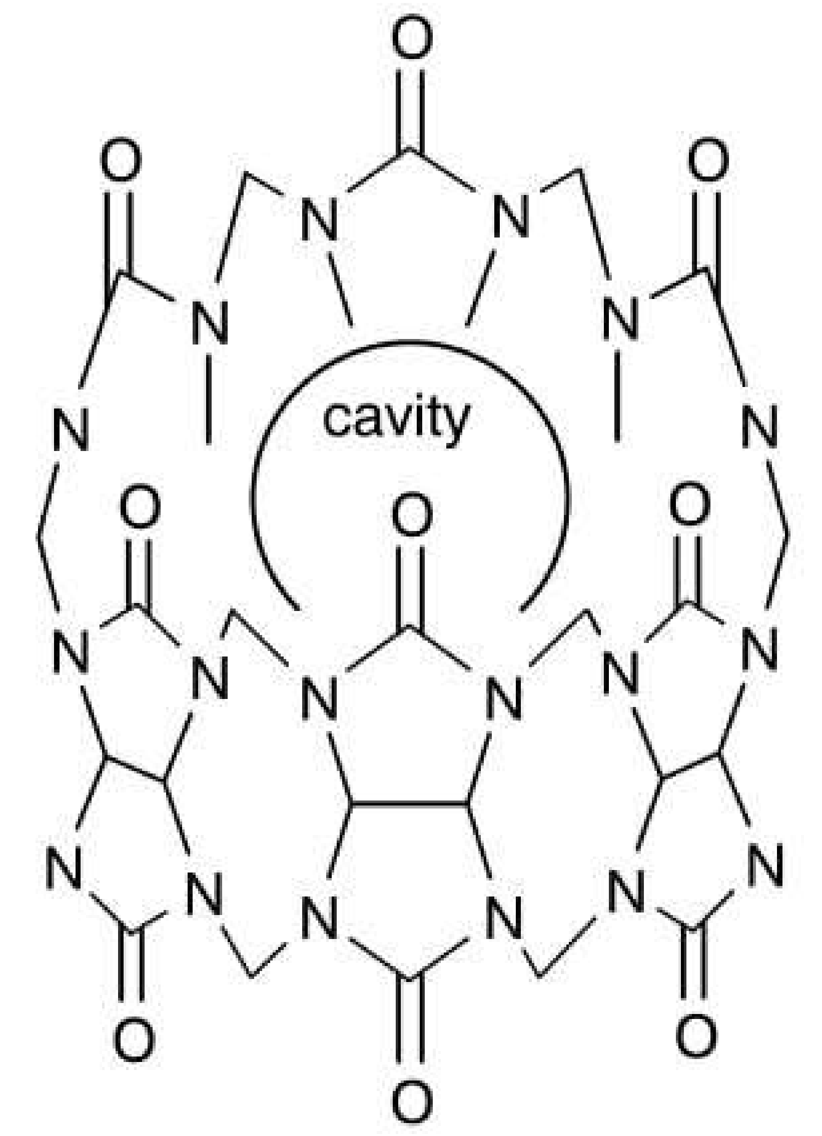
10.3.2 Cucurbituril

Cucurbituril, like cyclodextrin, is a macrocyclic complexing agent [46]. An advantage of this compound is its potentially low cost, being made from glyoxal, urea and formaldehyde. It is a cyclic hexamer (10.44) containing six acetyleneurein residues linked by methylene groups between the nitrogen atoms and is configured like a wristband (10.45), composed of six 8-membered rings alternating with pairs of 5-membered rings. Also like cyclodextrin, this cylindrical macromolecule has a hydrophobic cavity into which a dye molecule, or a part thereof, can be accommodated, the chemical structure of the dye having a distinct influence on the stability of the complex [46]. Cucurbituril can also complex with substances other than dyes, including alkaline-earth and alkali metal ions [47].

In the case of a typical dyebath composition containing dye, electrolyte and surfactants,



10.44



10.45
Cucurbituril

and possibly alkaline-earth cations from hard water, there are many competing concurrent interactions involving cucurbituril. For example, the following possibilities coexist [46]:

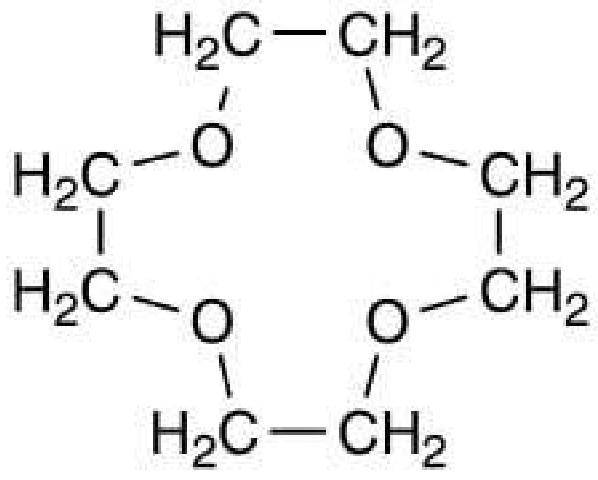
- the dye forms a complex with the cucurbituril and simultaneously is associated in micellar complexes with the surfactant
- the surfactant forms a complex with cucurbituril
- the electrolyte ions interact with cucurbituril.

Each factor may affect the others, depending on relative concentrations and pH. Cucurbituril requires quite strongly acidic conditions for solubilisation, hence its use in textile processing is likely to be very limited. It has mostly been investigated in connection with the removal of colour from textile effluents [46,48–53].

10.3.3 Crown ethers

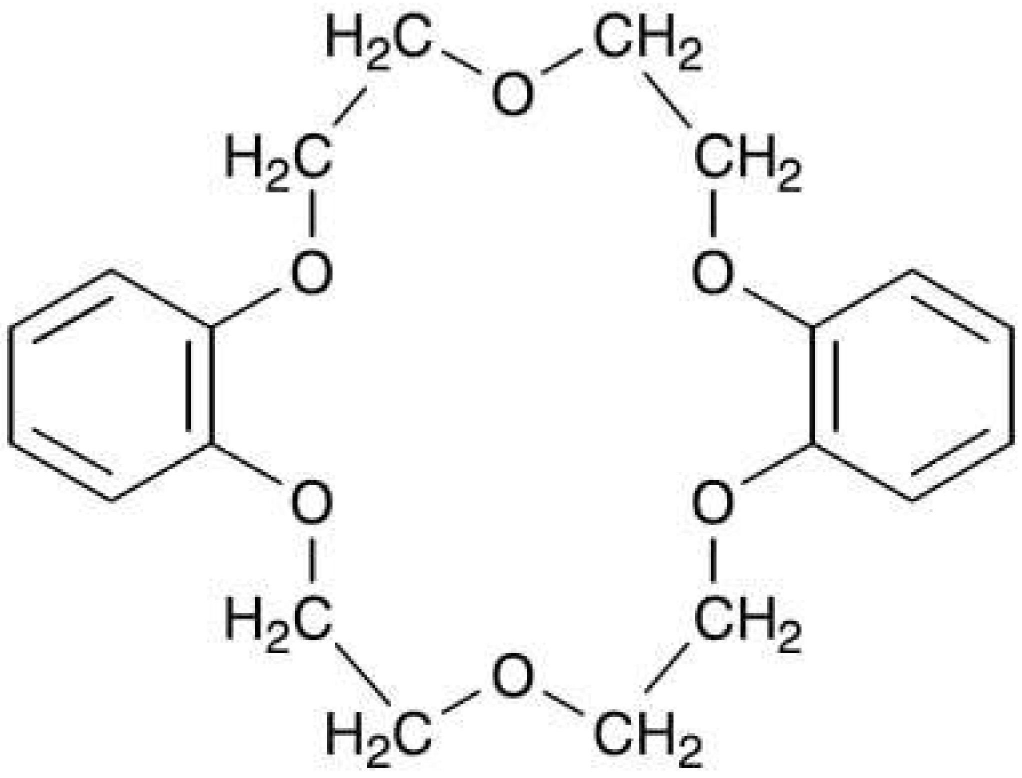
Crown ethers and related structures are macrocyclic organic compounds generally composed of repeating ethylene (CH_2CH_2) units separated by hetero atoms such as oxygen, nitrogen, sulphur or phosphorus [54]. Other alkylene sub-units such as methylene (CH_2) or propylene ($CH_2CH_2CH_2$) may also be included but are less common. In contrast to the cyclodextrins and cucurbituril, these macrocyclic complexing agents possess an electron-rich and highly polar cavity and a hydrophobic exterior. Usually they are readily soluble in organic solvents. They have been known since the 1930s. Two typical structures are 10.46 and 10.47. Oxygen is the hetero atom most commonly incorporated into the ring, but nitrogen (azacrowns), sulphur (thiacrowns) or phosphorus (phosphacrowns) are also known. Organic moieties sterically equivalent to the ethylene unit (such as 1,2-benzo) can be incorporated, as can most carbohydrates with vicinal dihydroxy groupings. Crown ethers are usually named as *x*-crown-*y*, from the number (*x*) of atoms composing the macrocyclic ring and the number (*y*) of hetero atoms contained within it. If one of the oxygen atoms in structure 10.46 is substituted by nitrogen, it becomes monoaza-12-crown-4.

Not all crown ethers have been tested for ecological or toxicological properties. Some are irritants and some are known to be toxic, although those tested do not show high toxicity. Nevertheless, amongst those that have not been tested, some may be hazardous to health.



10.46

12-crown-4



10.47

Dibenzo-18-crown-6

The functional characteristic of these compounds that is of interest from the viewpoint of textile processing is their capability to accommodate alkaline-earth and alkali metal cations, as well as a variety of other species, within their cavities. Stability constants (Equation 10.3) are again used, both as a measure of ligand strength and as a hierarchical indicator of complexing capability.

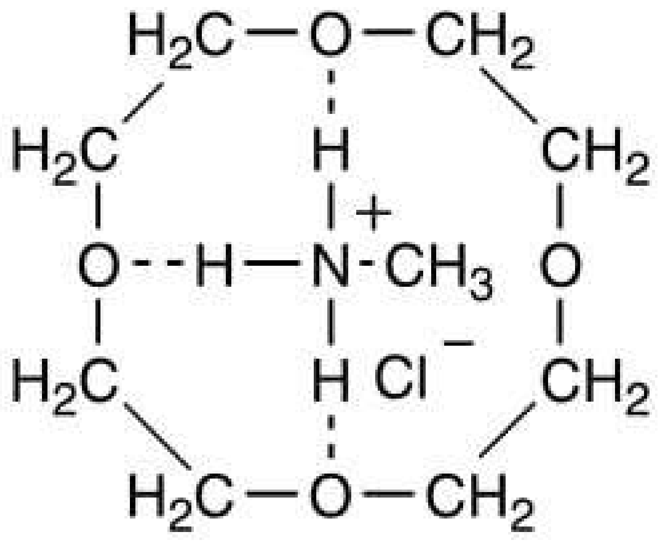
$$K_s = \frac{k_c}{k_d} \tag{10.3}$$

k_c = rate constant for complex formation
k_d = rate constant for dissociation of the complex
K_s = stability constant

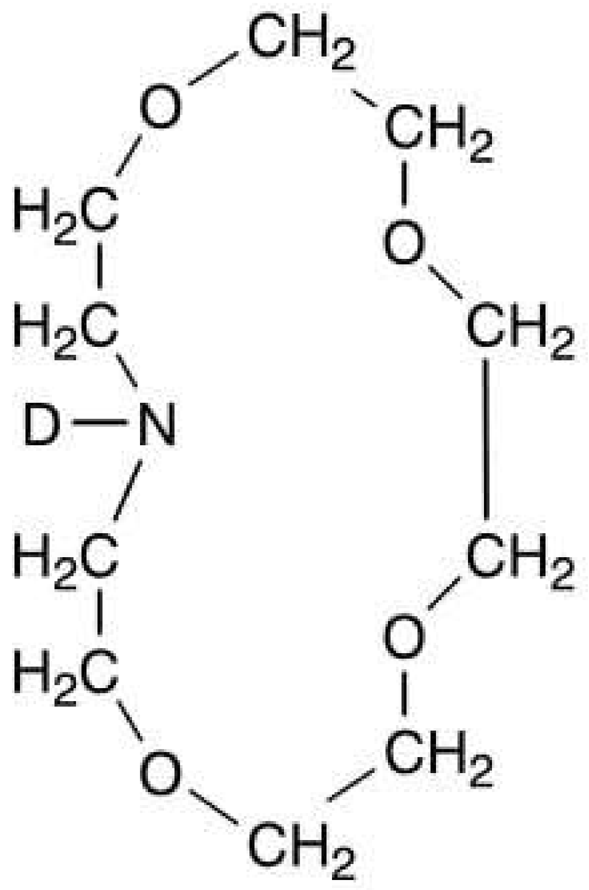
The stability constant is dependent, amongst other things, on the solvating medium. For example, for a simple crown ether k_c is usually very large and k_d also large, but in nonpolar solvents k_d is much smaller than k_c, so that K_S increases with decreasing polarity of the solvating medium.

It is generally accepted that for complexing to occur the cavity of the crown ether must contain convergent binding sites (as, for example, the inwardly directed oxygen atoms in 10.46 and 10.47), whilst the entity to be complexed must have divergent binding sites. An example is shown in 10.48, the formation of which is facilitated by the hydrogen atoms diverging from the central nitrogen of the methylammonium cation. It is the three N–H–O hydrogen bonds that stabilise the complex.

The potential of crown ethers for use as auxiliaries in textile coloration processes does not appear to have been evaluated recently, although their potential to complex with alkaline-



10.48



10.49 D = Styryl dye chromogen

earth and alkali metal ions has been demonstrated with styryl dyes containing an aza-15-crown-5 macroheterocyclic moiety (10.49) [55].

10.3.4 Liposomes

Liposomes, also known as lipid vesicles, are aqueous compartments enclosed by lipid bilayer membranes [56,57]. Figure 10.11 shows how lipid bilayers are arranged in the liposome and the lipid structures in large unilamellar vesicles and multilamellar vesicles. Lipids consist of two components:

- an elongated hydrophobic moiety
- a hydrophilic end group.

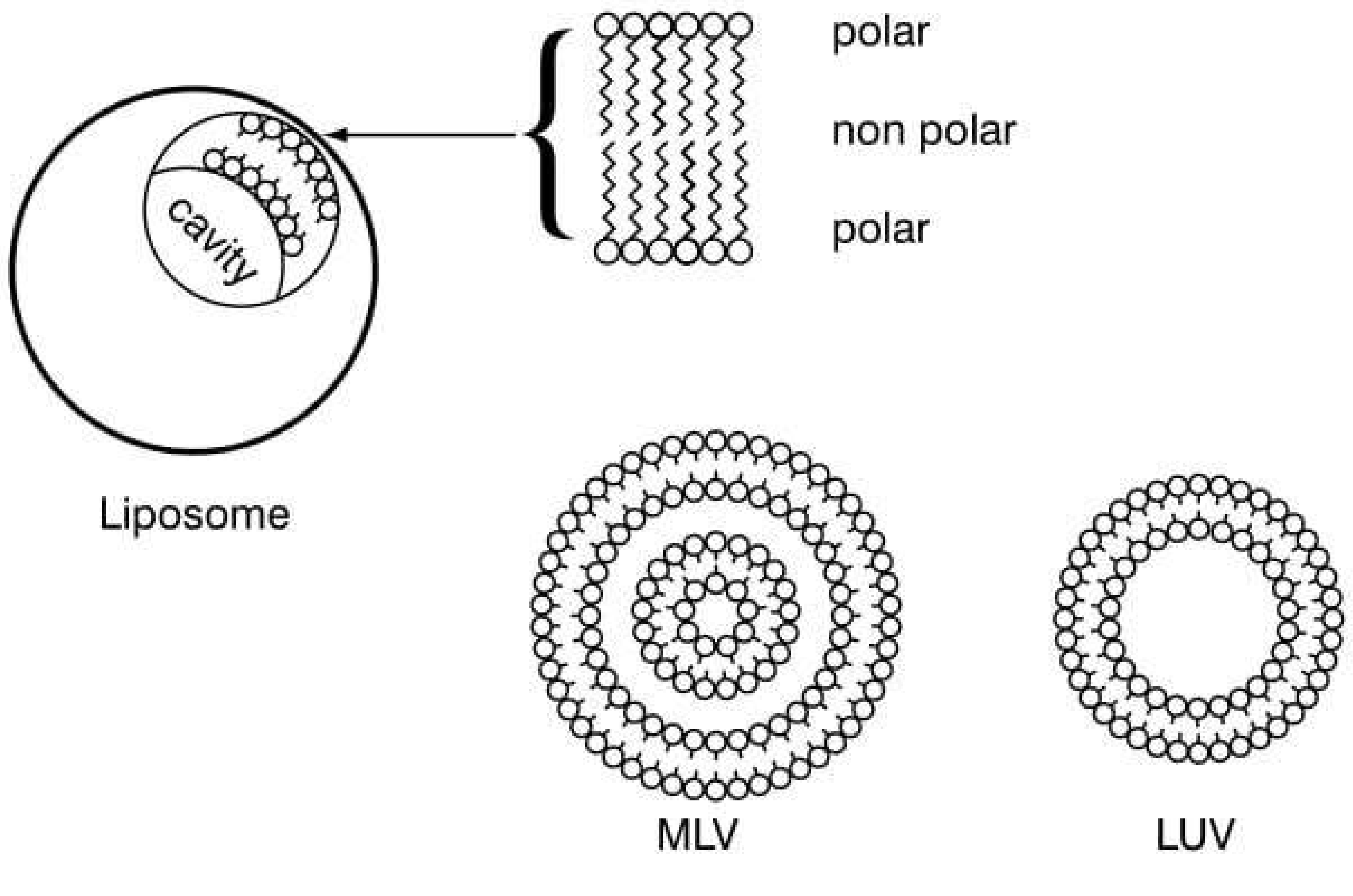
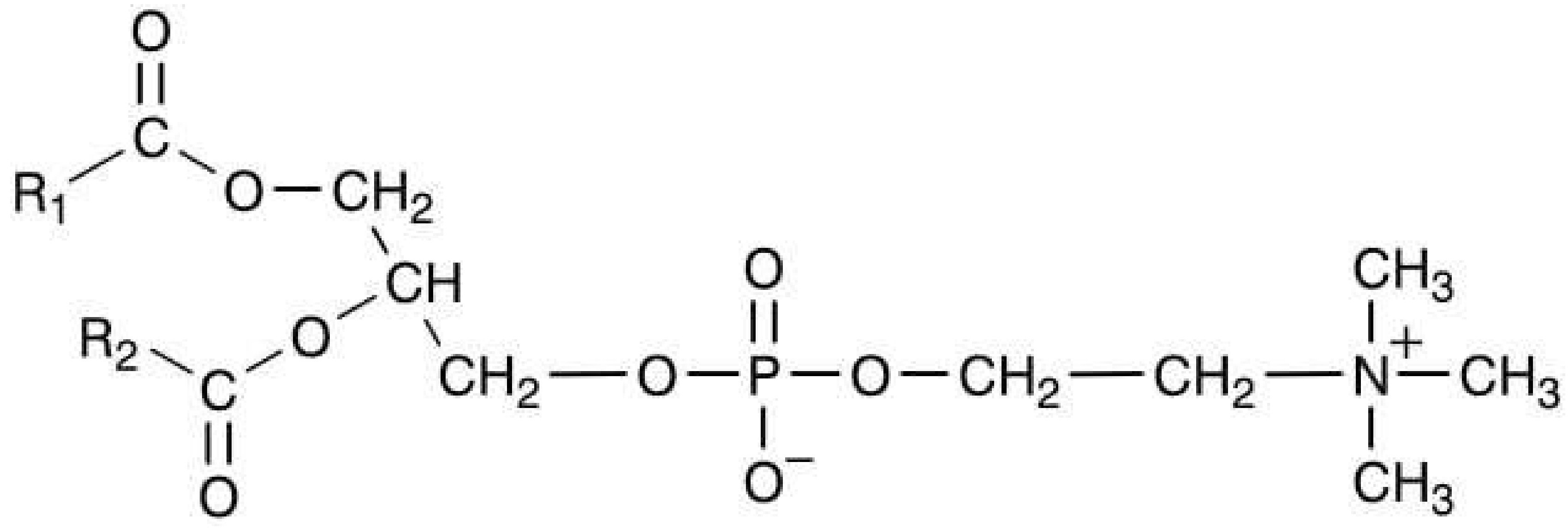


Figure 10.11 Liposome structures, including multilamellar vesicles (MLV) and large unilamellar vesicles (LUV) [57]

When these lipids are dispersed in water, they spontaneously form bilayer membranes (also called lamellae) which are composed of two monolayer sheets of lipid molecules with their hydrophobic surfaces facing one another and their hydrophilic surfaces contacting the aqueous medium. In the case of phospholipids such as phosphatidylcholine (10.50), the structure consists of:

- hydrophobic component: two hydrocarbon chains (R_1 and R_2)
- hydrophilic component: glyceryl ester, phosphate and choline groups.



10.50

Phosphatidylcholine

These structures are effective encapsulating systems for either hydrophilic or hydrophobic compounds. They can be obtained not only in uni- or multilamellar forms but also in different particle sizes with varying degrees of aggregation. They are particularly useful in biological and pharmacological applications. Recent research in various areas of textile wet processing has revealed further potential in these sectors. However, the methods of preparing liposomes so far reported are not readily adaptable to commercial processing conditions, as can be seen from the following typical procedures used by de la Maza *et al.* [57–60]. Clearly, substantial development work is needed before these techniques become compatible with bulk-scale textile wet processing.

Large unilamellar vesicle liposomes

Reverse-phase evaporation in a nitrogen atmosphere was used to prepare lipids. A lipid film previously formed was redissolved in diethyl ether and an aqueous phase containing the dyebath components added to the phospholipid solution. The resulting two-phase system was sonicated at 70 W and 5 °C for 3 minutes to obtain an emulsion. The solvent was removed at 20 °C by rotary evaporation under vacuum, the material forming a viscous gel and then an aqueous solution. The vesicle suspension was extruded through a polycarbonate membrane to obtain a uniform size distribution (400 nm).

Multilamellar vesicle liposomes

A lipid film was formed from a chloroform solution of egg phosphatidylcholine by rotary evaporation in a nitrogen atmosphere and under vacuum. An aqueous phase containing the dyebath components was then added to the lipid film. The solution was swirled to transfer the lipid from the flask and to disperse lipid aggregates; glass beads being added to facilitate dispersion. The resulting milky suspension was centrifuged for 5 minutes and then extruded through a polycarbonate membrane to obtain a uniform size distribution (400 or 800 nm).

Liposomes made from pure phosphatidylcholine or containing lipids that are found in the cell membrane complex of wool (e.g. cholesterol) have been used to encapsulate aqueous chlorine solutions in chlorination processes [61,62]. The results showed improvements in the uniformity and homogeneity of oxidative treatment, minimising degradation of the wool and facilitating subsequent treatments.

The application of acid dyes to wool using liposomes has also been researched. The dyes used were the milling acid dye CI Acid Blue 90 [57] and the neutral-dyeing 1:2 metal-complex dye CI Acid Yellow 129 [60]. Dyeing conditions were 90 °C and pH 5.5, using various ratios of phosphatidylcholine:dye. In the work with CI Acid Blue 90, both uni- and multilamellar vesicles were used. Dye exhaustion decreased with increasing concentration of phospholipid (Figure 10.12) but the amount of bonded dye increased with increasing lipid concentration (Table 10.4). The percentage of dye bonded to wool (C_b) was expressed by Equation 10.4:

$$C_b = \frac{100(C_a - C_e)}{C_a} \tag{10.4}$$

where C_a = mg/g dye absorbed by wool
and C_e = mg/g dye extracted from wool by ethanol and ammonia.

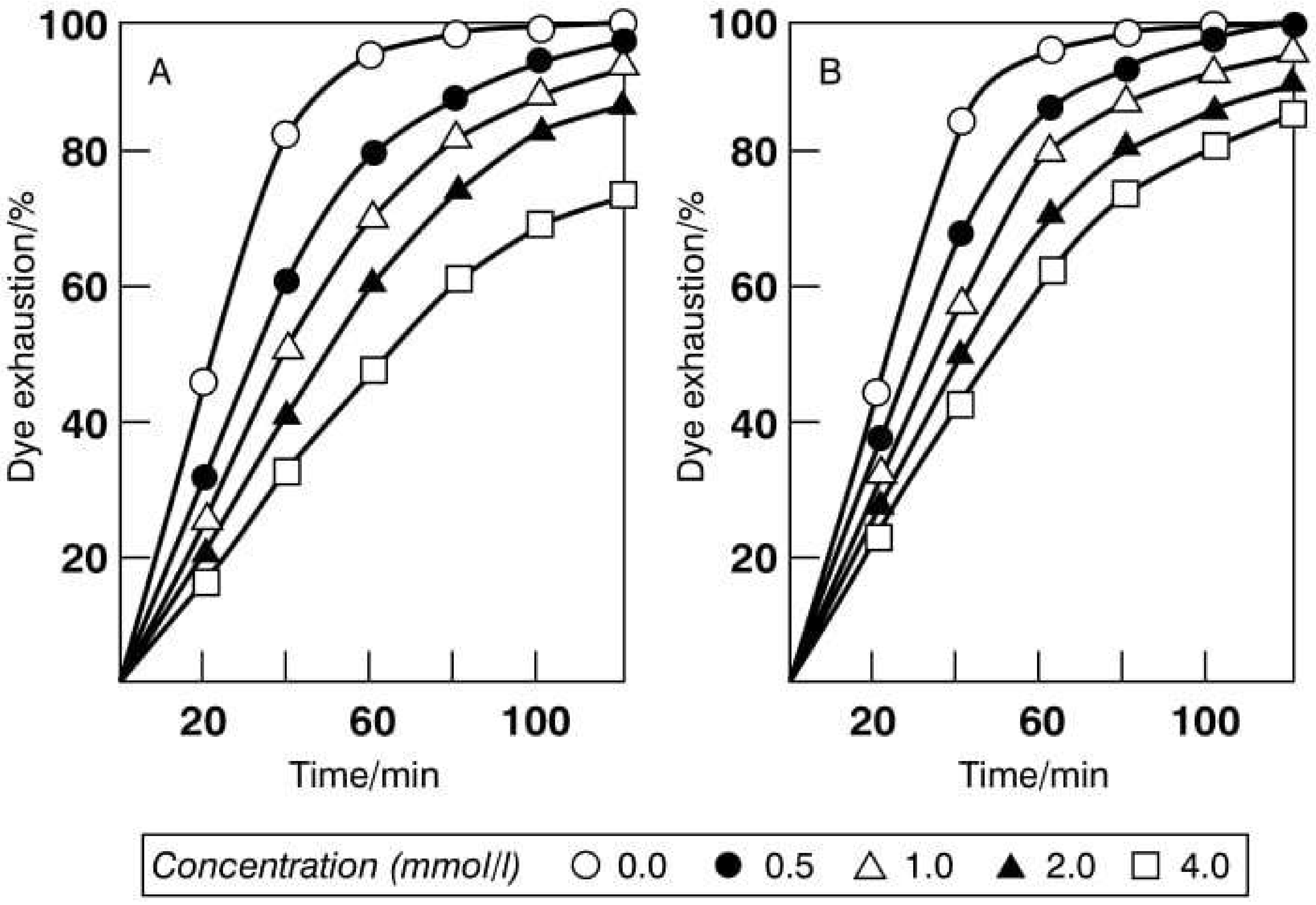


Figure 10.12 Exhaustion of CI Acid Blue 90 by untreated wool in dyeing with LUV (A) and MLV (B) liposomes [57]

Table 10.4 Amounts of dye bonded to wool using LUV and MLV liposomes at different lipid concentrations with CI Acid Blue 90 [57]

Lipid concentration (mmol/1)	Bonded dye (%)	
	LUV	MLV
4.0	84	77
2.0	78	74
1.0	77	73
0.5	68	68
0	62	62

The work with CI Acid Yellow 129 used only unilamellar vesicles. The liposomes again suppressed exhaustion but increased dye–fibre bonding, leading to better fastness properties. It is claimed that liposomes can be used to control the rate of exhaustion.

The application of CI Disperse Violet 1 to wool with phosphatidylcholine [58] and phosphatidylcholine/cholesterol [59] liposomes has been investigated. Figures 10.13 and 10.14 show that exhaustion decreases with increasing concentration of liposome, an effect which may be used to control exhaustion rate. It is claimed that liposomes enhance the dye dispersion efficiency, being superior to conventional dispersing agents. Dye–fibre bonding forces and levelling of the dye are also said to be improved.

Exploration of the use of liposomes in wool processing stems from the similarity that exists between the bilayer structure of the cell membrane complex of wool and that of the liposomes. Merino wool contains about 1% by weight of lipids, these forming the hydrophobic barrier of the cell membrane complex. Cholesterol is one of the main lipid

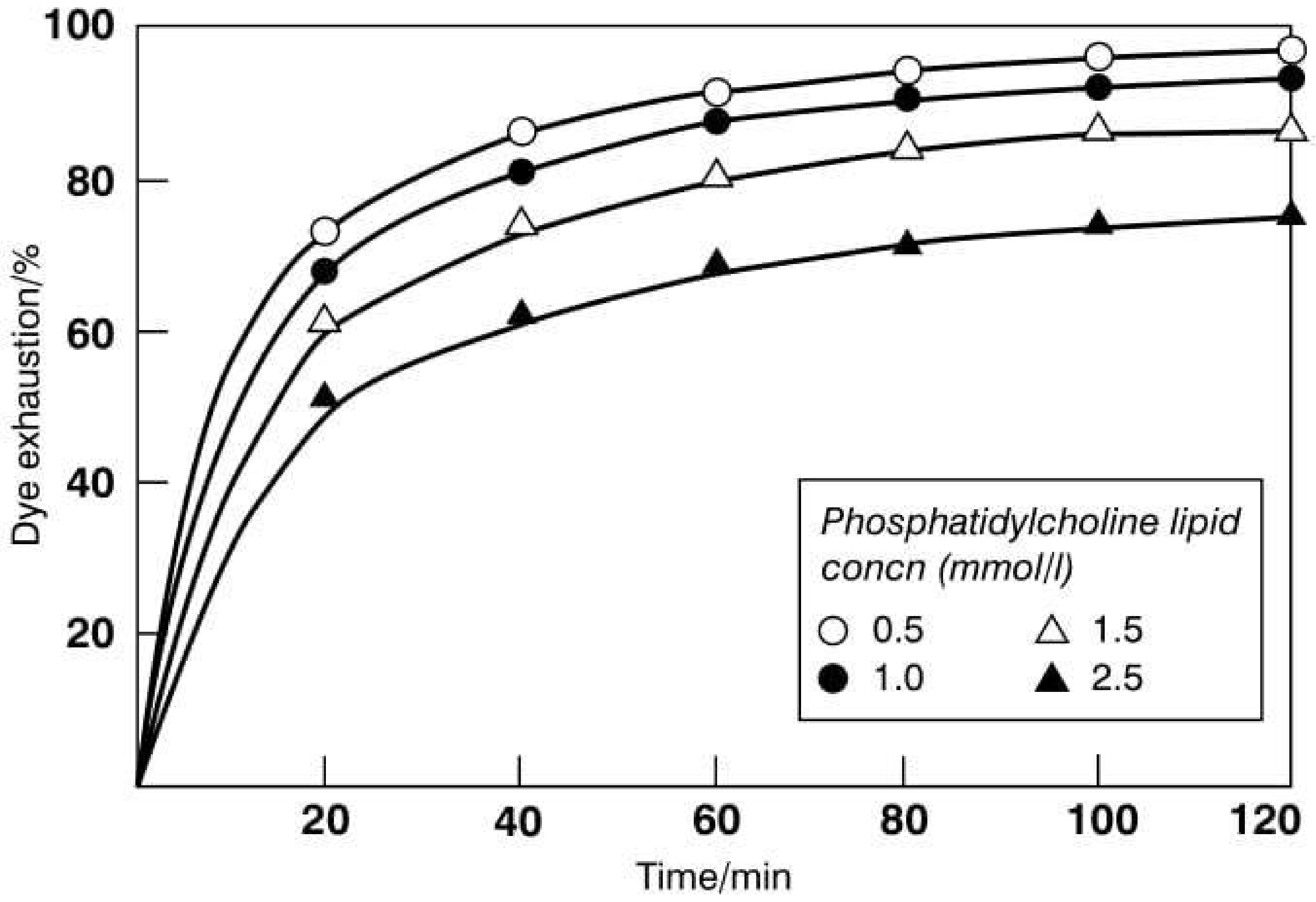


Figure 10.13 Exhaustion rates of CI Disperse Violet 1 on untreated wool in dyeing using liposomes at different lipid concentrations and constant dye concentration [58]

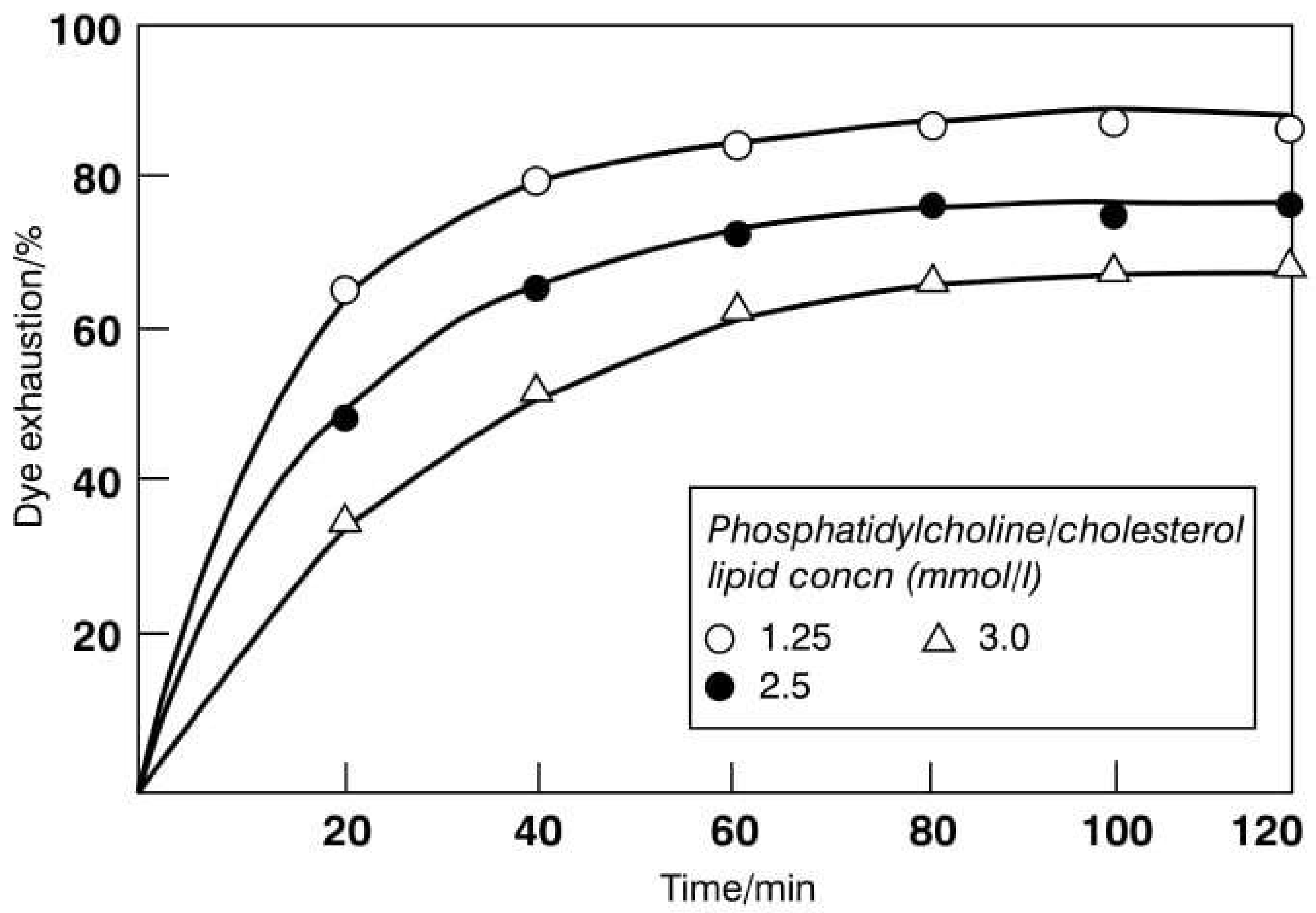
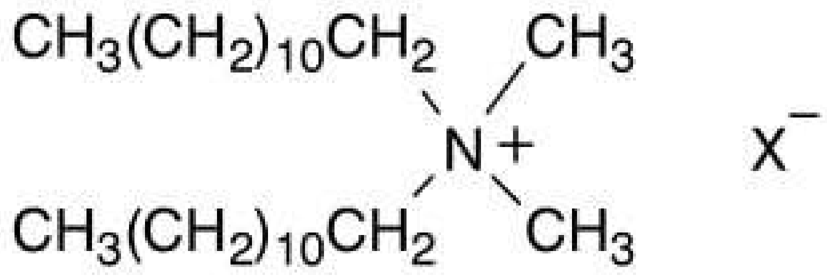


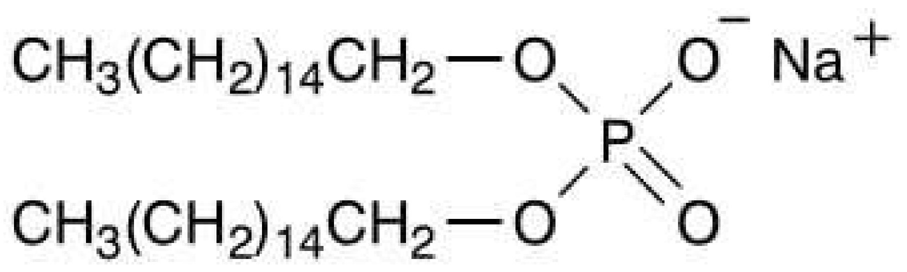
Figure 10.14 Exhaustion rates of CI Disperse Violet 1 on untreated wool during dyeing in the presence of MLV liposomes at different lipid concentrations and constant dye concentration [59]

components in wool; hence its use in combination with phosphatidylcholine (Figure 10.14). One of the ideas behind this research, which remains valid despite limited commercial prospects as yet, is to focus attention away from electrostatic forces of attraction towards hydrophobic interactions, which are now accorded greater importance. In dyeing, for example, the idea is that the hydrophobic liposome will encapsulate dye molecules by means of hydrophobic interaction, the liposome–dye complex then being absorbed into the hydrophobic centre of the cell membrane complex via further hydrophobic interaction. This is why claims are made for increased hydrophobic bonding of the dyes to the fibre.

Along similar lines, synthetic cationic (10.51) and anionic (10.52) double-chain surfactant vesicles have been investigated for the dyeing of polyester with a monoazo disperse dye [63]. The results were moderately encouraging from technological, economical and environmental viewpoints, although problems and inconsistencies were observed. It is often difficult to explain results with disperse dyes on the basis of structural chemistry alone, since they can be influenced by variations in dispersion characteristics and instability during dyeing.



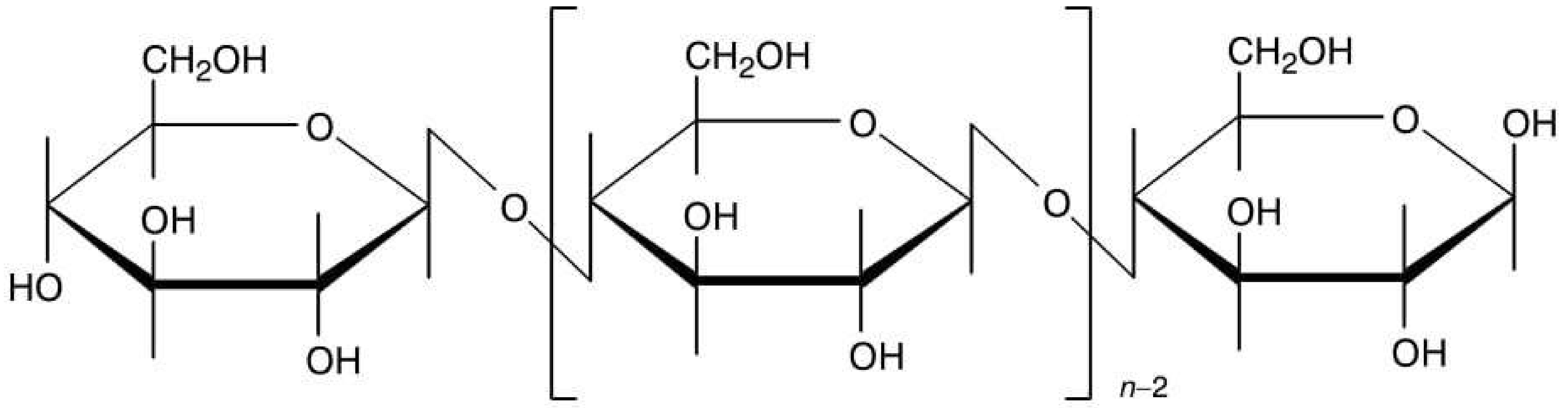
10.51 X = Br or Cl



10.52

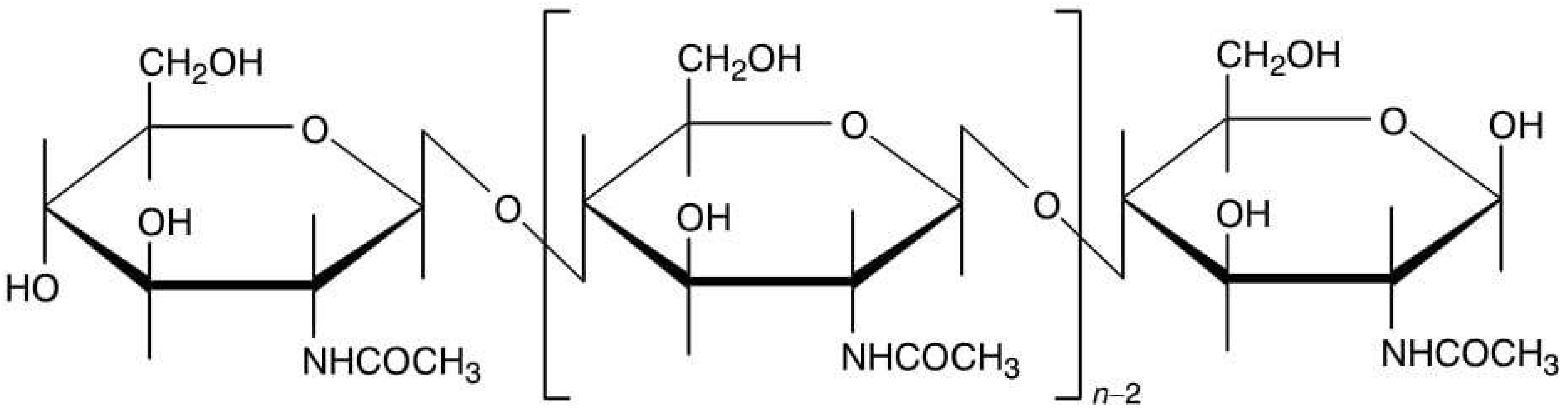
10.3.5 Chitin, chitosan and their derivatives

Chitin is the second most important natural polysaccharide produced by biosynthesis, exceeded only by cellulose, to which it is closely related in structure. It was first isolated by Braconnot in 1811 and thus its 'original and spectacular' properties have been recognised for a long time [64]. Chitin is found in crabs, lobsters and other crustaceans, spiders and other arthropodic insects, and the cell walls of fungi. Like cellulose (10.53), chitin (10.54) is a 1,4-β-D-glucopyranose. Both have a linear sequence of pyranose rings linked by 1,4-glycosidic bonds, a non-reducing end group and a reducing end group in the cyclic hemiacetal form. The characteristic difference between them is that chitin has an acetylamino group in the 2-position, compared with the 2-hydroxy group in cellulose. Chitin exists in three polymorphic forms, depending on the directions of adjacent polymer chains, the alternating α-chitin structure being the most common [64].



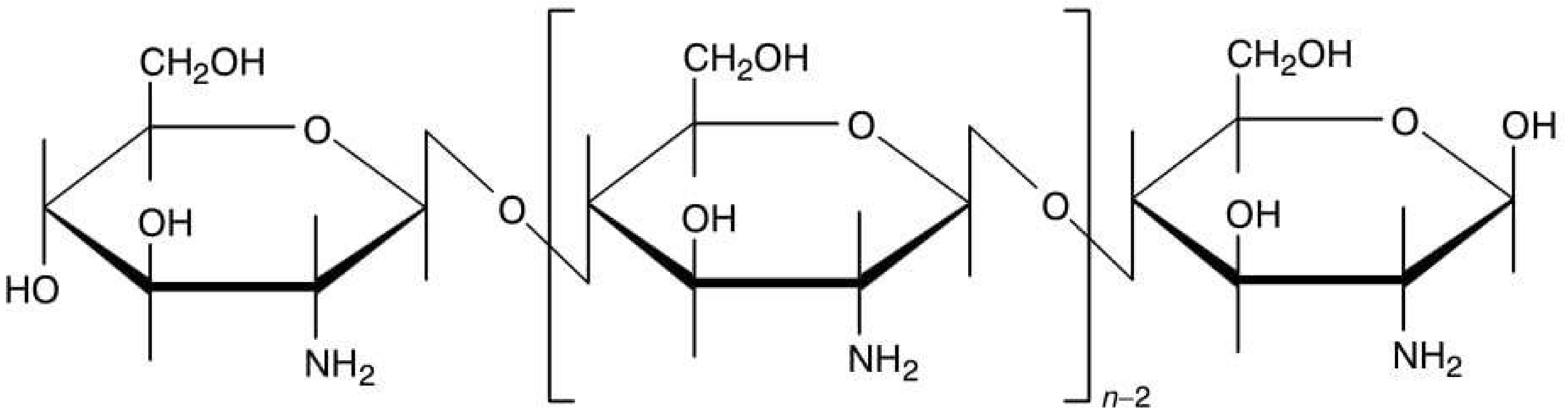
10.53

Cellulose



10.54
Chitin

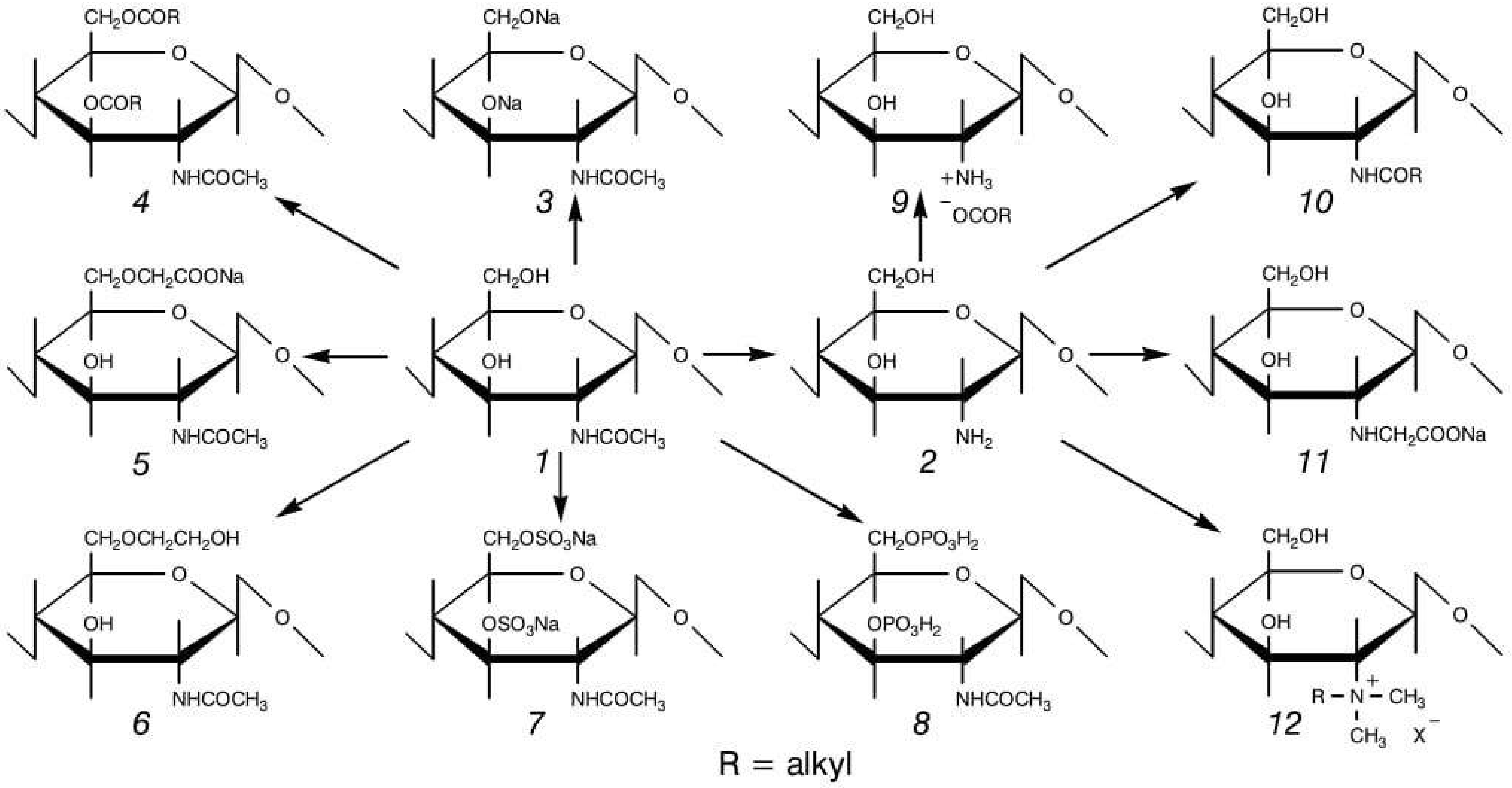
Chitosan (10.55) is a derivative of chitin made by alkaline hydrolysis resulting in deacetylation to give a primary amino group in the 2-position. Chitin is less hydrophilic than cellulose, whilst chitosan is more basic than either of the others. Structures 10.53–10.55 are representative only. Variations occur, depending on the source of the chitin and its treatment during and after harvesting. Chain length, average molecular mass and molecular mass distribution vary. There is also the question of impurities and the degree of deacetylation of chitosan, which is usually 75–95% [65]. Knittel and Schollmeyer [65] have outlined the nature, properties and uses of chitin and chitosan, including indications of their uses in textile processes [65]. Roberts has provided an excellent textbook [64]. There are also the proceedings of two symposia, although these do not deal with textile processing applications [66,67].



10.55
Chitosan

Numerous substituted derivatives of chitin and chitosan are known [67]; some important examples are shown in Scheme 10.9. The possibility of forming either anionic (5,7,8,11) or cationic (9,12) derivatives should be noted. The *O*-carboxymethyl (5) and *N*-carboxymethyl (11) polymers are of particular interest as they have stronger complex-forming capabilities with metal ions than either unsubstituted chitosan or EDTA [65]. In practice, derivatives formed by substitution via the 2-amino group of chitosan are more common than those substituted via the 6-hydroxy position of the glucopyranose grouping [65].

Chitosan features far more than chitin in research into applications. This is largely due to their difference in solubility characteristics, chitosan being more amenable to practical manipulation. Chitin is in fact rather more intractable than cellulose, since it is insoluble in those solvents, such as cuprammonium hydroxide, that are commonly used to dissolve cellulose. Chitin is soluble in hot concentrated solutions of certain inorganic salts capable of



Typical derivatives of chitin (*1*) and chitosan (*2*) [67]: alkali-chitin (*3*), *O*-acylchitin (*4*), *O*-carboxymethylchitin (*5*), *O*-hydroxyethylchitin (*6*), chitin *O*-sulphate (*7*), chitin *O*-phosphate (*8*), chitosan salt (*9*), *N*-acylchitosan (*10*), *N*-carboxymethylchitosan (*11*), trialkylammonium salt (*12*)

Scheme 10.9

a high degree of hydration, the order of effectiveness being: lithium thiocyanate > calcium thiocyanate > calcium iodide > calcium bromide > calcium chloride. Chitin also dissolves, with some degradation, in concentrated hydrochloric acid, sulphuric acid (some *O*-sulphation taking place) or phosphoric acid, but not in nitric acid. Certain organic carboxylic acids, such as formic, dichloroacetic or trichloroacetic, will also dissolve chitin.

Chitosan, on the other hand, interacts with inorganic acids to yield cationic polyelectrolytes, their solubility depending on the nature of the anion. Thus it is soluble in dilute hydrochloric, hydrobromic, hydroiodic, nitric or perchloric acid, but may be precipitated from hydrochloric or hydrobromic solutions as the acid strength is increased. Chitosan forms water-soluble salts with most carboxylic acids. Hence it is chitosan, rather than chitin, that has come to the fore in a remarkably wide range of end-uses, including such diverse fields as medicine, personal care, contact lenses, biotechnology, food, agriculture, effluent treatment, analysis, textile finishes and coatings. Although usage in textiles is relatively small as yet, its availability, environmental compatibility and remarkable versatility offer considerable potential.

Both chitin and chitosan are manufactured commercially on a large scale. Chitosan is available in powder, gel, solution, film, membrane, fibre and bead forms. Interest in all forms and levels of purity is high and continuing to expand [67]. Chitosan is produced from amply replenishable biological sources and is readily biodegradable, non-toxic and non-allergenic. It has bactericidal and fungicidal properties and actively promotes wound-healing.

The ability of chitosan to form complexes is of particular interest. Being slightly basic, it will readily form complexes with anionic compounds. Initially it forms into micelles with small amounts of anionic surfactants, leading to precipitation of a complex as the concentration of the anionic surfactant increases. Chitosan will complex with anionic polyelectrolytes leading to the formation of polycationic/polyanionic complexes of high molecular mass. This capability to complex with anionic substances is further enhanced if cationic derivatives of chitosan are used. The degree and strength of complexing depends on:

- the nature and ionic strengths of the cationic and anionic species
- the spacing of the charged ionic groups, as influenced by the relative molecular masses and spatial configurations of the components.

This property is clearly of interest for the removal of anionic substances from effluent streams, for example. However, since such complexing often results in an increase in viscosity as complexing proceeds, such systems can be used to produce gels or viscous liquids. Hence there is the possibility of using these complexes as print–paste or pad–liquor additives to control migration. Weakly basic chitosan or its more strongly basic derivatives will complex with anionic fibres and can therefore be used as finishes or pretreatments to modify selected properties of the fibres. They are already used, for example, in hair sprays or for complexing with and isolating proteins.

It is not surprising, therefore, that chitosan and its basic derivatives will complex with anionic dyes. Giles *et al.* [68,69] researched the use of chitosan for the removal of dyes from effluent as long ago as 1958. The binding capacity of chitosan for anionic dyes is pH-dependent, but it has been reported [65] that in effluent treatment as much as 10 g dye per kg chitosan can be complexed at pH values above about 6.5. Similarly, chitosan has been used for the aftertreatment of direct dyeings on cotton to improve their fastness.

The complexing of chitosan and its basic derivatives with anionic substances is paralleled by compatibility with cationic and nonionic compounds. Similarly, the anionic derivatives of chitosan show complex formation with cationic agents and are compatible with anionic and nonionic compounds. The capability of these chitosan derivatives to complex with certain metal ions, notably those of the transition series, is also important, having possibilities for the removal of metal salts from effluent. The hierarchy in terms of binding capacity is: $Cr(III) < Cr(II) < Pb(II) < Mn(II) < Cd(II) < Ni(II) < Fe(II) < Co(II)$.

Chitosan will readily react with formaldehyde via its primary amino groups [65]. The capability of chitosan and its basic derivatives to complex with anionic fibres has already been mentioned. In this context, the bactericidal and fungicidal properties of these chitosan compounds are useful. The fact that fibre-reactive chitosan derivatives can be prepared further increases these possibilities. Chitosan compounds containing long-chain alkyl groups exhibit fabric-softening properties and can be incorporated into finishing formulations for this purpose. The fact that charged chitosan derivatives can interact with appropriate fibre types gives scope for their use as levelling agents and to modify dye absorption in either a positive or negative sense, depending on circumstances and dyeing requirements. For example, they are claimed to reduce dye uptake variations between mature and dead cotton.

The use of chitosan derivatives in print pastes, to reduce the content of the environmentally unfavourable hygroscopic agent urea necessary when applying reactive dyes, has been evaluated [43]. It was found that in recipes normally requiring 300 g/kg urea this could be reduced to 75 g/kg by adding either 20 g/kg chitosan or 4 g/kg *N*-hexylchitosan. Although this did not give a significant increase in dye yield, the replacement of most of the urea by a biodegradable chitosan polymer offered significant promise.

10.3.6 Summary

In conclusion, it is noteworthy that cyclodextrins, liposomes and chitin derivatives are all readily available from renewable biochemical sources and offer advantages of biodegradability and safety in use. However, it needs to be borne in mind that this fact alone does not necessarily mean that they are entirely environmentally innocuous in the long run. Demands on resources for the husbanding and processing of bioforms that may be necessary in order to sustain demand for commercially viable qualities and quantities can exert deleterious effects, not least because they may give by-products that present problems of utilisation or disposal [70].

10.4 ENZYMES

10.4.1 Structure and properties of enzymes

Enzymes are proteins, i.e. sequences of amino acids linked by peptide bonds. The sequence of amino acids within the polypeptide chain is characteristic of each enzyme. This leads to a specific three-dimensional conformation for each enzyme in which the molecular chains are folded in such a way that certain key amino acids are situated in specific strategic locations. This folded arrangement, together with the positioning of key amino acids, gives rise to the remarkable catalytic activity associated with enzymes.

Their molecular masses range from about 10 000 to more than 1 000 000. Each enzyme can catalyse an indefinite amount of chemical change without itself being consumed or degraded by the reaction, although most enzymes lose their activity gradually under the conditions of use due to an inherent instability. Enzymes are produced by all living cells and are of two types:

- exoenzymes: these are expelled by the manufacturing cell into the surrounding environment, where they can break down organic compounds such as proteins, starches and fats into more soluble components of lower molecular mass; and
- endoenzymes: these remain within the living cell and are transformed or broken down by the action of coenzymes to produce relatively large amounts of energy and the cell components needed for cell processes.

Clearly, it is the exoenzymes that are of interest in textile processing, an area which has seen considerable development in recent years. Originally used only in the preparatory processes of scouring and desizing, they are now also used to modify textile surfaces in finishing as well as in effluent treatment.

Although enzymes are present in living systems they can exhibit powerful activity under certain conditions. Their behaviour within the cells of a correctly functioning (i.e. healthy) living entity is controlled by a sophisticated biochemical system designed to maintain optimum activity according to the needs of the living cells. In an external application such as textile processing, such biochemical control is not in place. Hence care is needed in the use of enzymes. Repeated inhalation of enzyme dust is associated with a comparatively high risk of respiratory allergy in susceptible persons. Undue exposure can cause irritation of moist skin, eyes and mucous membranes. The manufacture and use of enzymes is usually government-controlled.

More than 3000 different enzymes have been extracted from animals, plants and microorganisms. Traditionally, they have been used in impure form since purification is expensive and pure enzymes may be difficult to store and use. There is usually an optimum temperature and pH for maximum activity of an enzyme. Outside these optimum conditions, activity may simply be held in check or the enzyme may become 'denatured', i.e. altered in such a way that activity is lost permanently, although some forms of denaturing are reversible. Many enzymes are also sensitive to transition-metal ions, the effect being specific to particular metal ions and enzymes. In some cases, certain metal ions are essential for the stability and/or activity of an enzyme. In other cases, metal ions may inhibit the activity of an enzyme. Similarly, certain organic compounds can act as enzyme inhibitors or activators.

An enzyme consists of a polypeptide chain with a particular spatial configuration specific to that sequence of amino acids. The molecule twists and turns, forming structural features that are catalytically active, these being known as active sites. There may be more than one active site per enzyme molecule. Sometimes an auxiliary catalyst, known as a coenzyme, is also needed. Apparently, only the relevant active site of the enzyme comes into contact with the substrate and is directly involved in the catalysed reaction. The active site consists of only a few amino acid residues. These are not necessarily adjacent to one another in the peptide chain but may be brought into proximity by the characteristic folding of the enzyme structure. The active site may also include the coenzyme. The remainder of the enzyme molecule fulfils the essential function of holding the components of the active site in their appropriate relative positions and orientation.

Thus the alkaline protease obtained from *Bacillus licheniformis* with a molecular mass of about 27 000 consists of 274 amino acid residues and has serine and histidine as active sites. Pancreatic trypsin with a molecular mass of about 24 000 contains 230 amino acid residues and also has serine and histidine as active sites. Papain (molecular mass about 23 000 and 211 amino acid residues) has cysteine and histidine as active sites.

The molecular folding of the backbone chain of the enzyme, as well as the distribution and content of amino acids [71] plays a decisive role in determining the characteristic specificity of an enzyme with regard to its reactions. This folding is markedly affected by temperature, for example. As the temperature rises, the chain gradually unfolds until a point is reached at which the enzyme becomes 'denatured' and the catalytic activity is lost.

Most enzymes are highly specific, catalysing only one specific reaction. They may act upon only one isomer of a particular compound and are then described as stereospecific. Others are less specific, being able to catalyse several (usually related) reactions. Part of the active site is involved in binding to the substrate and another part is responsible for making or breaking chemical bonds. It appears that, for some enzymes, binding of the substrate produces a change in conformation which brings the key functional group of the enzyme into the required position for reaction to take place. Thus there must exist between the enzyme and the substrate a close stereochemical fit or complementarity, analogous to the situation between a lock and its key. Regarding stereospecific behaviour, certain enzymes exhibit a remarkable ability to discriminate between asymmetric right-hand and left-hand molecular configurations.

Enzymes may be named trivially or more formally. Trivial naming tends to predominate in industry and two trivial systems exist:

(1) a suffix (*-in* or *-ain*) is added to a root indicating the source of the enzyme, e.g. papain from papaya or pancreatin from pancreatic cells

(2) the suffix *-ase* is added to a root indicative of the substrate or reaction involved, e.g. lactase acts on lactose, cellulase hydrolyses cellulose and glucose oxidase oxidises glucose.

In formal nomenclature, a decimal numbering system is used. Only a brief description can be given here; more complete accounts can be found elsewhere [72,73]. The system requires four numbers. The first number gives the class of enzyme according to the following scheme:
(1) Oxidoreductases
(2) Transferases
(3) Hydrolases
(4) Lyases
(5) Isomerases
(6) Ligases.

The second and third numbers give the subclass according to the type of reaction which is characteristic of the enzyme, e.g.
1. Oxidoreductases
  1.1 acting on the CH–OH group of donors
    1.1.3 with O_2 as acceptor
The fourth number is the serial number of the enzyme in its subclass.

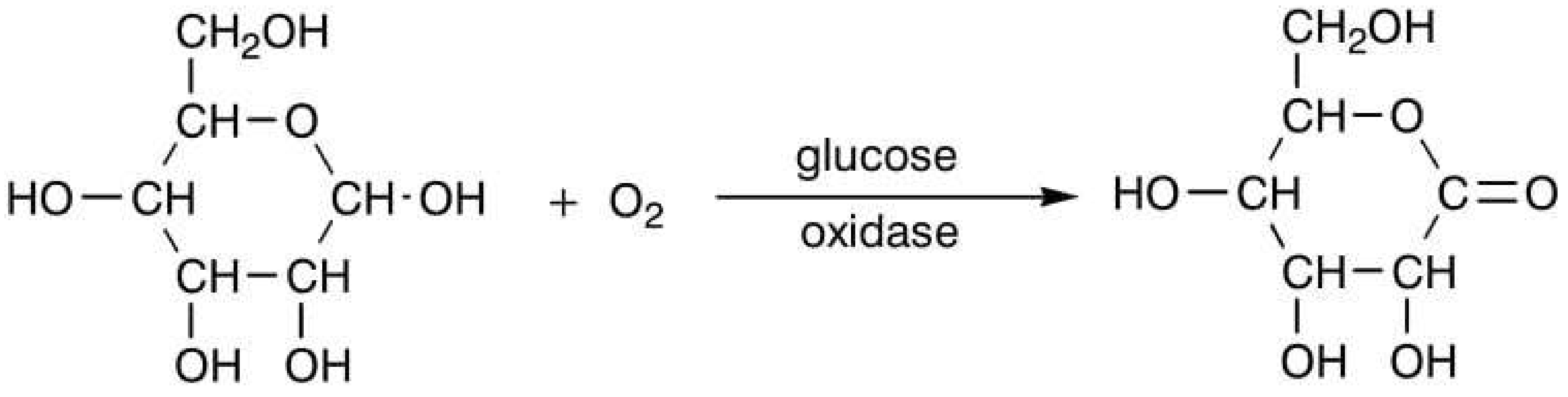
With regard to the specificity of enzymes, there are four main types:
(1) Enzymes that catalyse the reaction of only one substrate are known as absolute enzymes.
(2) Stereospecific enzymes catalyse reactions with one type of optical isomer but may also react with a series of related compounds of the same configuration. Many proteolytic enzymes hydrolyse only peptide bonds linking laevorotatory (L-) amino acids.
(3) Enzymes that react with a specific type of ester linkage are known as general hydrolysing enzymes. Thus lipases hydrolyse a wide range of organic esters. Generally, phosphatases will break down phosphate esters into phosphoric acid and an alcohol.
(4) This group is characterised by enzyme attack at a certain specific point in a molecule. Examples are:
  (a) Some proteolytic enzymes act at a location where the adjacent amino acid (e.g. phenylalanine) contains a benzene ring.
  (b) Some hydrolytic enzymes attack the interior bonds of a molecule. Thus α-amylase attacks the mid-chain region of the starch molecule and of glucosidic fragments formed from starch.
  (c) Other hydrolytic enzymes attack the end groups of saccharidic macromolecules. Thus β-amylase attacks the end groups in starch molecules, splitting off two glucose units in the form of a maltose residue. Amyloglucosidase attacks the non-reducing ends of starch or its hydrolysis products to split off single glucose units.

As mentioned above, certain metal ions may be necessary for activity or stability. Thus calcium is needed for bacterial α-amylase. Magnesium or cobalt is needed with glucose isomerase. Calcium stabilises the starch-liquifying bacterial α-amylases but inactivates the glucose isomerase that may be used subsequently. Many enzymes contain an additional nonprotein component, referred to as a coenzyme or prosthetic group. This may be an organic molecule, a vitamin derivative or a metal ion. In most cases the coenzyme participates directly in the catalytic reaction.

The four main groups of enzyme activity mentioned above are covered by the six classes of enzymes already listed.

Oxidoreductases

Such enzymes catalyse reactions involving electron transfer. Oxidases use molecular oxygen as an electron acceptor (Scheme 10.10). Dehydrogenases remove hydrogen atoms from the substrate and transfer them to an acceptor other than oxygen.



10.56
D-Glucose

10.57
D-Gluconolactone

Scheme 10.10

Transferases

These catalysts bring about the transfer of a particular chemical group from one substance to another. Examples of groups that can be transferred include alkyl, formyl, carboxyl, aldehyde, keto, acyl, glucosyl, nitrogen-, phosphorus- or sulphur-containing groups. Thus a transaminase transfers an amino group and a transmethylase transfers a methyl group. Scheme 10.11 shows the transfer of an amino group using a transaminase.

α-Amino acid α-Keto acid

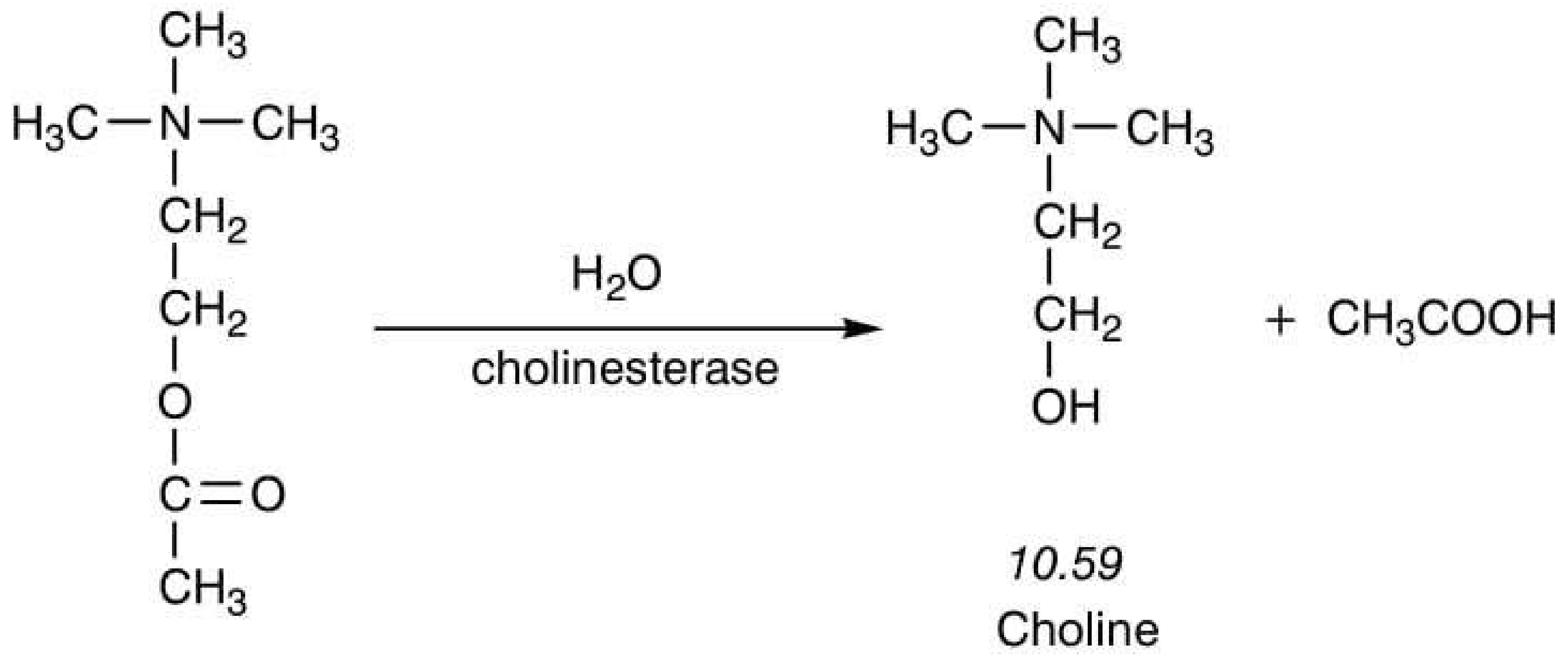
Scheme 10.11

Hydrolases

Enzymes in this group are capable of hydrolysing a substrate. Examples include:

Substrates	*Types of enzyme*
starch	amylases
proteins	proteinases and peptidases
nucleic acids	nucleases
fats	lipases
esters (e.g. phosphates)	esterases (e.g. phosphatases)

Scheme 10.12 shows the action of cholinesterase in the hydrolysis of acetylcholine (10.58) to choline (10.59).



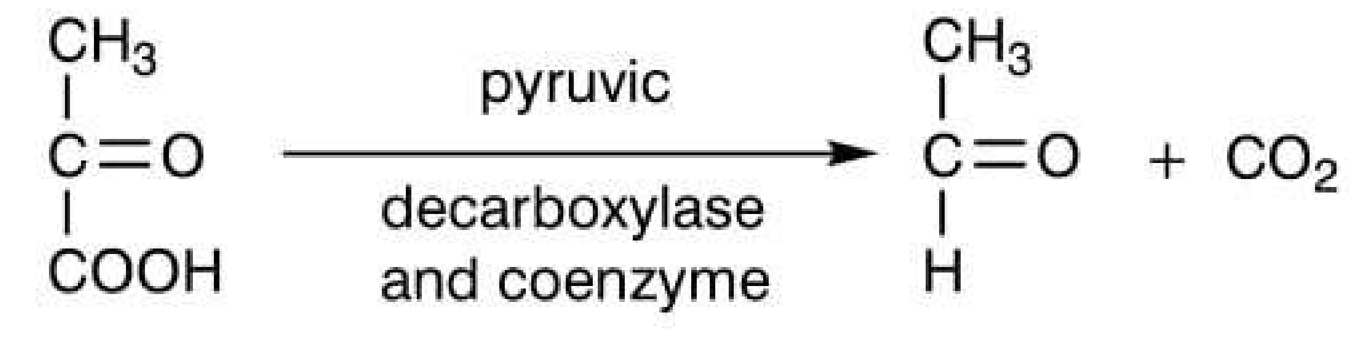
10.59
Choline

10.58
Acetylcholine

Scheme 10.12

Lyases

These enzymes catalyse the non-hydrolytic cleavage of bonds in a substrate to remove specific functional groups. Examples include decarboxylases, which remove carboxylic acid groups as carbon dioxide, dehydrases, which remove water, and aldolases. The decarboxylation of pyruvic acid (10.60) to form acetaldehyde (10.61) takes place in the presence of pyruvic decarboxylase (Scheme 10.13), which requires the presence of thiamine pyrophosphate and magnesium ions for activity.



10.60
Pyruvic acid

10.61
Acetaldehyde

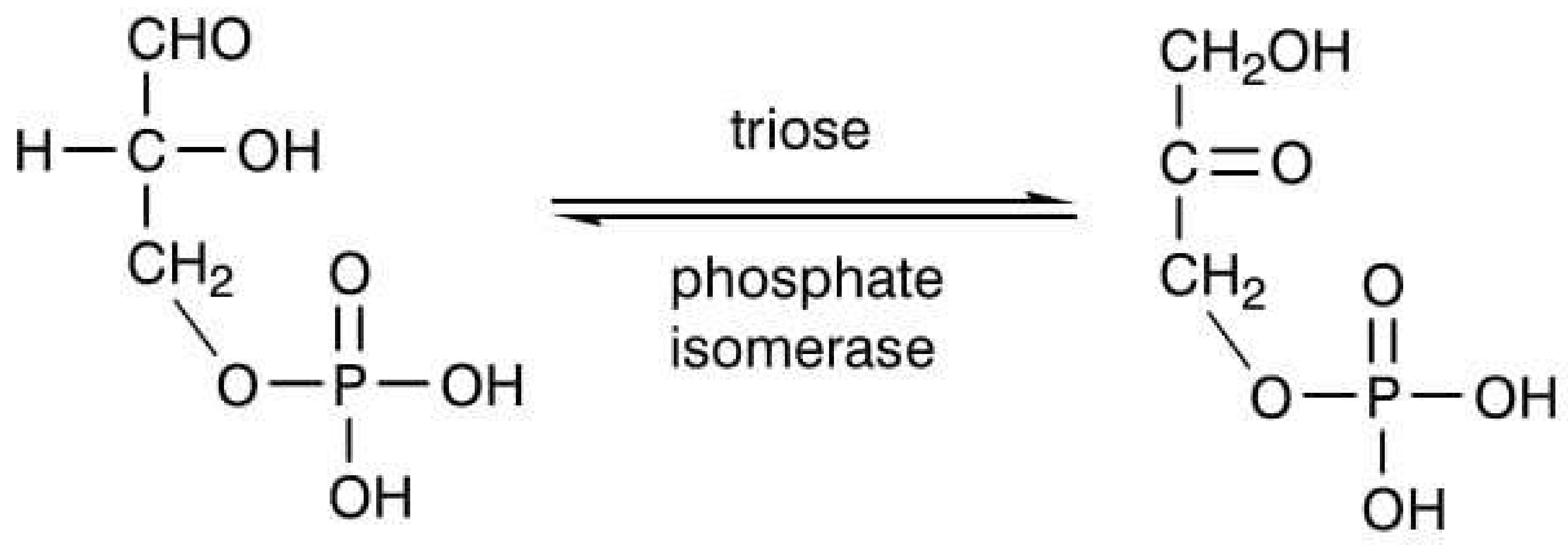
Scheme 10.13

Isomerases

These catalysts facilitate the interconversion of isomeric compounds and include racemases, optimerases, *cis-trans* isomerases, intramolecular oxidoreductases and intramolecular transferases. Scheme 10.14 shows the conversion of an aldehyde to a ketone by triose phosphate isomerase.

Ligases or synthetases

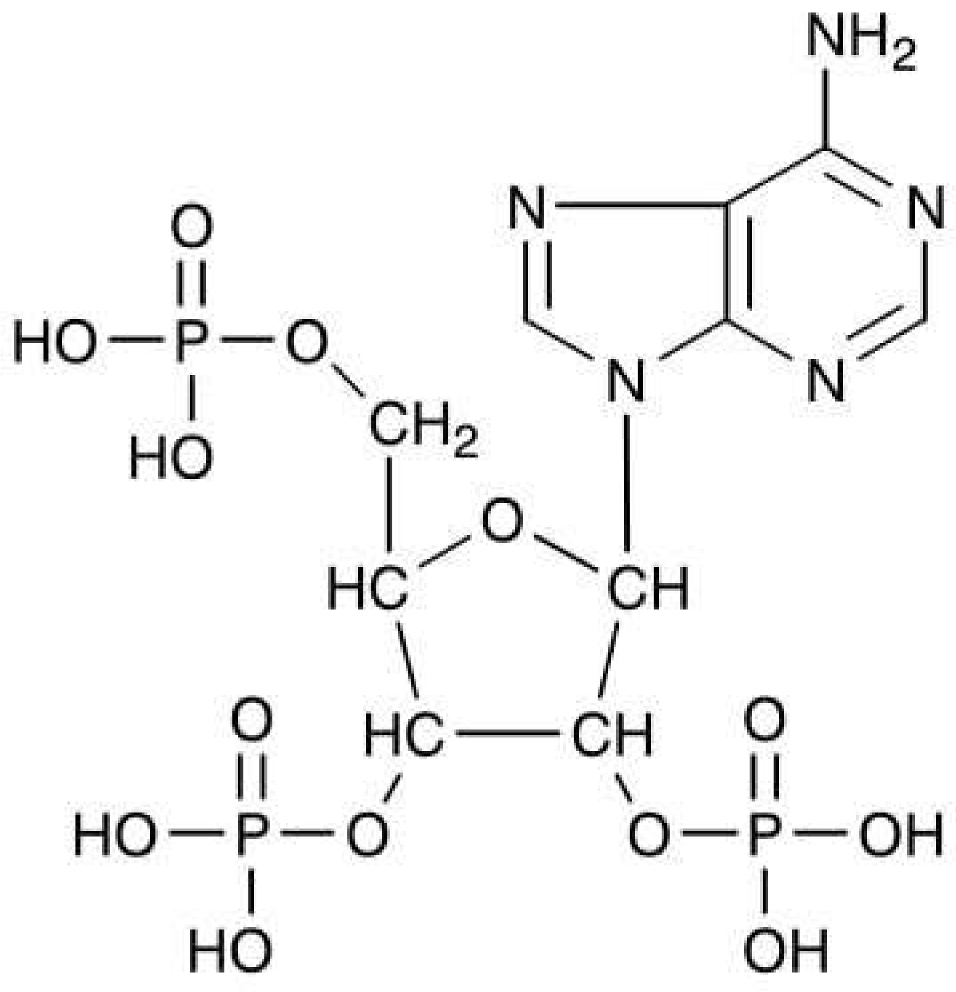
Such enzymes catalyse the condensation of specific compounds, accompanied by the breakdown of a pyrophosphate bond in adenosine triphosphate (10.64). Adenosine is the condensation product of a pentose (D-ribofuranose) and a purine (adenine). Scheme 10.15 shows the action of glutamine synthetase on a mixture of L-glutamic acid (10.65) and



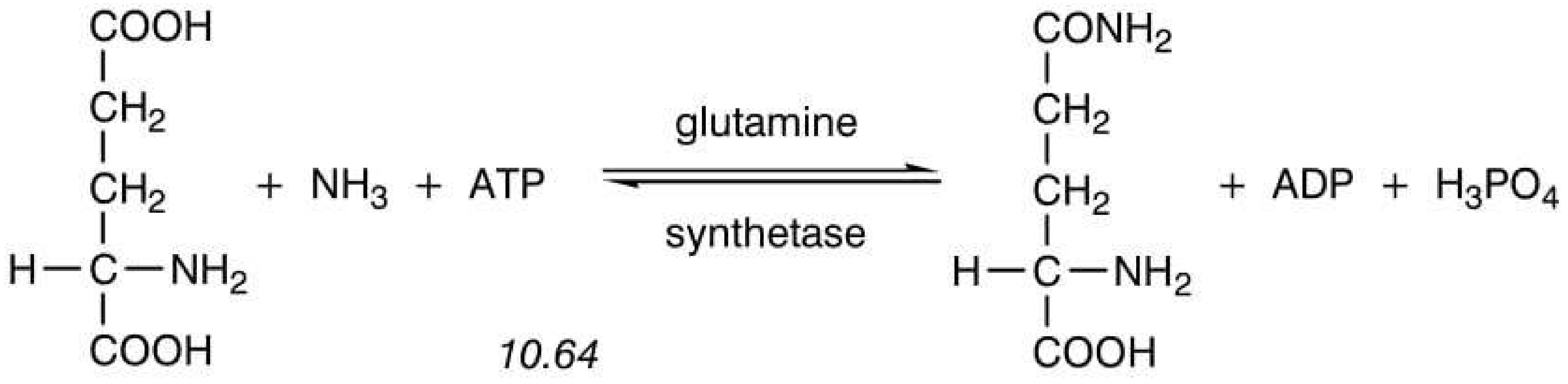
10.62
D-Glyceraldehyde phosphate

10.63
Dihydroxyacetone phosphate

Scheme 10.14



10.64
Adenosine triphosphate



10.65
L-Glutamic acid

10.66
L-Glutamine

Scheme 10.15

ammonia. Adenosine triphosphate (ATP) is converted into the diphosphate (ADP) and phosphoric acid is formed.

More comprehensive accounts of enzyme chemistry, behaviour and technology are available [71,73–75]. In addition, general biochemistry textbooks contain more or less detailed accounts of these topics.

10.4.2 Enzyme applications in textile processing

Enzymes have traditionally been closely associated with the desizing of cellulosic fabrics. In recent years, however, the sphere of possible, if not actual, uses has widened considerably.

Further developments can reasonably be expected, particularly as much of this vigorous research is motivated by environmental concerns. An overview of this activity is given below.

Mercerisation, scouring and alkali boiling of cellulosic fibres

The traditional mercerising of cotton presents quite hostile conditions for enzymes. Hence it is not surprising that little use of enzymes has been reported, either in traditional mercerising or as an alternative means of obtaining similar effects. Cegarra [76] has concluded that, because of the strongly alkaline nature of mercerising solutions and the resultant transformation of the cellulose structure, it seems rather unlikely that enzymes will provide alternatives to alkali in the near future. Even so, it is pertinent to study the effects that mercerisation may have on any subsequent enzyme treatment. It has been shown [77] that enzymatic hydrolysis is accelerated on cellulose that has been mercerised without tension compared with stretch mercerisation.

Possible uses of enzymes in scouring or alkali boiling offer somewhat more scope, although conditions can still be rather hostile as regards alkalinity and temperature. Nevertheless, there are some emergent signs. Various enzymes, such as cellulases, pectinases, lipases and proteases, have been compared [77], leading to the tentative conclusion that cellulases give the best results for the removal of impurities, together with slightly inferior whiteness, a similar loss in strength and less contaminated effluents, compared with the traditional alkaline scour. Use of either a pectinase or a pectinase/cellulase mixture for the removal of pectin from cotton has also been studied [78]. Effective removal using such enzymes was found at 40 °C and pH 4.5, giving a higher degree of whiteness than alkaline washing at the boil for the same degree of cellulose degradation. Cellulase can facilitate the alkaline scouring of viscose [79], enabling the concentration of alkali (36–60 g/l) traditionally used to be reduced by 5–10 g/l, and giving, moreover, a more uniform and consistent swelling process than when alkali is used alone. Another study [80] also demonstrated possibilities for using enzyme formulations in cotton scouring.

Desizing of cellulosic fabrics

The enzymatic desizing of cellulosic fabrics is a long-established standard process. Amylolytic enzymes are used to convert any type of starch size into water-soluble products without affecting the cellulosic fibres. Using enzymes in their natural or modified state, products are available to allow desizing at 20–70 °C, 70–90 °C or 85–115 °C [81]. Cegarra [76] has intimated that, given the availability of such products, further studies are likely to be concentrated on formulations allowing simultaneous desizing and scouring in an alkaline medium, replacing the present two-stage process.

Nevertheless, research continues to explore improved desizing processes. Advantages have been claimed for lipases [82] and traditional amylase desizing can be improved with the help of a thermostable lipase, giving both technical and environmental advantages [83]. Cotton sized with poly (vinyl alcohol) (PVA) is generally desized in water at about 80 °C. However, a mixture of two different PVA-degrading enzymes gives equivalent desizing at only 30–55 °C and pH 8.0. Extending the enzymatic treatment time to 4–6 hours (compared with one hour) resulted in minimum residual PVA [84]. Environmental benefits were also found, since the PVA content in the liquid waste after desizing for four hours was negligible. Advantages for oxidoreductases over amylolytic enzymes have been observed, since they break down lignin impurities and are effective over a wider range of temperature and of pH [85].

Bleaching of cellulosic fibres

The possibility of catalysing the action of hydrogen peroxide by enzymes is an interesting one, but the need to avoid fibre damage is critical and so such catalysis by a peroxidase is not currently practical. However, the careful use of glucose oxidase in conjunction with an enzymatic desizing process is reported [86] to permit the novel and eco-friendly use of starch-containing effluent liquors for subsequent bleaching. This allows the use of hydrogen peroxide as the oxidising agent, together with gluconic acid (10.28) which has outstanding sequestering properties and good biodegradability. Ecological and economic advantages are claimed, including minimising the effluent pollution load, reducing chemical consumption and processing under mild conditions.

After bleaching it is important to ensure that the fibre does not contain residual hydrogen peroxide since this can interfere with subsequent processes, particularly coloration. Certain enzymes, particularly catalases, used to eliminate peroxide are bio-friendly and time-saving [87], thus having significant advantages over traditional methods [88]. Such a technique can be used in either batchwise or continuous washing-off after bleaching to give rapid and complete decomposition of any residual peroxide [89].

Dyeing of cellulosic fibres

Enzyme processing before, during or after dyeing is an active area of study. Enzyme pretreatment may have beneficial or adverse effects on subsequent coloration. The action of enzymes during coloration may improve the coloration process or provide a combined process, such as desizing/coloration or coloration/biofinishing. With the emergence of biofinishing techniques, it is important to know how such enzyme treatments are affected by any prior coloration process. Most of the published work deals with enzyme pretreatments or aftertreatments.

In one study [90], enzyme pretreatment increased colour yield without affecting fastness properties. However, pretreatment of cellulosic fibres with cellulase lowered the subsequent fixation of homobifunctional triazine reactive dyes but did not impair the fixation of other types of reactive dyes [91]. Another study suggested that the enhanced brightness of reactive dyeings was greater with triazine dyes than with vinylsulphone types when cotton was pretreated or aftertreated with cellulase [92].

The enzyme biofinishing of cotton after dyeing was found to be inhibited by direct or reactive dyes but not by vat dyes [93]. In another investigation of reactive dyes in this context, biofinishing was variously influenced by the type of dye–fibre bond, the type of chromogen, the presence of metal ion, the number of reactive groups per molecule and even by the dye application method [91]. Yet another study [94] showed that cellulase pretreatment boosts dye exhaustion and cellulase aftertreatment increases the apparent depth of the dyeing. Interactions between cellulase enzyme pre- or post-treatments and reactive or direct dyes have been studied by Buschle-Diller *et al.* [95], with the objectives of elucidating the mechanism of enzymatic degradation and specifying optimum conditions for a combined dyeing/biofinishing process.

Denim washing

The practice of stonewashing of dyed cotton denim fabrics to give a 'distressed' or washed-down appearance was traditionally carried out with pumice stones. This was labour-intensive, time-consuming, caused abrasion of the fabric surface and created debris. Several authors have described how the stonewashed effect can be produced more advantageously using cellulase enzymes to partially or wholly replace the stones [76,96–101]. The enzymes provide a controllable means of surface attack of the fibres, thus bringing about the desired uneven appearance. Advantages claimed include savings in time and labour, much less fabric abrasion and no debris. The enzymes used are neutral or acidic cellulase preparations, which may contain endo-, exo- or beta-gluconases. The finisher can exploit the differing characteristics of acidic and neutral cellulases by employing washing procedures that take advantage of each type of formulation [98].

Biofinishing of cellulosic fabrics

Biofinishing, or 'biopolishing' as it is more popularly known, is similar to denim washing in its use of cellulase enzymes, although the effects intended are quite different. The process is designed to eliminate, by dissolution, the cellulosic fibrils projecting from the surface of the fabric. This treatment results in [76]:

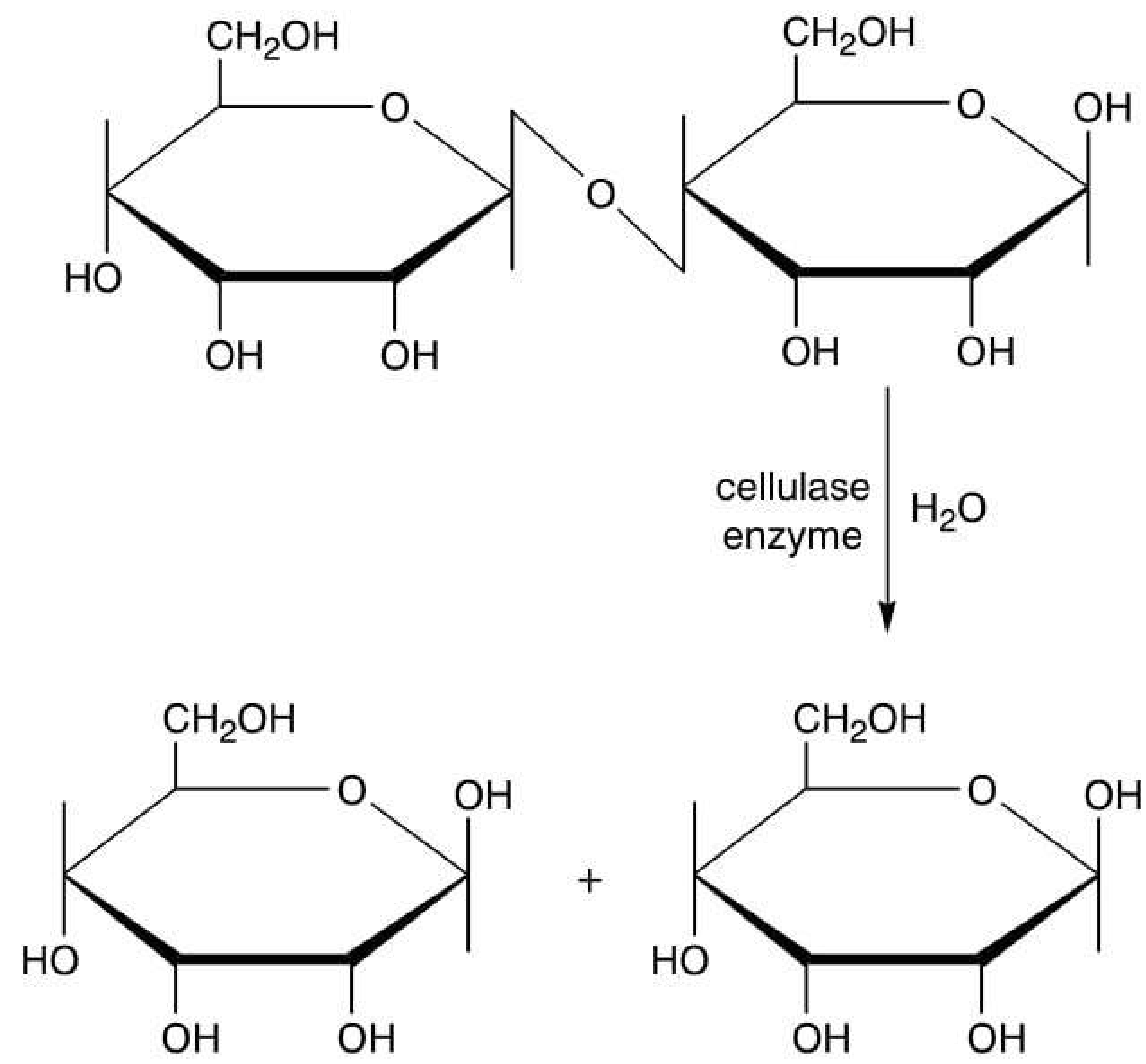
- a cleaner, smoother surface
- a softer, cooler feel
- improved resistance to pilling
- brighter, sometimes deeper colours.

The precise effects obtained are dependent on the fabric quality, the type of cellulase enzyme and the application conditions, but no mechanical forces are involved in removal of the fibrils. The process has attracted considerable attention and is now one of the main methods of defibrillating lyocell fabrics [94,101–114]. Simultaneous treatment with cellulase and protease enzymes has been applied to the biofinishing of wool/cotton blends [115].

Acidic cellulases at pH 4.5–5.5 and 45–55 °C or neutral cellulases at pH 6–8 and 50–60 °C are effective in biofinishing [106,107]. Heavier fabrics and lower enzyme concentrations need longer treatment times but 30–60 minutes is a typical duration. The treatment is terminated by inactivating the enzyme, either by raising the pH to 10 or by increasing the temperature to 75 °C for 10–15 minutes. The process is usually monitored by assessing the weight loss of the fabric; a weight loss of 3–5% usually represents an adequately finished effect without excessive loss of fabric strength [107]. Dissolution of the cellulose involves depolymerisation as illustrated in Scheme 10.16 [107].

Wool processing

It is more difficult to control the enzymatic processing of wool. Hence there is a greater danger of fibre damage compared with cellulosic fibres. Since cellulose is a highly crystalline



Scheme 10.16

material possessing only limited amorphous regions, it is relatively easy to restrict the action of enzymes to the surface of the fibre and to the amorphous material, thus leaving the strength of the fibre unchanged [116] In the case of wool, however, proteases and lipases catalyse the degradation of different components of the fibre. Proteases, having diffused into the interior of the fibre, hydrolyse parts of the endocuticle and proteins in the cell membrane complex. This is difficult to control and can lead to serious damage of the fibre. SEM micrographs have shown the complete damage of wool fibres and released cortical cells characteristic of uncontrolled attack by protease enzymes [116].

Three types of enzyme may be selected for the treatment of protein fibres [76,99]:

(1) Proteases, which can be classified as either peptidases or proteinases. These cleave polypeptide chains eventually into their component amino acids. Peptidases can be further classified as endopeptidases (which act on the main-chain amido groups along the polypeptide molecule) or as exopeptidases (which act only at terminal amino acid residues).
(2) Lipases, which mainly hydrolyse fatty esters, especially triglyceride esters of fatty acids.
(3) Lipoprotein lipases, which act on the lipoproteic bonds of lipoproteins (combinations of proteins with fatty ester molecules), thus breaching the hydrophobic barriers formed by these compounds.

The most widely used of these types are the proteases, but the others may be useful in some circumstances. A characteristic feature is that individual enzymes are highly specific in their action, so that although one protease may yield the required effect, another may fail to do so.

Bleaching of wool

A serine protease that is stable to hydrogen peroxide and is active in an alkaline medium has been found and marketed [76,117,118]. In fact this enzyme becomes more active with increasing concentration of peroxide. This enzyme increases the whiteness of wool directly by decolorising the natural yellowish hue of the fibres. Hence, depending on the degree of whiteness required, this enzyme can be used either alone or in combination with hydrogen peroxide to effect the bleaching of wool. Serine protease can also be applied with bleaching agents that operate by a reductive mechanism.

Carbonising of wool

The traditional method of carbonising with sulphuric acid is environmentally undesirable and can easily lead to fibre damage. Hence it is not surprising that research has been directed towards alternatives in which enzymes are used to remove the cellulosic impurities from wool. Cellulases and lignases are mainly used but others have been proposed [116]:

(1) Removal of plant impurities by hydrolases, lyases or oxidoreductases.
(2) Cellulolytic and pectinolytic enzymes used to reduce the amount of sulphuric acid required.
(3) Incubation of wool with cellulases facilitated subsequent removal of burr with no chemical or physical damage to the wool.
(4) Application of a mixture of cellulases, pectinases and lignases, again without damage to the wool.

Dyeing of wool

The effects of enzyme treatments on the subsequent dyeability of wool have been evaluated. One investigation included both chlorinated and unchlorinated wool [119]. Wool was treated with a protease at 50 °C and pH 7.5, followed by dyeing with CI Reactive Reds 28 and 116. The enzyme-treated wool showed more rapid dyeing and higher absorption with no effect on fastness. These effects were greater on the chlorinated wool than on the unchlorinated control. Alternatively, the enzyme-treated wool could be dyed at a lower temperature. The effect of pretreatment with a neutral protease on dyeing with acid dyes has also been examined [90,120], increased colour yields again being observed. It is essential, of course, to determine whether the economies of increased yield or lower dyeing temperature exceed the additional cost of enzyme treatment, and whether the durability of the wool is adversely affected.

Shrink-resist finishing of wool

This is an area of considerable research activity, comparable with the enzymatic stonewashing and biopolishing of cotton. However, there has been less success in translating this research into commercial processes. Evidently, the technical use of enzymes for wool fabrics will not become widespread for another five to ten years [121]. Since certain enzymes can remove cuticular scales from wool fibres, it is not surprising that they are of interest for shrink-resist finishing, either alone or in combination with traditional chlorination or resin-application processes. Interest in this area is acute, because of the environmental disadvantages of chlorination procedures. These yield absorbable organohalogen (AOX) by-products, which accumulate in the effluent and ultimately may give rise to toxicity problems in the food chain if taken up by aquatic organisms [116]. Hence there is considerable commercial potential for an enzymatic descaling process that could wholly or even partially replace chlorination. The critical factor is to achieve the optimal degree of descaling reproducibility, with minimal effect on fibre strength.

Ideally, the anti-felting effect should be achieved using ‘soft chemistry’ without application of a synthetic resin and the entire process should be environmentally innocuous, producing no harmful substances [116,122]. This ideal has yet to be attained. It was originally thought that the large protease molecule would not be able to penetrate the fibre cuticle. If so, attack would be limited, as with chlorination, to the cuticular scales with only minor deterioration in mechanical properties attributable to damage in the interior [123] This proved to be too simplistic a viewpoint, however, as some proteases even attack the highly swellable cell membrane complex preferentially, possibly penetrating this region by channelling beneath the cuticular scales [123–125]. Moreover, microscopic examination has indicated that enzymatic action on wool is not uniform, some fibres remaining practically intact whilst others are damaged considerably [126]. Most anti-felting investigations have been carried out with proteases but other types have also been examined, e.g. a protein disulphide isomerase which rearranges the disulphide bonds of cystine residues [127] and transglutaminase which introduces new crosslinks into the keratin structure [128].

Protease activity towards wool can be increased by addition of sodium sulphite or bisulphite, either with the enzyme treatment or as a pretreatment [122]. Pretreatment with oxidising agents may also increase the effect of certain enzymes; hydrogen peroxide, dry chlorine, peracetic or performic acid, wet chlorination, potassium permanganate and peroxymonosulphuric acid (H_2SO_5) have been used in this way [122]. Sulphite reduction increases proteolytic activity by cleavage of cystine disulphide bonds in the cuticle to form thiosulphonic acid groups, a reaction known as sulphitolysis [122,129,130]. When preceded by oxidative treatment, the action of sulphite yields electron-withdrawing sulphonic acid groups in the sulphur-rich cuticular layers, selectively activating the nucleophilic degradative reaction catalysed by the protease and thus preferentially directing the enzyme action to the cuticle [122,129,131]. Not all proteases are activated by sulphite, however [126].

Although the present situation and the way ahead appear uncertain, it is clear that enzyme treatment alone does not fulfil the technical requirements for shrink-resist finishing. Even with enzyme treatment, some degree of chlorination (with the attendant AOX problems) and/or application of a resin will still be required. Two-stage or even three-stage processes have been proposed [116]:

(1) (i) Treatment with permanganate; (ii) proteolytic enzyme treatment; This gave complete descaling.
(2) (i) Treatment with papain (protease), monoethanolamine hydrosulphite and urea; (ii) treatment with dichloroisocyanuric acid; (iii) a second enzymatic treatment.
(3) (i) A combined protease treatment; (ii) wet chlorination or oxidative treatment (using sodium hypochlorite and potassium permanganate); (iii) application of a polymer.
(4) (i) Enzyme treatment; (ii) treatment in saturated steam.
(5) (i) Enzyme treatment; (ii) high-frequency radiation.
(6) The Schoeller Superwash 2000 process [132]: (i) so-called ‘black box’ pretreatment; (ii) enzyme treatment; (iii) application of a low-AOX polyamide resin.

Most enzyme treatments of wool are carried out at about 50 °C for 30–60 minutes. The amount of enzyme required depends on the specific enzyme type and its commercial strength. Optimal pH also depends on the enzyme type. In a study of sixteen commercial proteases for which the optimal pH varied from 3 to 10.5 [122], it was found that only papain (optimal pH 6.5–7) and alkaline proteases conferred shrink-resistance on sulphite-treated wool and these tended to cause too much fibre damage. It is thus clearly apparent that in this area of enzyme activity there is still scope for further development to meet the desired targets.

Biofinishing of wool

Enzymes can be used to modify the surface of wool fibres in order to improve lustre, softness, smoothness or 'warmth' of the fabric. Since such processes involve attack on the cuticular scales of the fibre, there is clearly a resemblance to shrink-resist treatments and similar methods are used [116]:

(1) (i) Treatment with potassium permanganate, ammonium sulphate, acetic acid and bisulphite; (ii) treatment with a proteolytic enzyme.
(2) Descaling by application of a heat-resistant neutral protease to confer a cashmere-like feel.
(3) Combined use of dichloroisocyanurate and a proteolytic enzyme.
(4) Complete removal of degraded or damaged portions of the wool (not merely the cuticle) using: (i) protease treatment; (ii) formic acid rinse and application of a softener.
(5) (i) Treatment with dichloroisocyanurate; (ii) neutralising and incubating with papain; (iii) steaming at 100 °C.

Only empirical tests have so far been carried out, however [76]. In a detailed but small-scale study, various options were examined for the sequence: (i) oxidative treatment; (ii) protease treatment; (iii) application of softener, including exhaust or pad application [133].

The following products were examined:

Oxidising agents

(a) dichloroisocyanuric acid,
(b) potassium peroxymonosulphate,
(c) magnesium monoperoxyphthalate hexahydrate,
(d) sodium hypochlorite.

Enzymes

Papain and four protease formulations that varied from neutral to alkaline as regards optimal pH for activity.

Softeners

(a) a weakly cationic softener,
(b) a cationic silicone micro-emulsion,
(c) a cationic emulsion modified with a silicone elastomer.

The results varied widely:

- descaling: from none to full
- fibre damage: from none to severe
- strength loss: from -6% (i.e. a slight increase in strength) to +30%
- Whiteness Index (original value -2): from -1.9 to +25.8.

Irrespective of the descaling effect, development of a 'soft lustre' depends on application of a softener. These experiments were positive in demonstrating the possibility of descaling the fibres and in perceptibly improving lustre under mild conditions. In particular, it was shown that papain is effective at the remarkably low concentration of 50 mg/l, showing a high degree of specificity after chlorination.

Degumming and desizing of silk

The use of enzymes in silk degumming or desizing is well-established [76,99,134–136]. In a study of eight enzymes under optimised conditions [137], weight losses of 24 ± 3% were observed in most cases but trypsin and pepsin gave extremely poor results. Increasing the treatment time at the optimal concentration of enzyme gave no further significant weight loss. There was no significant strength loss in the case of degummed silk and lustre was improved. In earlier work, degumming with papain was as effective as alkaline degumming and superior to other methods [138]. Nevertheless, all the parameters must be carefully controlled to prevent attack on the silk itself [76].

Dyeing of silk

Enzymes have been used to facilitate the dyeing of silk with reactive dyes [139].

Application of enzymes in laundering

As surfactants are often used in textile processing, it is important to note that anionic or cationic surfactants can inhibit the action of enzymes, as has been reported in the case of cellulases used for the treatment of cotton [140]. Dyes can also inhibit enzyme activity: for example, CI Direct Red 28 has been shown to have a much greater inhibitory effect than CI Acid Orange 7 [141].

Many domestic and laundry washing formulations contain at least one enzyme. Alkaline proteases, with serine active sites and optimal activity at pH 9–10.5, are mostly used [73]. Much attention is given to the degree of temperature toleration and to compatibility with other components of the commercial product. In some countries (e.g. the USA) it is sufficient to have temperature tolerance up to 50–55 °C, whereas elsewhere (e.g. in Europe) toleration to 100 °C may be required for laundry detergent formulations. Papain, for example, has broad activity and is thermally stable but is unsuitable, as is trypsin, on account of incompatibility with perborate, many boosters and all bleaches. A protease derived from *Bacillus licheniformis* is much more suitable, this being compatible with surfactants, chelating agents such as phosphates, EDTA and NTA, as well as with fluorescent brightening agents and perfumes.

Rather more offbeat investigations have centred on micro-organisms belonging to the group

Archaea or *Archaebacteria*, which live in sulphurous waters around undersea volcanic vents. An extraordinarily stable enzyme which functions even at 135 °C and survives at pH 3.2–12.7 has been identified [142]. This enzyme has been termed STABLE (**s**talk-associated **a**rchae**b**acteria**l** **e**ndoprotease). It is suggested that such exceptional stability may be attributable to unusually large M_r and tight folding of the protein chain. Suggested uses include washing powders and detergents, as well as industrial catalysts. It is even proposed that such remarkable properties may have contributed to the early evolution of life on earth [142].

10.5 PREPARATION OF SUBSTRATES

By one of those perversities of terminology often encountered in textile wet processing, the term 'auxiliaries' generally includes all chemicals used in preparation and finishing processes, even though in these cases such chemicals often provide a primary rather than a secondary (auxiliary) function as in coloration processes. Thus the chemicals used in preparation are discussed in this section. It cannot be overstressed that the success of any coloration process relies on the state of the substrate presented for coloration; moreover, thorough preparation can often do much to reduce the need for auxiliaries in subsequent processes. Methods of preparation for cellulosic and wool substrates are also discussed elsewhere [11,143]. In this chapter the emphasis is on the chemistry of the products used rather than on the technology of processing.

10.5.1 Scouring

The purpose of scouring is to reduce to an acceptable level the amounts of fats, waxes, oils and dirt present. Apart from the aesthetic benefits of a clean substrate, the major technical reason for scouring is to improve the extent and uniformity of absorbency for subsequent processes, especially coloration. Usually the objective is the complete removal of all extraneous matter but on occasion only partial removal is the aim, since a certain residue of oils, for example, will aid such processes as spinning, weaving or knitting. Scouring is particularly important with natural fibres, which obviously contain much more extraneous matter than do synthetic fibres.

In scouring, surfactants function as primary, rather than auxiliary, agents. The basic requirements are for good wetting power and detergency, the latter property generally including the ability to remove, emulsify and suspend the extraneous matter in the liquor. Not all effective detergents possess good wetting properties; hence a combination of surface-active agents to provide both wetting and detergency may be preferable. Detergency can be significantly improved by the use of additional compounds usually referred to as 'builders', the chief of which is undoubtedly alkali in the form of sodium carbonate or hydroxide. Alkaline phosphates such as sodium orthophosphate, sodium pyrophosphate or sodium tripolyphosphate may also be used in those countries where they do not contravene the local environmental regulations. Alkalis function mainly through saponification of the waxes, fats and oils on the substrate, thus. rendering them water-soluble and more amenable to removal and suspension by detergents.

If the processing water or the substrate contains cations such as those of calcium, magnesium or iron, a sequestering agent should be added to the scouring liquor. Apart from their ability to sequester metal ions, many of these agents also possess useful detergent-enhancing powers. The aminopolycarboxylates are generally preferred, both for their sequestering ability and for their stability in warm to hot alkaline liquors. Polyphosphates are occasionally used at lower temperatures but are less efficient in alkaline media. When incorporated in the scouring medium certain organic solvents, such as pine oil, trichloroethylene, perchloroethylene, triethanolamine or glycols, can greatly aid the removal of greasy matter, particularly mineral oil which may be a component of any lubricating oils present on the substrate. However, the use of these additives must be in accordance with local environmental regulations.

Soaps are occasionally still used for scouring, although anionic or nonionic synthetic detergents are almost always preferred. Among the anionics, fatty alkyl sulphates, sulphonates and phosphates are commonly used. Ethoxylated fatty alcohols are typical nonionic scouring agents. Ethoxylated nonylphenol was once the most common nonionic product used. This came under quite severe environmental scrutiny but, as explained in section 9.8.1, there is now a good deal of evidence to suggest that nonylphenol derivatives are not so environmentally damaging as at first thought.

Proprietary scouring agents range from single-component surfactants to complex, specially formulated mixtures that contain some or all of the above mentioned types of component matched to give a balanced or compatible product. As mentioned in section 9.8.3, better emulsifying properties are generally obtained with a carefully selected blend of surfactants rather than with a single product. It has been demonstrated [144] that in the case of ethoxylated nonylphenol and ethoxylated fatty alcohol surfactants, the broader the molar mass distribution of the combined surfactants the better is the scouring efficiency, and that it is inappropriate to aim at homogeneity of the nonionic formulation in scouring. In selecting a suitable product, thought should be given to the ease with which it can be rinsed out of the substrate and to any effects that residual quantities may have on subsequent processing. Fabrics destined for printing, in particular, need the highest degree of uniform absorbency and cleanliness [145], free from residual surfactants that may cause bleeding or haloing of the printed design into the surrounding area.

Scouring is of crucial importance in wool processing: important, because the raw fibre contains 20–60% of extraneous matter in the form of grease, suint, dirt, sand and vegetable matter; and critical, because the fibre is so easily damaged by hot alkaline treatments. There have been considerable changes in wool scouring practice, evolving mainly from corresponding changes in the types of lubricants used on the fibre, although environmental factors have also played a part. It has been pointed out that the pollution load from a wool scouring mill can be similar in magnitude to the average discharge from a small town [11]. Hence there are heavy environmental pressures on wool scourers. This impact has provided the impetus to develop systems which use as little water and energy as possible and reduce effluent contamination through the recovery of some of the components.

Examples of such comprehensive systems are the WRONZ and Siroscour (CSIRO) techniques, which use minimal volumes of water whilst producing wool of optimal quality. The essential feature of the WRONZ treatment [146] is the passage of the greasy liquor from the first stage through a heavy solids separating tank and a centrifugal separator, from which the partially degreased liquor is returned to the first stage. The Siroscour system depends on concentration destabilisation to increase centrifugal recovery of grease and dirt and to reduce water usage even further [146]. In concentration destabilisation wool grease, dirt and suint salts are allowed to build up to very high levels in the scour bowls so that the resulting unstable emulsion can be cracked easily by heating to 95 °C, allowing the grease and dirt to be centrifugally separated. Separation occurs in three stages [147]:

(1) superficial dirt (easy to remove)
(2) grease
(3) persistent dirt (difficult to remove).

Advantages claimed for this process [148] include: improved whiteness, decrease in ash content, improved grease recovery and quality, optimisation of water consumption, efficient dirt removal from effluent and a reduction in treatment costs. An excellent review of wool scouring (and of wool processing generally) up to 1984 is available [146].

Soap and alkali were traditionally used and very greasy wools were scoured with alkali alone, forming a soap *in situ* by saponification of the wool grease. Such methods are now rarely used, having been supplanted by nonionic surfactants under neutral or alkaline conditions. Octa- and nona-ethoxylated nonylphenols are the preferred nonionics, providing environmental considerations permit their use, since they are unsurpassed for detergency. Alternatively, ethoxylated straight-chain fatty alcohols are preferred on the grounds of superior biodegradability. The advantages of nonionic detergents over soaps include greater efficiency under neutral conditions, stability in hard water, lower cost and more efficient removal of grease (although this is one area where over-degreasing can be a disadvantage). Syndets are desorbed more easily in difficult rinsing situations (in yarn cheeses, for example), although they are not as efficient as soap for the suspension of dirt. In place of the alkaline sodium carbonate, the tendency is to use neutral sodium sulphate as a detergent builder.

Apart from the impurities present in raw wools, typical formulations [146] for lubricating wool fibres are:

(1) water-miscible polyglycol lubricants; these are mainly used on carpet yarns and can be readily removed using a neutral nonionic surfactant;
(2) mineral wool oil (mineral oil with a nonionic lubricant); normally extracted using a nonionic surfactant, although in some cases a little alkali may also be useful;
(3) a combination of mineral oil, olein fatty acids and triglycerides; nonionic surfactant with sodium carbonate can be used, but for more complete removal (as where subsequent shrink-resist processes are carried out) soap and sodium carbonate must be used;
(4) natural vegetable and/or animal oils; these are still used on woven worsteds scoured traditionally with soap and sodium carbonate, although even here there is a gradual trend towards more neutral systems.

Nowadays, proprietary mixtures of lubricating agents are formulated with ease of removal in scouring very much in mind. Consequently, scouring processes are generally mild, using a nonionic surfactant at about 50–60 °C [11].

Aqueous scouring is expensive in terms of water use and effluent treatment and it can cause entanglement of delicate wool fibres. Solvent scouring offers an effective alternative but it is essential that the solvent does not enter the environment. Earlier solvent-based processes included the use of perchloroethylene in which 8–18% water had been emulsified with a surfactant. Current processes are based on hexane (de Smet process), 1,1,1-

trichloroethane (Toa/Asohi process) [11,149] or a commercial product called Triwool (ICI) in the Wooltech process [150–152].

The Wooltech process is claimed to be environmentally friendly and to produce wool of superior quality. The Triwool solvent is non-flammable, does not deplete ozone from the upper atmosphere and is not a known carcinogen. The process specifically excludes water, being designed primarily to avoid fibre entanglement. Current use is for the scouring of wool tops, where it gives about 2–3% higher yields than aqueous scouring. The recovery of raw wool grease is claimed to be 99%. The process offers environmental advantages over conventional aqueous scouring and gives softer wool fibres of enhanced tensile strength and elasticity, which is beneficial for spinning and weaving.

In the laundering of garments and household textiles, as opposed to the scouring of in-process material, agents are often added to the liquor to prevent redeposition of soil extracted from the fabric during washing, typical products being the hydroxyethyl, hydroxybutylmethyl and carboxymethyl ethers of cellulose. It has been shown, using carbon black soiling on shrink-resist treated wool, that the lowest redeposition was obtained with hydroxybutylmethylcellulose and the highest with the carboxymethyl ether [153].

The other major natural fibre, cotton, contains a significant proportion of extraneous matter such as seeds, fats, waxes, colouring matter and dirt, as well as substances such as sizes and lubricants applied during processing. Unlike wool, however, it has outstanding stability in alkali and withstands strongly alkaline treatments ranging from severe caustic kier boiling to milder treatments with soap and soda [143,154]. It is difficult to detach the effect of scouring from the complete sequence of desizing, scouring, mercerising and bleaching, since they all contribute to improved absorbency and cleanliness. Traditional caustic treatment in kiers is carried out at the boil or in some cases at up to 120 °C, using 1–2% o.w.f. alkali. This treatment bursts the seed motes and saponifies fats and waxes, converting the fatty esters into sodium salts and glycerol. This *in situ* formation of soaps naturally aids cleaning. Nevertheless, synthetic detergents are often added to aid penetration through wetting and to increase detergency.

The surfactants selected must be highly stable in the strongly alkaline conditions, as well as in hard water. Anionic surfactants of the fatty alkyl and alkylaryl sulphate types have been preferred, although the use of phosphate esters is increasing. A synergistic mixture is beneficial, one component (C_{10}–C_{13}) to aid wetting, the other (C_{14}–C_{16}) as a detergent. The sulphosuccinates, often a first choice for wetting ability, cannot be used here as they are hydrolysed under such strongly alkaline conditions. A sequestering agent is usually added in order to remove metal ions that would create problems in subsequent bleaching. Addition of a mild reducing agent guards against alkaline oxidative tendering of the fibre through oxycellulose formation and also promotes a degree of bleaching. The reducing agent will also reduce any iron(III) contamination to iron(II) ions, which are easier to remove by the sequestering agent. A commercial kier boiling additive may contain some or all of these components. Suppression of foam may also be a requirement. Semi-continuous and continuous scouring systems are more common nowadays [154]. The auxiliary needs in these pad–steam processes are generally the same as those for batch scouring, except that the selection and balancing of components is much more critical in order to secure optimal treatment during the short dwell times.

Contrary to the usual practice of scouring cotton and its blends under alkaline conditions, McCaffrey and Santokhi [155] have cogently argued the case for scouring knitgoods under acidic conditions. This starts from the assertion that the degree of impurity removal resulting from conventional alkaline scouring is probably not really necessary for cotton knitgoods. In the case of knitgoods, as opposed to woven fabrics, a milder scour is desirable to retain some of the natural fats and waxes, resulting in a fabric with a softer handle and improved sewability [143]. It has been demonstrated [155] that acidic scouring (pH 4.5 with acetic acid) in the presence of a self-emulsifiable knitting lubricant can give results as good as traditional processes on knitgoods, except that impurity removal is inferior but acceptable. In addition there are significant advantages, particularly from economical and environmental aspects. Acidic scouring uses approximately one-third less water than an alkaline scour. Alkaline processes often require a separate acidic rinse to neutralise the alkali, whereas residual acid is easily rinsed out. Acidic scouring also offers an opportunity to reduce chemical consumption and hence costs. These savings minimise effluent treatment and reduce the effects of effluent on the environment. Acidic scouring gave a reduced processing time and lower weight losses, both factors that contribute to improved productivity.

Compared with wool and cotton, the scouring procedures for synthetic fibres are relatively simple since these fibres contain fewer impurities. Most of these have at least some degree of water solubility; the most important are sizes and lubricants. The major sizes used are poly(vinyl alcohol), carboxymethylcellulose and poly(acrylic acid), all of which are completely or partially water-soluble. Sometimes aliphatic polyesters are used.

Secondary acetate and triacetate fibres generally respond to a light scour with soap or synthetic detergent, usually at 60–75 °C, this being sufficient to remove soil, oil, sighting colour and any antistatic agent, although temperatures can range from 30 to 90 °C [156]. Anionic synthetic detergents, such as the poly(oxyethylene) sulphates, are preferred before dyeing with disperse dyes since low cloud-point nonionic scouring agents, if carried over into the dyeing process, can interfere with the stability of the dye dispersion at higher temperatures. Addition of a sequestering agent is helpful in hard water. Care should be taken if alkali is added, especially on secondary acetate, since these ester fibres can be hydrolysed to cellulose under hot alkaline conditions. Nevertheless, in the S-finishing process this alkali sensitivity is exploited to effect a carefully controlled surface saponification of the fibres to improve drape and antistatic properties [157]. Sodium hydroxide is applied together with an anionic surfactant to aid wetting and uniformity of treatment. S-finishing is more usually carried out on triacetate fibres, reducing the total acetyl content from about 62 to 59%.

When scouring synthetic fibres that are to be dyed with disperse dyes, nonionic scouring agents are best avoided unless they are formulated to have a high cloud point and are known not to adversely affect the dispersion properties of the dyes. Conversely, when scouring acrylic fibres, anionic surfactants should be avoided [156] because they are liable to interfere with the subsequent application of basic dyes. These fibres are usually scoured with an ethoxylated alcohol, either alone or with a mild alkali such as sodium carbonate or a phosphate.

Polyamide and polyester fibres are generally scoured using an alkyl poly(oxyethylene) sulphate and sodium carbonate. Some polyester qualities are subjected to a causticisation treatment with sodium hydroxide in the presence of a cationic surfactant to give a lighter fabric with a silkier handle [154,156]. This treatment involves etching (localised saponification) of the polyester surface and is broadly analogous to the S-finish used on triacetate fibres. The process has attracted considerable interest in recent years but its popularity is likely to decline as the availability of polyester microfibres increases. If the weight loss during caustic reduction of polyester is restricted to 15–17% there is little effect on the breaking strength or the viscosity of the fibre [158], since hydrolysis is limited to the surface of the fibre. If the weight loss is greater than 20%, however, deeper layers of the fibre are attacked and the fibre strength and viscosity are reduced. The crystalline regions of the fibre show considerable resistance to hydrolysis. These factors, however, may vary quantitatively depending on the structure and morphology of the particular polyester.

The cationic surfactant normally used with the alkali acts as a catalytic accelerant [159]; quaternary ammonium compounds are most often used. The kinetics of the process have been studied [159], showing that careful control of all parameters is essential. The treatment results in an increase in surface polarity of the fibre. The substantivity for dyes and the rates of wetting-out and dyeing are increased. The increase in wettability arises from the formation of free carboxyl and hydroxy groups [160]. Although sodium hydroxide is the preferred alkali, other alkalis have been investigated [161], the order of activity being: KOH > NaOH >> Na_2CO_3. Saponification also increased at lower liquor ratios.

Cationic accelerants vary in their efficacy [161]. Other types of accelerant have also been evaluated. In one study [162], comparisons were made between tetra-ethylammonium bromide, benzyltriethylammonium chloride, poly(diallyldimethylammonium chloride) and the diethyldimethylammonium derivative of a benzenesulphonate polyglycol ester. It was found that the cationic polymers had a greater effect than the simple quaternary ammonium compounds of lower molecular mass. This effect was attributed to the capability of the polymers to enter into hydrophobic interaction with the fibre surface. Ethylenediamine has also been found to accelerate the alkaline hydrolysis of polyester [163].

Alkaline hydrolysis in a solvent (dimethylformamide, dimethylsulphoxide or dimethylacetamide) containing sodium hydroxide has been investigated [164]. Fabric geometry [165] and the degree of heat setting of the polyester also influence the results. As the temperature of heat setting was increased, the accelerating effect of dodecylbenzyldimethylammonium chloride decreased [166]. Basic-dyeable polyester is particularly sensitive to alkaline hydrolysis [167]. In some cases, saponification has been used to produce special effects such as a leather-like finish [168].

10.5.2 Desizing

Desizing is an essential part of the purification process for woven fabrics. Sizes perform an adhesive and lubricating function. After drying, the size forms a protective film on the surface of the warp yarns, bonding the protruding fibrils to produce a smoother yarn with improved tensile strength and abrasion resistance. The objective of sizing is to improve weaving efficiency by reducing the number of yarn breakages, reducing frictional wear of loom parts and allowing increased running speeds.

Individual size polymers may be used alone or in combination with one another and their performance may be further improved by the addition of other components such as waxes and lubricants. However, whilst sizing offers many benefits in the subsequent weaving of the yarns, it is anathema as far as wet processing is concerned. A typical sized yarn may contain as much as 34% of impurities, distributed as shown in Figure 10.15. These impurities can interfere with wetting-out and with bleaching. They may also affect coloration processes. Depending on the type of size and the dyes used, dye uptake may be increased or resisted;

hence uneven distribution of size may lead to unlevel coloration. There may also be a deleterious effect on fastness properties, since coloured size is likely to be attached to the fibre only superficially. Consequently, it is invariably essential to remove sizes and lubricants thoroughly before further wet processing.

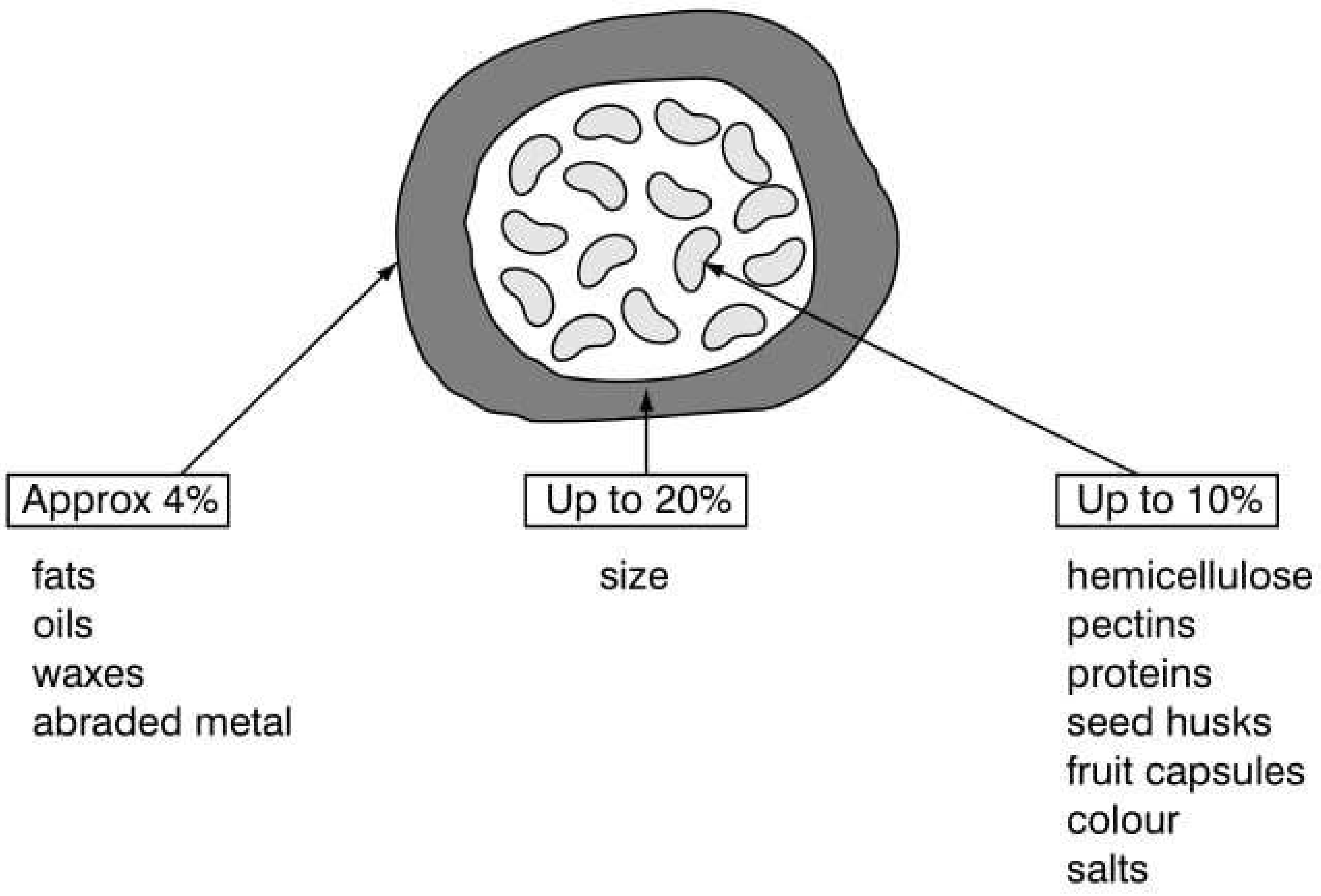


Figure 10.15 Cotton warp yarn and its impurities [169]

This removal of size residues inevitably raises environmental questions. Unfortunately, the various size polymers and their associated additives respond to different methods of removal. It is therefore highly desirable to know which sizes and other components have been used in a given case so that appropriate methods of removal can be formulated. This is not always easy, particularly in commission dyehouses or printworks where sizing has been carried out elsewhere. Analytical procedures are available but these require appropriate facilities and expertise. Once desizing has been carried out there arises the question of how to dispose of the effluent.

The range of size polymers available has expanded to the point of being extremely complex [169], both in terms of the main types of size and the numerous combinational possibilities that they represent. The present overview of salient aspects covers the following: chemistry of size polymers, the use and properties of sizes, desizing methods, analysis of size polymers and environmental aspects. A summary of the equipment used for sizing is available [170].

Chemistry of size polymers

Recent reviews dealing with the chemistry of size polymers are available [169,171]. Sometimes a distinction is made [172] between primary sizes, secondary sizes and binders. This distinction appears to be an arbitrary one depending mainly on the proportions present in a mixture, although other factors may also be pertinent. There is a great deal of similarity in essential chemistry between typical size polymers, thickening agents used in printing and migration inhibitors used in continuous dyeing. An overall summary [169] of the main types of size polymers available is given in Table 10.5. Similar but less comprehensive lists are given elsewhere [171,172].

Table 10.5 Chemical types of main size polymers [169]

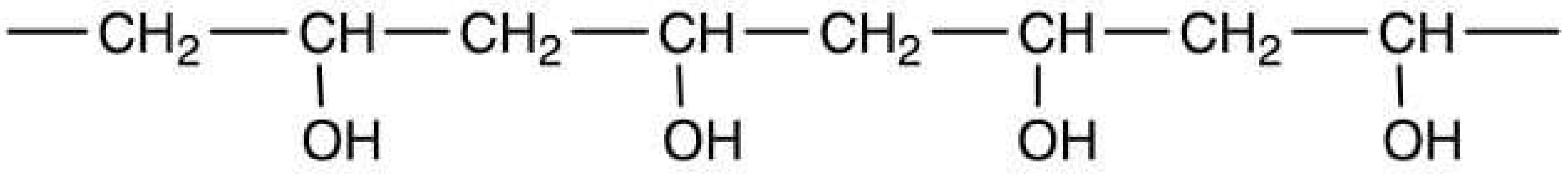
Vegetable products			
Native	Starches	Potato, maize, wheat, rice, sago, tapioca	
	Resins		
	Vegetable gums	Arabic, Locust bean, Senegal, Tragacanth	
	Mosses and algae	Moss starch, sodium alginate	
	Pectin		
Modified	Starch derivatives	Water-soluble starches	
		British gum	
		Starch ethers	Hydroxyethyl starch
			Hydroxypropyl starch
		Starch esters	Carboxymethyl starch
			Phosphate starch
			Starch carbamate
	Cellulose derivatives	Cellulose esters	Carboxymethyl cellulose
			Methyl cellulose
Animal products			
	Glue		
	Gelatin		
	Casein		
Synthetic products			
	Polyvinyl compounds	Partially saponified poly(vinyl acetate)	
		Fully saponified poly(vinyl acetate)	
		Copolymers with crotonic acid	
		Copolymers with vinyl acetate	
	Acrylic acid copolymers	with methacrylic acid	
		with acrylic acid esters	
		with acrylonitrile	
	Maleic acid copolymers	with styrene	
		with ethyl vinyl ether	
		with butadiene	
	Poly(ethylene glycol) copolymers	with isophthalic acid	

It is important to recognise that the molecular characteristics (average molecular mass and distribution, possible degree of substitution) of such polymers can be varied quite widely, with attendant changes in properties. Thus polyacrylic acids and their salts may be described as either sizes or binders. The distinction is related to the proportions used: to be effective as a binder [171] such a polymer must constitute at least 10% of the dry weight of a size formulation. A product marketed specifically as a binder may have molecular characteristics that provide properties different from those of a similar product marketed as a size component. For example, an acrylic size may be engineered specifically for adhesion and film-forming properties whereas an acrylic binder may be designed to enhance film elasticity when added in smaller quantities (about 10%) to a size formulation. It is therefore important to bear in mind that different polymers based on similar chemistry can be engineered to provide suitability for specific uses.

The chemistry of starches, galactomannans, modified starches, modified celluloses and alginates is discussed in section 10.8.1 on natural thickeners. The main starches used are potato starch in Europe, maize starch in America, and rice, maize, tapioca or sago starches in the Far East [169].

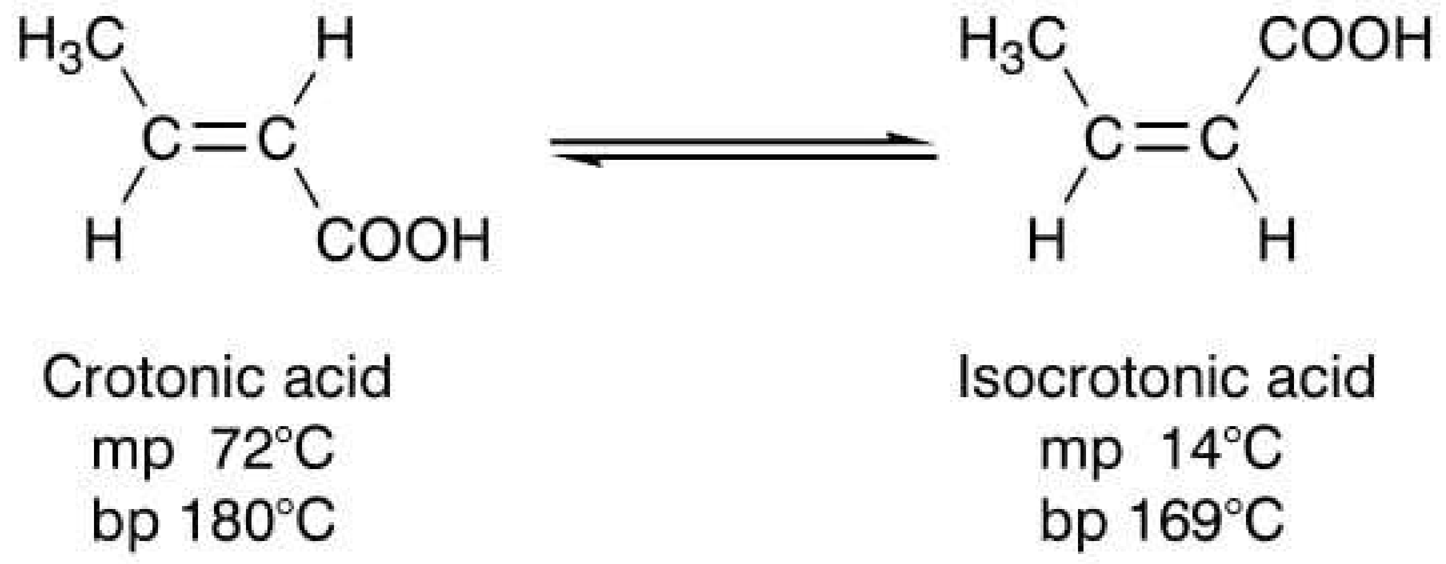
Animal glue is a complex colloidal mixture of proteins. The related gelatins are also complex heterogeneous mixtures of proteins. They are strongly hydrophilic and rich in the amino acids glycine, proline, lysine, hydroxyproline and hydroxylysine. Casein is a phosphoprotein obtained from the milk of mammals.

Poly(vinyl alcohol) has the structure 10.67. Poly(vinyl acetate) is the fully esterified derivative of poly(vinyl alcohol), in which the –OH groups are replaced by $-OCOCH_3$ groups. As indicated in Table 10.5, commercial polyvinyl sizes are effectively copolymers of poly(vinyl acetate) and poly(vinyl alcohol) that vary in the degree of saponification of the ester groups. These products may comprise 100% of either polymer, or combinations of the two monomers in any proportions. Crotonic acid (2-butenoic acid), widely used in the preparation of resins, may also be a component. This compound exhibits *cis–trans* isomerism (Scheme 10.17). The solid *trans* form is produced readily by catalysed rearrangement of the liquid *cis* isomer.



$$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-$$

10.67

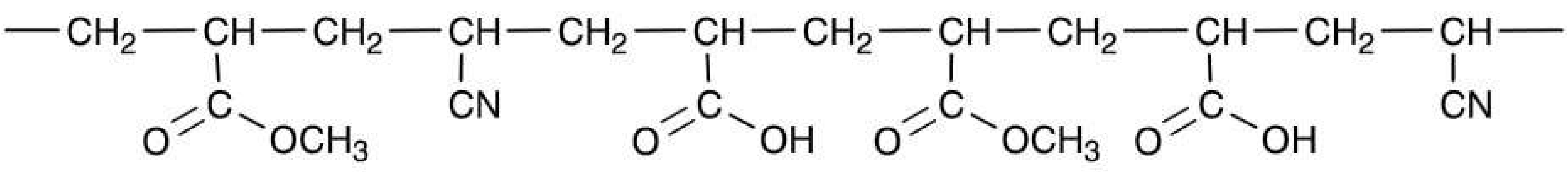


Crotonic acid
mp 72°C
bp 180°C

Isocrotonic acid
mp 14°C
bp 169°C

Scheme 10.17

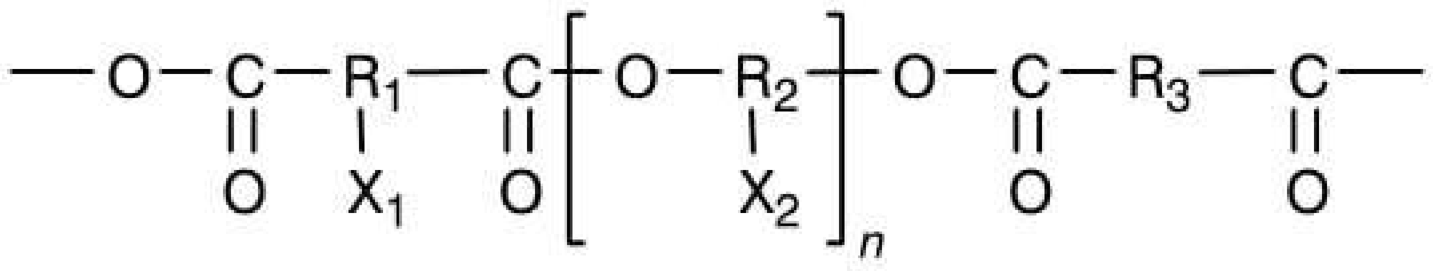
Polymers based on acrylic acid have gained considerable importance in recent years. Their essential chemistry is discussed in section 10.8.2 on synthetic thickeners. Copolymers of acrylic acid with acrylonitrile and methyl acrylate (10.68) contain a random distribution of cyano, ester and acidic sidechain groups [169].



$$-CH_2-\underset{O=C-OCH_3}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}-CH_2-\underset{O=C-OH}{\underset{|}{CH}}-CH_2-\underset{O=C-OCH_3}{\underset{|}{CH}}-CH_2-\underset{O=C-OH}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}-$$

10.68

The polyester sizes used have a much lower average molecular mass than polyester fibres. These structures (10.69) contain sulphonic acid groups and may be water-soluble or water-dispersible types. The degree of sulphonation is low [171]. If these resins are subjected to a high pH, the sulphonate groups can be hydrolysed, giving an insoluble resin that is very difficult to remove from the fibres.



10.69

(1) R_1 = Aromatic ring
(2) X_1 = $—SO_3^-$, $—OCH_2CH_2CH_2SO_3^-$ or $—CO_2CH_2CH_2SO_3^-$ substituent on the aromatic ring R_1
(3) R_2 = CH_2CH_2 (n = 2–10), $CH_2CH_2CH_2$ (n = 1–2) or CH_2—cycloalkyl—CH_2
(4) X_2 = $—CH_2OCH_2CH_2CH_2SO_3^-$ substituent on aliphatic group R_2, in which case X_1 = H
(5) R_3 = Cycloaliphatic or aliphatic hydrocarbon of 2–6 carbon atoms

Rather more specialised sizes are used in certain applications. For example, a reactive poly(dimethylsiloxane) (section 10.10.2) is recommended for the sizing of some industrial textile fabrics [173].

The application and properties of sizes

As already mentioned, the essential aim of sizing is to increase productivity in weaving. This is achieved through a reduction in yarn breakages that permits increased running speeds. Indeed, the high speeds of modern weaving processes could not have been realised without corresponding improvements in sizing technology. The most important requirements of a size formulation can be summarised as follows [174]:

- high adhesion and good film-forming properties on the yarn, together with good elasticity of the applied film
- low tendency to foam in the application liquor
- freedom from skin formation in the application liquor
- good storage stability
- good compatibility of wash-off liquors containing different size components
- appropriate compatibility with alkalis and bleaching agents if desizing is not carried out separately from scouring and bleaching.

To these may be added economy and ease of removal from the substrate, as well as a favourable response to effluent treatment.

The adhesive strength of a size film is an important consideration as it has a bearing on stability during weaving [175]. Adhesive strength depends on such factors as type of size polymer, additives present (e.g. wetting agent), sizing liquor temperature, yarn characteristics, viscosity index of the size formulation and degree of saponification of poly(vinyl acetate) sizes. Size dissolution rate is also an important factor; this needs to be known if desizing is to be carried out effectively and efficiently [176].

Many factors will determine the choice of size type and formulation. A general scheme of size use relative to different fibre types is given in Table 10.6. It is useful to classify sizes according to those physico-chemical properties that largely determine the method of desizing, as shown in Table 10.7. Evidently, some degree of synergistic chemistry is involved in determining the specific suitability of size polymers for certain fibres. For example, there is an obvious similarity of molecular structure between starch and cellulosic fibres, offering substantial scope for hydrogen bonding between hydroxy groups. The similarity in molecular structure between polyester sizes and synthetic fibres facilitates hydrophobic bonding between hydrocarbon segments of the polymer chains.

Table 10.6 Sizing agents for different substrates [169]

Size:	Natural				Synthetic				
Substrate	Starch	CMC	Gums	Glue	AACo	AECo	PVA	PE	PVCo
Staple fibre yarns									
Cellulosic	+	+	+		+	+	+		
Polyester/cellulosic	o	o	o		+	+	+		
Nylon/cellulosic	o	o	o		+	+	+		
Wool	o	o		+		+	+		
Polyester/wool	o	o				+	+		
Polyester, nylon	o	o				+	+		
Filament yarns									
Viscose				+	+	+	+		+
Acetate						+	+		+
Triacetate						+	+		+
Nylon					+	+			
Polyester						+	+	+	

\+ Alone
o Only in combination with synthetic size

CMC	Carboxymethylcellulose	Gums	Galactomannans
AACo	Acrylic acid copolymers	PVA	Poly(vinyl acetate)
AECo	Acrylic ester copolymers	PE	Polyesters
PVCo	Polyvinyl copolymers		

Table 10.7 Size properties and methods of removal [169] (slightly modified)

Physico-chemical characteristics	Type of size	Method of removal
Chemically degradable	starches modified starches	enzymatic or oxidative
Water-soluble	acrylic acid copolymers poly(vinyl acetate/alcohol) carboxymethylcellulose certain modified starches	rehydration and dissolution
Water-resistant	polyesters certain acrylic acid copolymers	neutralisation and dispersion

Economic factors play a major part in the selection of sizes. For this reason, starch sizes and their mixtures continue to be the most widely used, particularly on cellulosic substrates. Nevertheless, more costly size polymers may be economically justifiable if this can be offset by higher productivity in weaving. High productivity generally demands high elasticity and strong adhesion, provided mostly, if not exclusively, by synthetic sizes. Water-jet weaving machines require water-resistant sizes. Some sizes are adversely affected by high temperatures (as in heat setting) or by treatment at inappropriate pH values and these effects can make their removal more difficult.

The choice and combinations of different size components must take account of many factors if optimum results are to be obtained. Much has been published regarding the optimisation of size formulations in relation to desizing processes [177–183]. Cotton warp yarns sized with starch are normally woven at high humidity (80% and above) to keep yarn breakages low, as the starch film is brittle at low humidity. It has been shown [183], however, that improved weavability at moderate relative humidity (e.g. 65%) can be obtained using: (a) starch/acrylamide or hydroxyethyl starch at not less than 15% add-on; or (b) poly(vinyl alcohol), which gave excellent results even at a low add-on of 5–6%.

Addition of acrylamide to starch improved the performance of cotton yarn more than acrylamide alone, but addition of poly(vinyl alcohol) to starch lowered the performance of the yarn compared with poly(vinyl alcohol) alone. Overall, taking into account economic considerations, stringent pollution requirements and the needs of desizing, the single-component hydroxyethyl starch showed optimum acceptability for weaving performance at moderate relative humidity.

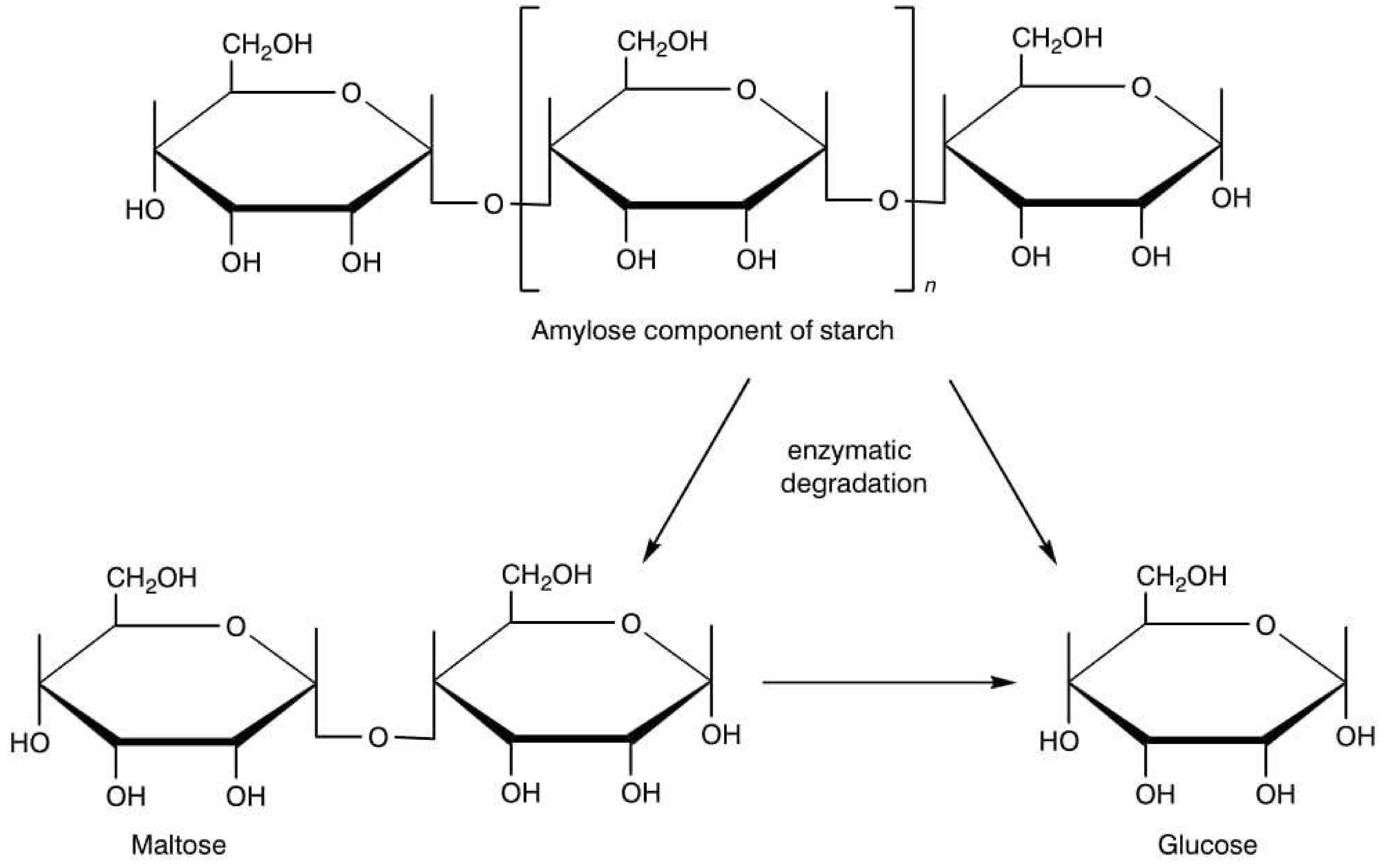
The incorporation of waxes or lubricants (section 10.10.1) is an important consideration that should not be overlooked. These components exert a significant influence on weavability and on the conditions and efficiency of desizing. The lubricant may be added as a component of the size formulation, or applied separately by kiss-roll after sizing. Lubricants may themselves be used as sizing agents, particularly on synthetic warp yarns. Indeed, it has been argued [184] that such treatments give results comparable with traditional sizes as regards fibre strength and weaving performance. They offer advantages of savings in heat energy during drying and in manpower and space, as no special sizing unit is required.

Desizing methods

As indicated earlier in Table 10.7, it is helpful to select desizing methods according to whether size polymers are chemically degradable, water-soluble or water-resistant.

Desizing by chemical decomposition is applicable to starch-based sizes. Since starch and its hydrophilic derivatives are soluble in water, it might be assumed that a simple alkaline rinse with surfactant would be sufficient to effect removal from the fibre. As is also the case with some other size polymers, however, once the starch solution has dried to a film on the fibre surface it is much more difficult to effect rehydration and dissolution. Thus controlled chemical degradation is required to disintegrate and solubilise the size film without damaging the cellulosic fibre. Enzymatic, oxidative and hydrolytic degradation methods can be used.

The traditional approach is enzymatic desizing, in which an α-amylase or diastase enzyme is used to attack the 1:4-glycosidic links in the starch, breaking down the macromolecules into small soluble saccharides such as maltose and glucose. Scheme 10.18 is a simplified representation based on hydrolysis of the amylose component of starch; similar reactions take place with the amylopectin component (section 10.8.1). In addition to the enzyme a surfactant is required to ensure rapid and thorough wetting, including penetration of the size film, and emulsification or solubilisation of lubricants. Nonionic surfactants are less likely to deactivate the enzyme than anionic agents. The enzyme liquor is generally applied by impregnation immediately after singeing. With modern equipment running at speeds up to 170 m/min, the role of the surfactant is a critical one [169]. A carefully formulated mixture of surfactants may give the best balance of properties for rapid and thorough wetting, together with the removal of lubricant waxes or oils. The concentration of enzyme needed depends on the type and amount of size present and particularly on the potency of the commercial brand used.



Scheme 10.18

Temperature and pH are critical parameters that are also brand-related. Enzymes are available covering the range 20–120 °C [143,169] and from acidic to alkaline pH. Those requiring mildly alkaline conditions are usually preferred, since the degraded fragments from the branched amylopectin component of starch usually require such conditions for solubilisation, rice and tapioca starches having rather higher amylopectin contents [143]. The presence of salt or calcium ions can also influence the behaviour of the enzyme. Hickman [143] has summarised typical conditions (Table 10.8). The effect of electrolytes (NaCl, Na_2SO_4, $CaCl_2$ and $MgCl_2$) on the aqueous solubility of saccharidic size polymers, including potato starch, starch esters and galactomannans, has been studied in detail [185]. It is important to know whether a fungicide, such as a halogenated phenol, has been added to protect the size formulation against mildew, since such fungicides are toxic to enzymes.

There are some circumstances in which enzymatic desizing is inefficient:

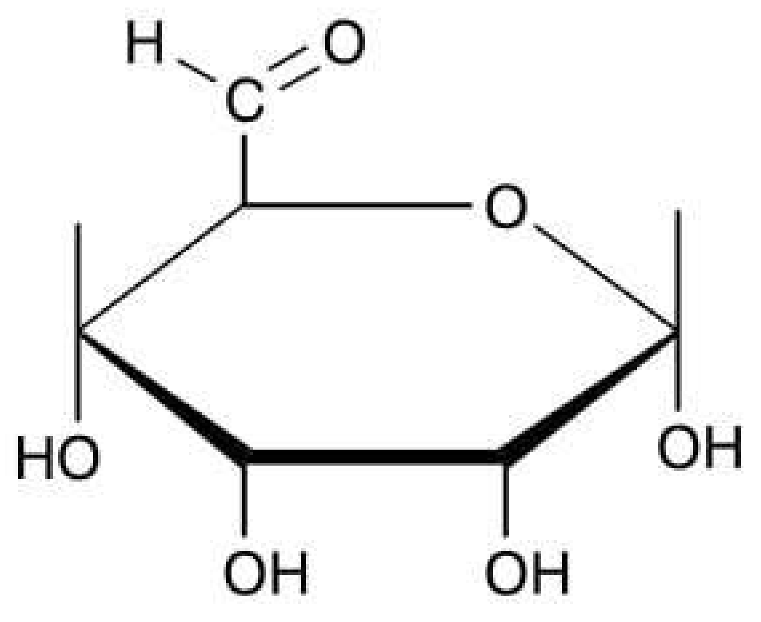
- if insufficient space is available for the batching of enzyme-impregnated fabric
- if branched-chain starches such as tapioca are present they can be difficult to degrade, depending on the degree of ageing
- if fungicides have been used to protect the starch from mildew attack
- if oxidative desizing can be adopted and combined with scouring or bleaching, thus minimising energy requirements.

Table 10.8 Optimum conditions for enzymatic desizing [143]

Enzyme	Optimum pH	Optimum temperature range (°C)	Effect of		Time
			NaCl	Ca ions	
Malt diastase	4.5–5.5	55–65	o	+	12–24 h
Pancreatic amylase	6.5–7.5	40–55	+	+	12–24 h
Bacterial amylase	6.5–7.5	65–75	+	+	1–4 h
Bacterial amylase	7.0–8.0	100–120	+	+	1–2 min

+ Improved desizing
o No effect

The primary alternative to enzymatic treatment is oxidative desizing. This is extremely popular worldwide, especially in the Far East [169], and its popularity is increasing [143], mainly for the economic reasons outlined above. The oxidants most often used are hydrogen peroxide and sodium or potassium persulphate. There may be a considerable risk of fibre damage by persulphate, however, as this oxidant tends to degrade both starch and cellulose. The mechanism of degradation includes the hydrolysis of amylose (see Scheme 10.18) and amylopectin, as well as the formation of aldehyde (10.70), carboxylic acid (10.71), keto (10.72) and diketo (10.73) groups. There may also be ring cleavage [169] to give diacids such as tartaric (10.74) and oxalic (10.75).



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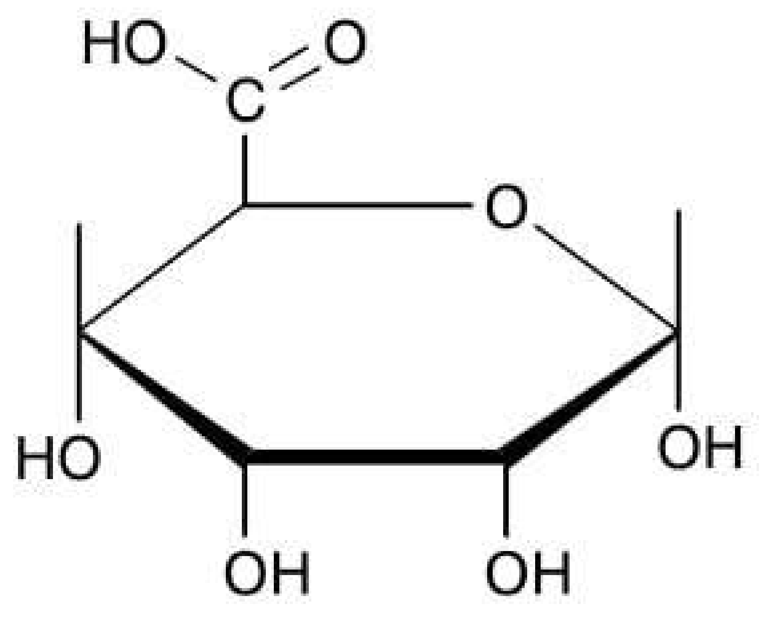

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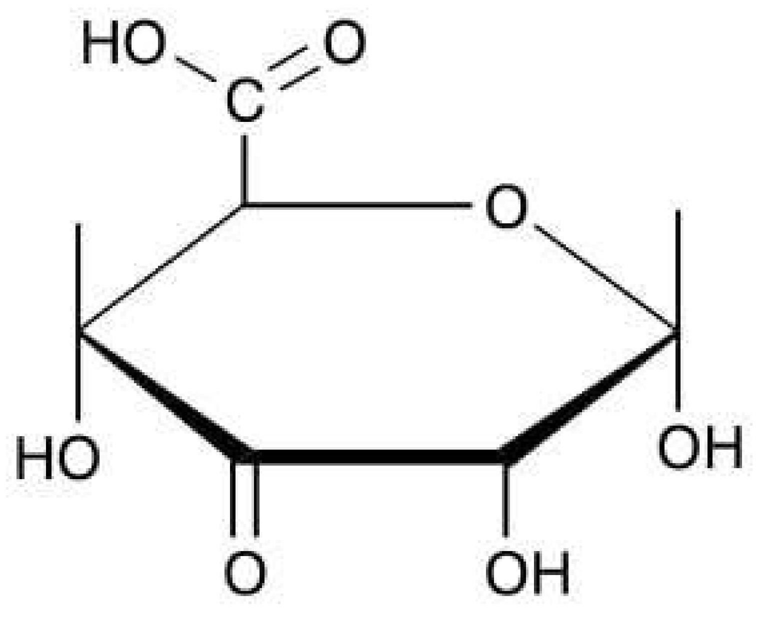
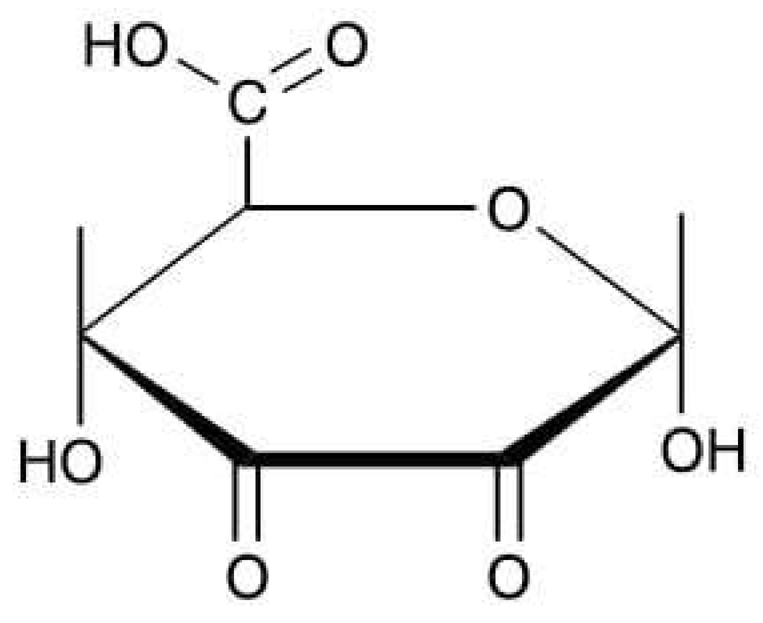


10.72

10.73 is placed next:



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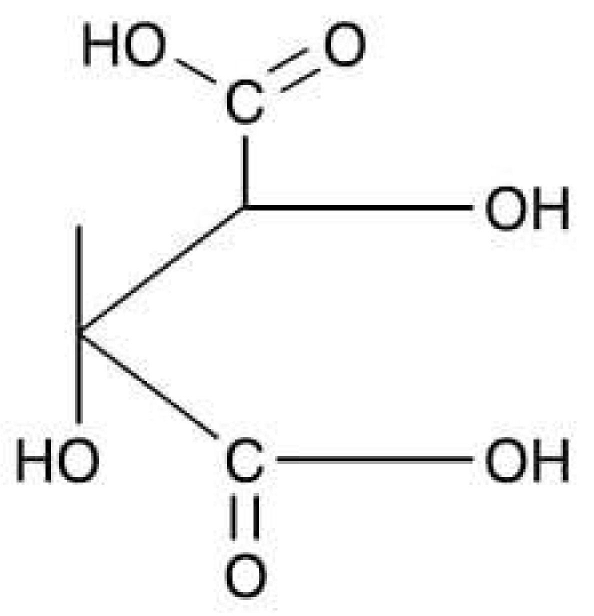

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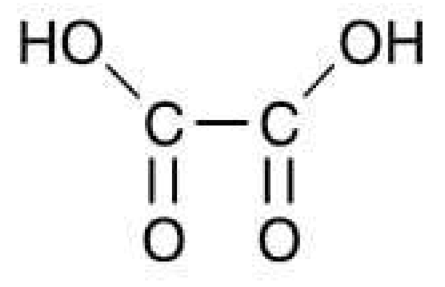


10.75

This oxidative reaction is generally carried out simultaneously with a caustic scour at 100–130 °C, offering the economic advantages of a combined scouring and desizing process. If peroxide is selected as the oxidant, this also exerts a bleaching action. In addition to oxidant and sodium hydroxide, the auxiliaries required include a magnesium salt, sodium silicate or an organic stabiliser for the oxidant, a sequestering agent (e.g. DTPA;

diethylenetriaminepenta-acetic acid) and a wetting agent. The role of the magnesium salt and oxidant stabiliser is discussed elsewhere (section 10.5.3). Recommended conditions for batchwise oxidative desizing at high temperature are given in Table 10.9.

Table 10.9 Oxidative desizing at high temperature [143]

	Concentrations (% owf)		
Magnesium sulphate heptahydrate	0.005	0.005	0.005
Sodium hydroxide (100%)	2–6	2–4	9–12
Stabiliser	0–1	0–1	0–1
DTPA (40% solution)	0.2	0.2	0.2
Hydrogen peroxide (35%)	5–15	5–15	5–15
or sodium persulphate	0.2–0.5	0.2–0.5	0.2–0.5
Wetting agent	0.2–0.5	0.2–0.5	0.2–0.5
Temperature (°C)	100	100	120–130
Time (min)	<15	15–60	1–2

In this table, the lower amounts of sodium hydroxide provide desizing only, whereas the higher concentrations provide oxidative scouring. The concentrations of the various components are critical to ensure efficiency of action without fibre damage. Hickman [143] gives the following guidelines:

(1) Rapid desizing treatments require more critical control of alkali and oxidant concentrations.
(2) Increased alkalinity for a given oxidant concentration tends to increase chemical damage.
(3) Increased oxidant concentration above the minimum required for desizing increases chemical damage.
(4) Persulphates promote desizing, rather than bleaching, and require more critical control of concentration than does hydrogen peroxide.
(5) Mixing of persulphates and hydrogen peroxide is not recommended in pad–steam desizing.
(6) To desize oxidatively by a batchwise process, the oxidant must be added when the alkaline fabric reaches top temperature.

It is possible to degrade and solubilise starch size residues using cold peroxide and alkali but batching times are long (typically 16–20 hours). This simultaneous desizing and bleaching process requires 30 g/l sodium hydroxide (100%) and 50 ml/l hydrogen peroxide (35%), together with wetting agent, detergent, stabiliser and sequestering agent. The desizing effect can be improved by addition of persulphate without risk of significant fibre damage at this temperature [169].

It has been demonstrated [186] that the inclusion of polyacrylamide in either enzymatic or oxidative desizing formulations results in increased pick-up of the liquor by the sized warp yarns. Desizing by hydrolytic degradation of starch during the traditional kier-boiling treatment using 3°Bé sodium hydroxide liquor at 110 °C is now rarely encountered as it is a slow and expensive process [169].

In Table 10.7 are listed the following size polymer types in the water-soluble category: acrylic acid copolymers, poly(vinyl acetate/ alcohol), carboxymethylcellulose and certain modified starches. It is necessary to clarify what is meant by water-soluble in this context. All these polymers form colloidal solutions and the dissolving process is not instantaneous. When films formed by such polymers come into contact with water, there is an initial period during which they absorb water. The rate at which water diffuses into the polymer film varies widely, depending on the polymer structure and the heat treatments that the film has received. This phase is known as rehydration and is characterised by the formation of a gel. Only when the polymer has absorbed sufficient water does it actually begin to disintegrate and dissolve to give a viscous colloidal solution. Higher temperatures and the presence of surfactants generally increase the rates of rehydration and dissolution. Figure 10.16 illustrates relative dissolution rates in cold water of various water-soluble size polymers prepared as 60 × 15 mm films of 200 μm thickness [169]. The disintegration level represents the completion of rehydration. Thus in any desizing process relying solely on aqueous dissolution, it is always important to allow adequate time for rehydration.

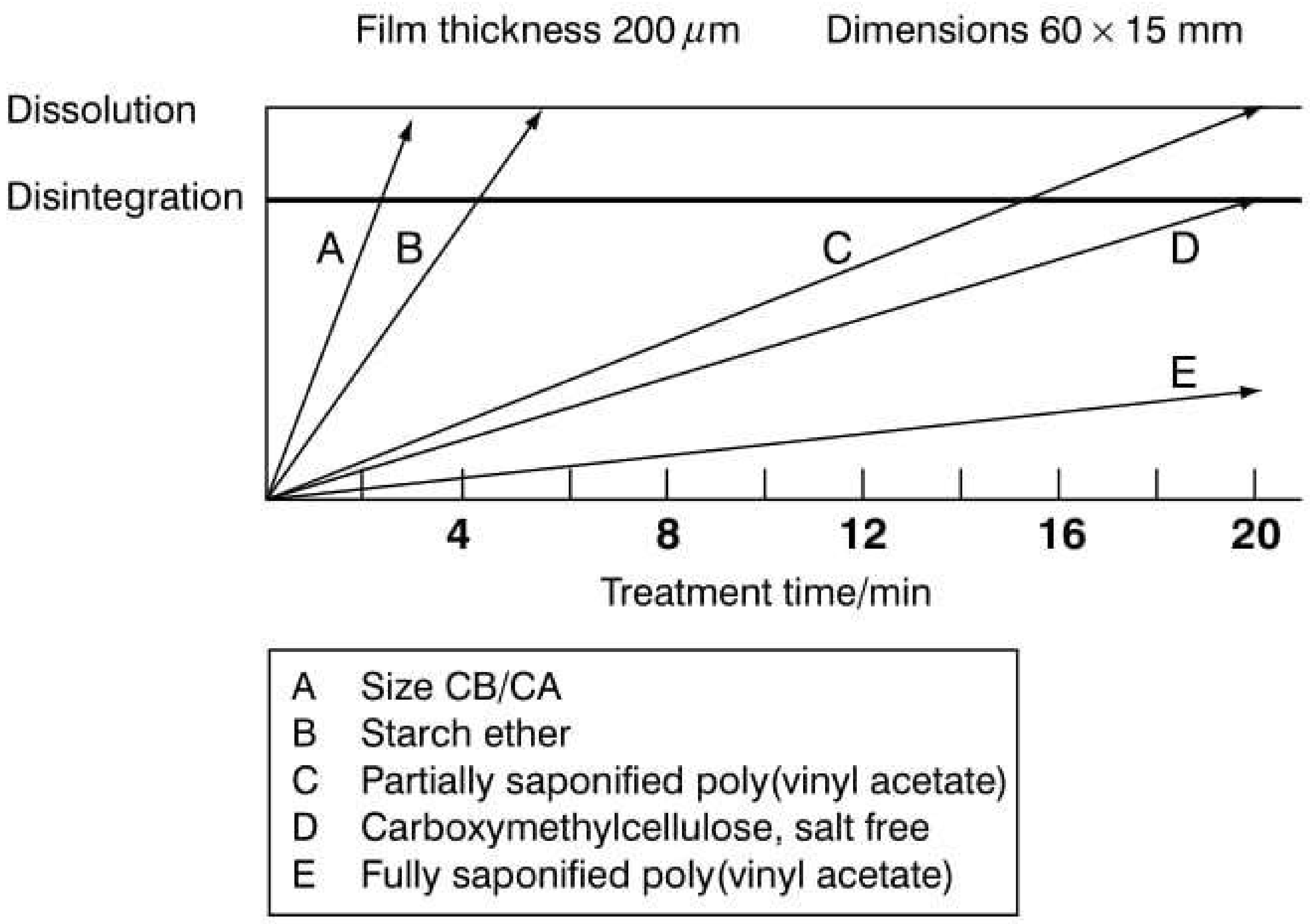


Figure 10.16 Dissolution rates of films of water-soluble sizing agents in water at 20 °C [169]

Not all modified starches are suitable for removal by aqueous dissolution alone. Such modifications of natural starches are carried out to reduce solution viscosity, to improve adhesion and ostensibly to enhance aqueous solubility. Commercial brands vary [169], however, from readily soluble types to those of limited solubility. Indeed, some may be as difficult to dissolve as potato starch if they have been overdried. It is thus very important to be sure of the properties of any modified starch present. If there are any doubts about aqueous dissolution, desizing should be carried out by enzymatic or oxidative treatment. Even if the size polymer is sufficiently soluble, it is important to ensure that the washing-off range is adequate. Whilst the above comments relate to modified starches, other size polymers such as poly(vinyl acetate/alcohol) and acrylic acid copolymers vary from brand to brand with regard to ease of dissolution.

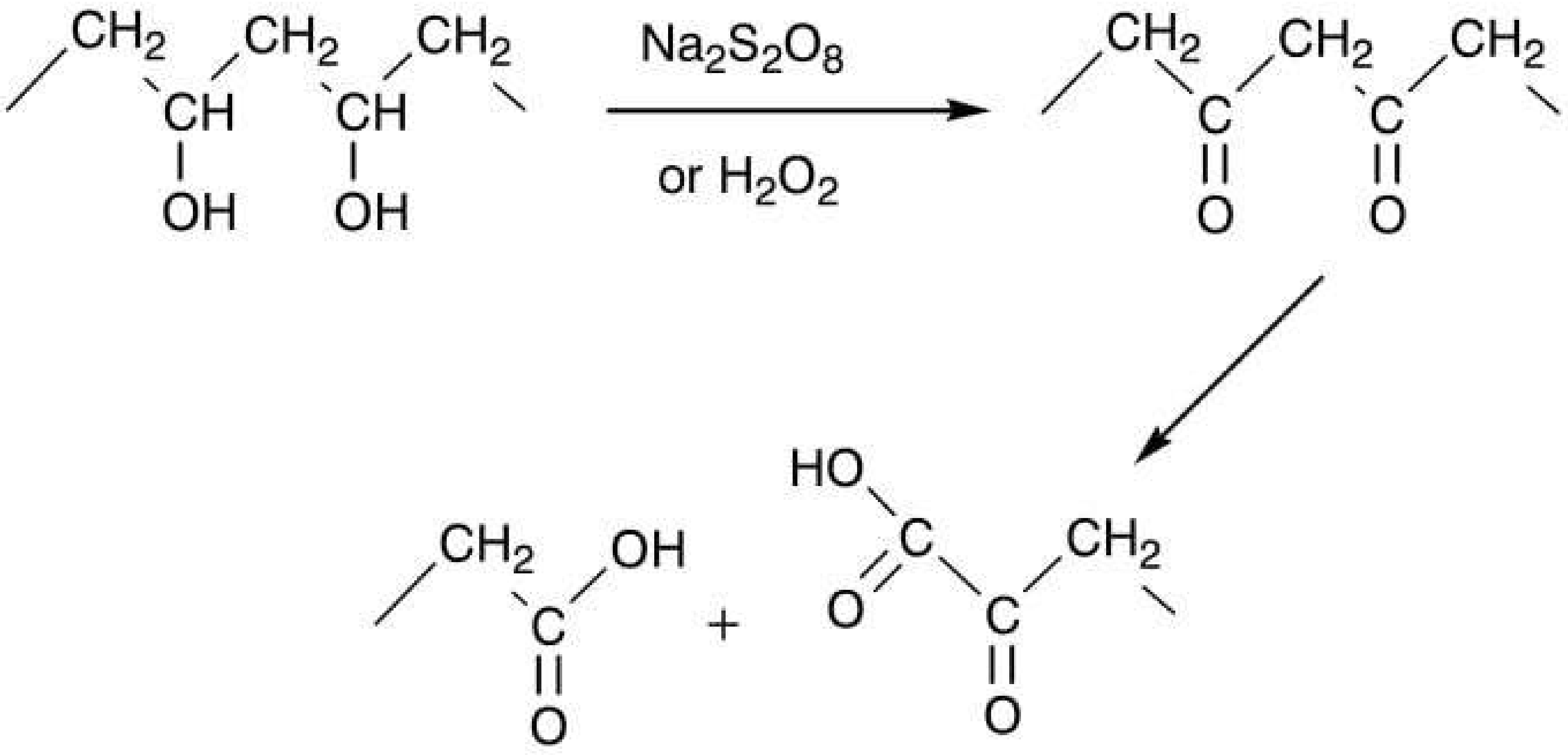
Carboxymethylcellulose, an excellent film-former, is a highly effective size on cellulosic substrates but has poor adhesion to synthetic fibres. It is easily desorbed, hot water generally being sufficient, although surfactant and alkali are usually added to increase the efficiency of removal. A further advantage of carboxymethylcellulose is that heat setting does not affect the ease of subsequent removal, nor is it sensitive to alkaline or acidic pH. Indeed, it has been stated [171] that if anyone has a problem removing a carboxymethylcellulose size, it is unlikely that they could remove much of anything from a piece of fabric! Nevertheless, Angstmann and Bassing [169] caution that this size does require much water and an initial swelling time.

The poor adhesion of carboxymethylcellulose to synthetic fibres means that where such fibres are present, it can only be effective in combination with a synthetic size polymer (Table 10.6). This needs to be taken into account when considering suitable desizing procedures. If this cellulose derivative is to be used in conjunction with an electrolyte-sensitive acrylic acid copolymer, it is advisable to choose a salt-free carboxymethylcellulose.

Poly(vinyl acetate/alcohol) sizes are also described as water-soluble and are widely used, either alone or in combination with most of the other types, across the whole range of fibres and blends [169,171]. However, this category covers a wide range of commercial products, differing greatly in quality and ease of removal. Indeed, some are quite difficult to remove, thus necessitating careful selection [187]. Detailed studies of factors affecting the removal of water-soluble sizes, particularly poly(vinyl alcohol) types, have been published [188–190].

Apart from molecular mass, the behaviour of polymers of this type depends strongly on alcohol group content, usually expressed as the percentage degree of saponification of the poly(vinyl acetate) from which it is derived. Poly(vinyl alcohol) forms a strong film that shows good adhesion to cellulosic fibres but poor adhesion to polyester. These films can usually be removed quite readily with hot water and detergent. The presence of a mild alkali may be acceptable [171] but is perhaps best avoided [169]. Poly(vinyl alcohol) is sensitive to alkali addition and is precipitated by strong alkali, making the residues very difficult to remove. The wash-off parameters should be optimised for efficiency of size removal, since high temperatures and long liquor ratios are environmentally and economically unfavourable. The amount of size polymer applied and the presence of any additives need to be carefully considered. Care should be taken in the heat setting of fabrics containing poly(vinyl alcohol) size. Too high a temperature for too long a time induces crystallisation, making the size residues much more difficult to remove.

Poly(vinyl alcohol) can be modified with crotonic acid (Scheme 10.17) to give size copolymers that have higher solubility and lower sensitivity to alkali [169]. Although these sizes are generally regarded as water-soluble, they are more readily removed by alkaline oxidative desizing methods using either persulphate or peroxide [169], the polymer being degraded into smaller segments as indicated in Scheme 10.19.



Scheme 10.19

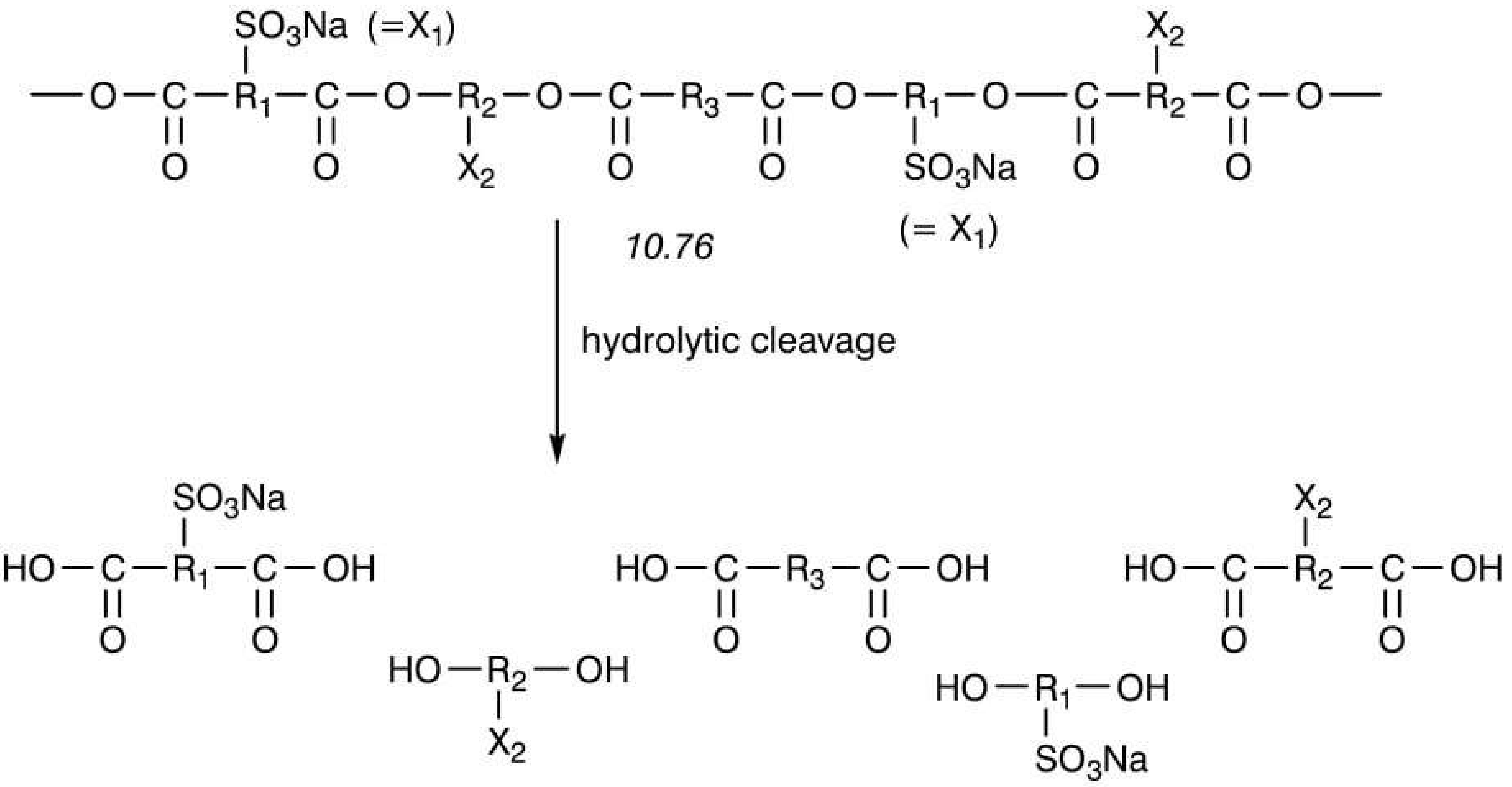
Many acrylic acid copolymers are water-soluble but unlike poly(vinyl alcohol) they are not degraded by alkali. In fact they need alkali for effective desizing as they are more soluble at alkaline pH than in neutral solutions. They are sensitive to acidic media, which should not be used. Solubilisation occurs by the formation of sodium carboxylate groups from the anionic polyacid. The polyelectrolyte formed in this way is readily soluble and shows a rapid rate of dissolution. However, the presence of electrolytes such as magnesium or calcium salts from hard water can inhibit removal [191].

The desizing of water-soluble size polymers can be summarised as follows. Batchwise or continuous methods can be used; in both cases an adequate supply of hot water is needed during the washing-off. Hot water and detergent are needed to remove poly(vinyl alcohol) or carboxymethylcellulose. The addition of alkali may be beneficial with carboxymethylcellulose. Alkali is essential with modified starches and acrylic acid copolymers. Poly(vinyl alcohol) can be degraded effectively by alkaline oxidation.

Water-resistant sizes include polyesters and certain acrylic acid copolymers. These are mainly used for the sizing of synthetic filament warp yarns, some formulations being particularly useful in water-jet weaving. The acrylic acid size copolymers described as water-soluble are generally partially neutralised during manufacture to give partial formation of the sodium salt; complete conversion to the sodium salt is carried out using alkali in desizing. Water-dispersible types, on the other hand, are normally partially neutralised with ammonia during manufacture and these are more suitable for water-jet weaving. When the sized yarn is dried the ammonia is evolved, leaving the less soluble acrylic acid form. This lower solubility is a significant advantage in water-jet weaving. A yarn sized with a sodium acrylate copolymer will have a typical pH of 6–7 when dry, compared with pH 4–5 for an ammonium acrylate type [171]. This difference in pH needs to be accounted for when desizing, so that more alkali is needed for the desizing of ammonium acrylate copolymer sizes. Typical desizing conditions include a detergent with up to 5 g/l sodium hydroxide or sodium carbonate at 70–90 °C [171]. The pH should be carefully monitored in order to maintain alkalinity throughout. A sequestering agent may be needed because transition-metal ions can insolubilise acrylic acid copolymers, one atom of trace metal reacting with two or three carboxylic acid groups in the size polymer.

Polyester sizes differ from acrylic acid sizes in the nature of the solubilising groups present, namely sulphonic acid rather than carboxylic acid groups, solubility behaviour being dependent on the degree of sulphonation with respect to the average molecular mass of the polymer (10.76). In general, however, the degree of sulphonation is low (10.69) and the polymer is rather sensitive to alkali. Too strongly alkaline conditions result in hydrolytic cleavage of the ester groups (Scheme 10.20) to give some fragments without solubilising groups and these are difficult to remove in desizing [169]. Consequently, although alkali and detergent are needed for desizing, the amount of alkali is less than that needed for acrylic acid sizes and the alkalinity should not be allowed to rise above pH 9. Typical conditions are 0.5–1.0 g/l sodium carbonate with detergent at 90–95 °C [169]. A sequestering agent may also prove useful. Batchwise treatment, or more usually a pad-wash range, can be used.

Polyester resins can be highly beneficial as additives to other size polymers, although a great deal of care and expertise is required in formulation [192]. Viscosity, for example, is an important factor in the warp sizing process. The viscosity of some sizes, such as poly(vinyl alcohol), is significantly affected by temperature fluctuations. The addition of a polyester resin tends to minimise such changes in viscosity. Surface tension is another important parameter



In structure *10.76* (see also *10.69*) either X_1 or X_2 contains a sulpho group, but not both.
R_3 is an unsulphonated aliphatic group

Scheme 10.20

that is subject to variability and polyester resins can help to stabilise it within the optimum range. Such resins have beneficial effects on rheological behaviour, film formation and film characteristics, giving significant improvements in yarn abrasion resistance, good surface lubrication and a softening of the surface fibres. Certain acrylic acid or vinyl copolymer resins behave in a similar way to polyester resins in enhancing the performance of conventional size formulations. The degree of expertise required in formulating such complex mixtures of size polymers for optimal performance has led Mayfield [192] to emphasise the advantages of using proprietary products formulated by specialists. These products may contain up to thirty ingredients, including trace additives that can effectively influence the many components present. These formulations can be very accurately combined and evaluated for chemical and physico-chemical compatibility by specialist suppliers.

Analysis and monitoring of size polymers and desizing processes

The many technical factors involved in desizing and the need for economy and environmental accountability emphasise the importance of monitoring and analysis. However, only a brief outline can be given here. A review of analytical procedures and simple laboratory methods for size determination is available [193]. Methods are given for size determination directly on the fibre surface, for the extraction of components of low molecular mass and for their subsequent estimation in solution.

Size polymers on polyester can be determined by staining tests with CI Basic Red 22, CI Reactive Red 12, iodine/potassium iodide solution, or a mixed indicator. The extraction of size components and their determination in solution using a variety of reagents to give a characteristic coloration or a coloured precipitate has been described. Methods using fluorescence spectroscopy with a fluorescent cationic dye (e.g. Pinacryptol Yellow or CI Basic Orange 14) were also described.

An extremely useful technique for measuring the amount of size applied is non-contact on-line determination of water absorption [194]. The moisture content of sized warps can be derived from microwave absorption by the water present.

The identification of anionic poly(acrylic acid) sizes can be carried out by staining with a fluorescent cationic dye (CI Basic Orange 14) followed by spectroscopic measurement of excitation wavelength and fluorescence emission [195,196]. Such methods can also be used (with CI Basic Orange 14 or CI Basic Red 1) to detect and estimate carboxymethylcellulose, poly(vinyl alcohol) and starch derivatives [197].

A method is available, utilising on-line near-infrared reflectance spectroscopy, for controlling the uniform application of poly(vinyl alcohol) size [198].

The desizing of cotton can be monitored using a dyeing test supported by assessment of wettability [199,200]. The dyeing test requires a 10 g/l solution of CI Direct Red 83. This test can usefully be supplemented by the TEGEWA drop test to determine wettability. A simple method of estimating the efficiency of desizing with poly(vinyl alcohol) and starch-based sizes depends on the determination of TOC (total organic carbon) and COD (chemical oxygen demand) [201].

Environmental aspects

Since size add-on is customarily in the region of 10–20%, desizing clearly produces quite a sizeable pollution load. Although many size polymers are biodegradable, they exhibit high biological oxygen demand (BOD) and chemical oxygen demand (COD). These high values are compounded by the major contribution of size residues. High liquor ratios or copious quantities of wash-off water facilitate the desizing process but these large volumes of waste liquor pose additional difficulties quite apart from the initial cost, both financially and environmentally. In Table 10.10 the water consumption, BOD and pollution load contributed by desizing are compared with those from other wet processes on cotton [202]. Typical BOD and COD values determined for the main classes of size polymers are given in Table 10.11 [203]. The COD of a typical cotton desizing effluent is composed of 42% from sizing agents and fibre fragments, 40% from impurities in the cotton and 8% from surfactants [204].

Table 10.10 Water and effluent data arising from the wet processing of cotton [202]

Process	Water consumption (% of total)	BOD (% of total)	Pollution load (% of total)
Desizing	5	22	>50
Scouring	1	54	10–25
Bleaching	46	5	3
Mercerising	2		<4
Dyeing	8	5	10–20
Printing	7	6	10–20
Washing-off	30	1	5
Finishing	1	7	15

Table 10.11 Specific COD and BOD values found for important sizing agents [203]

Sizing agent	Specific COD value (mg O_2/g)	Specific BOD value (mg O_2/g)
Starch	900–1000[a]	500–600
Carboxymethylcellulose	800–1000[a]	50–90
Poly(vinyl alcohol)	ca. 1700[a]	30–80[b]
Polyacrylate	1350–1650	<50
Galactomannan	1000–1150[a]	400
Polyester dispersion	1600–1700	<50
Protein size	1200	700–800

a Taking account of moisture content of commercial product
b With non-adapted inoculum

Clearly, one option to reduce the add-on is to use high-efficiency size formulations. However, there is a limit to what can be achieved by this approach. Even if the add-on is reduced to only 5%, the pollution load is still substantial. The two main options to facilitate disposal are: (a) recovery of size polymers; and (b) biological effluent treatment. Recovery of size polymers, particularly from water-soluble synthetic sizes, is based on extraction washing using the minimum quantity of water. Recovery rates in the region of 50% have been quoted for poly(vinyl alcohol) and carboxymethylcellulose size formulations. It is necessary to apply one of three concentration techniques: precipitation, condensation or ultrafiltration [205].

Precipitation is only really possible with poly(vinyl alcohol) and is seldom applied to textile effluents, normally only to eliminate size residues from effluent liquors. The condensation technique exploits heating to drive off water. This is energy-intensive and is therefore in decline. Ultrafiltration is long-established commercially and is the preferred concentrating technique. The principle of ultrafiltration, capable of separating particles in the range 0.05–0.15 μm, has been compared with other systems of filtration, such as reverse osmosis, nanofiltration and microfiltration [206]. A sequence of treatments can be used, such as ultrafiltration to recover most of the size followed by biological treatment of the residue. In some cases ultrafiltration renders an effluent acceptable for discharge to the municipal water treatment system, but this depends on local regulations.

One major advantage of ultrafiltration is that it can facilitate the reuse of recovered materials [207]. In the case of sizing, however, this clearly depends crucially on the composition of the recovered material. If a blend of sizing agents is present, it does not necessarily follow that the recovered material will contain these components in the original (required) proportions for reuse. Nor is reuse a possibility where desizing has been carried out by a degradative process, such as enzymatic or oxidative desizing. Thus the scope for reuse is favoured where single-component formulations of non-degraded size polymer can be recovered. Simple formulations, however, may not meet all the weaving requirements. Hence arguments for and against the relative merits of simple and complex formulations are common.

The basis of ultrafiltration is that a liquor is passed through a membrane many times until the required concentration of the permeate is attained. Fouling of the membrane can be a problem and regular cleaning and disinfection of the membrane is recommended. Ultrafiltration of poly(vinyl alcohol) and starch sizes offers economic advantages over discharge to the sewer [208,209]. A starch carbamate size effluent had its entry COD of 19 159 mg O_2/l reduced by ultrafiltration to 672 mg O_2/l, a recovery yield of almost 97%. Starch ethers, such as hydroxypropyl and carboxymethyl derivatives, have given recovery values of 92–97% [209]. Size polymers suitable for recovery by ultrafiltration must exhibit the following characteristics: water solubility, thermal and mechanical stability, bioresistance, good washing-out properties and low to moderate viscosity [210]. Poly(vinyl alcohol), carboxymethylcellulose and certain acrylic sizes meet these demands. The ultimate benefits of ultrafiltration from economic and environmental aspects are that not only can size be recovered for reuse but also the water that passes through the membrane can be recycled into the washing-off range [211].

Biological treatment of a desizing effluent usually involves a two-stage anaerobic treatment using cultivated methane bacteria, possibly followed by a final aerobic treatment [209]. Typically, a dwell time of 12–17 days will give about 80% degradation of a starch size. Such treatment usually gives an effluent acceptable for discharge to the municipal sewage system. Several factors other than the nature of the size polymer can affect the efficiency of biological treatment, notably the degree of adaptation of the biological inoculum and the temperature at which digestion takes place. The method of evaluation can also influence the results obtained. Figures 10.17 and 10.18 illustrate the effects of adaptation of the inoculum on the bioelimination of a modified poly(vinyl alcohol) size [212], as assessed by the Sapromat [213] and Zahn–Wellens [214] test protocols respectively. The effect of digestion temperature on the same polymer using optimally adapted inoculum is shown in Figure 10.19. Thus seasonal temperature fluctuations need to be considered. It is possible to formulate mixtures of size polymers so that the effect of digestion temperature is minimised. Data showing the effects of temperature on the rates of biodegradation of hydroxypropyl starch and of a formulation containing poly(vinyl alcohol) and hydroxypropyl starch [215] reveal that the polymer mixture is much less sensitive to the temperature of digestion. The rate of influx and even of rainfall can also exert some influence on the rate of elimination.

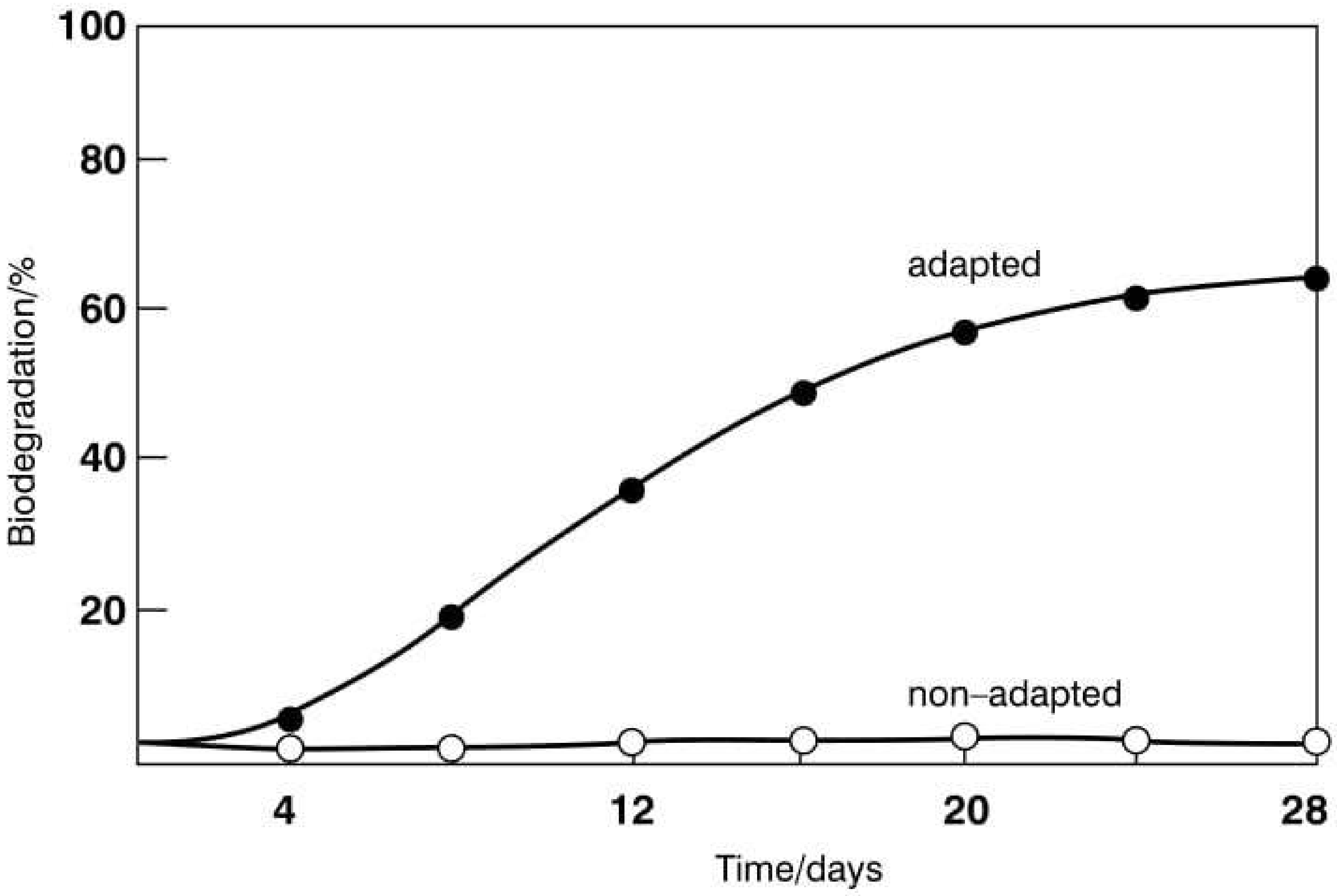


Figure 10.17 Biodegradation rate curves for poly(vinyl alcohol) with adapted and non-adapted inoculum according to the Sapromat test [212]

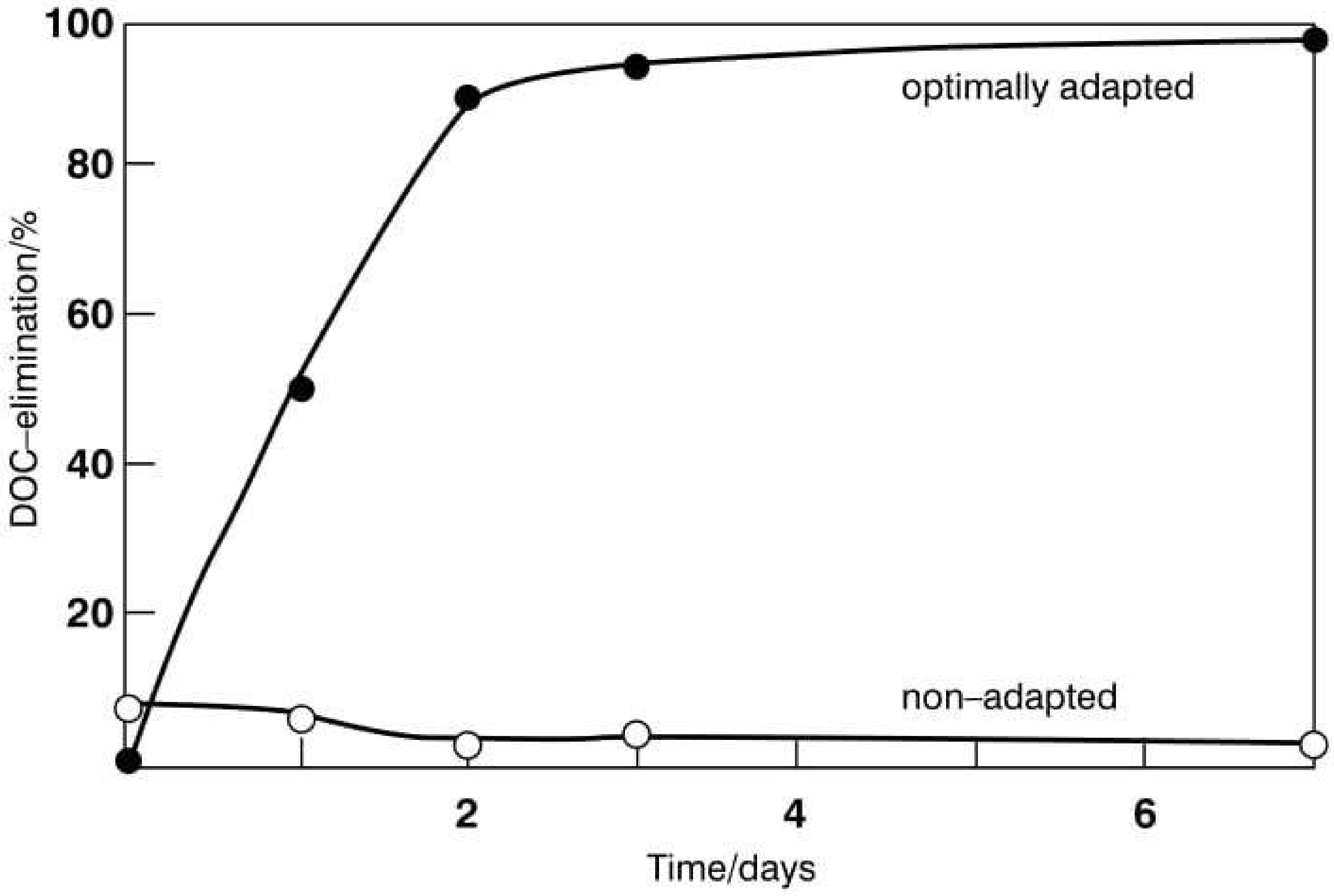


Figure 10.18 DOC-elimination rate curves for poly(vinyl alcohol) with optimally adapted and non-adapted inoculum according to the Zahn-Wellens test [212]

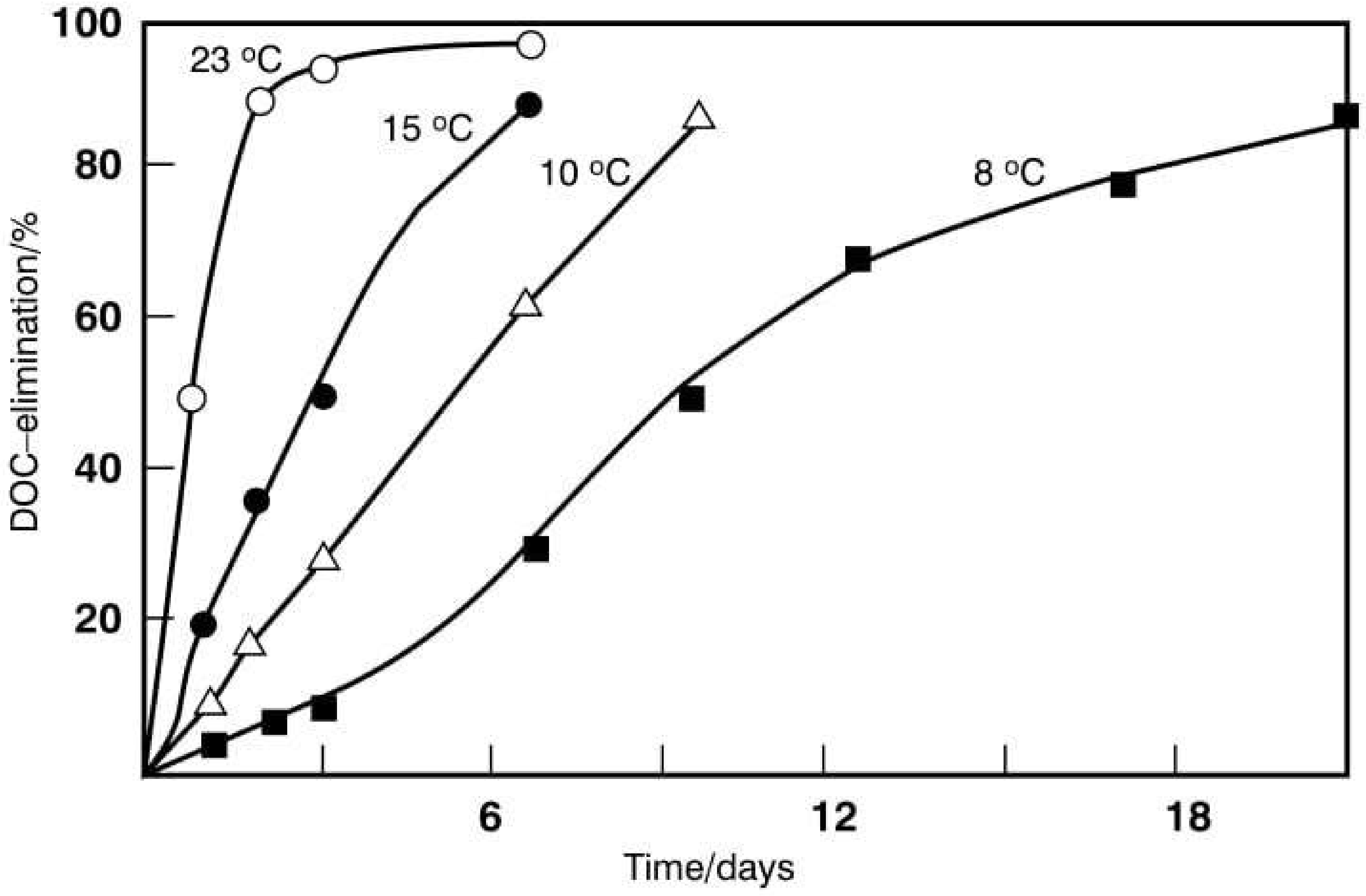


Figure 10.19 DOC-elimination rate curves for poly(vinyl alcohol) with optimally adapted inoculum at various temperatures [212]

The following scale has been proposed to assist discussions of biodegradability [216,217]:

Degree of biodegradation after 14 days	*Description*
80–100%	easily biodegradable
60–80%	moderately biodegradable
0–60%	difficultly biodegradable

Many starches and modified starches are easily biodegradable, although some are less so. In an evaluation of the biodegradability of ten starch-based sizes over seven days [218], four were degraded to 95–100%, two to 80–95%, three to 60–80% and only one to less than 60%. Whilst carboxymethyl starches are easily biodegradable [218], carboxymethylcelluloses are generally difficult to degrade [211,217]. The biodegradation of carboxymethylcellulose can be as low as 8–13% under aerobic conditions, although up to 54% can be eliminated under anaerobic conditions [211]. Galactomannan sizes are biodegradable to 80% within seven days [216,217].

It was mentioned earlier that poly(vinyl alcohol) sizes show wide variability in aqueous solubility. They are also extremely variable with regard to biodegradation characteristics, from 15% to 95%. It is not surprising, therefore, that they have been the subject of much research [187,203,211,212,219] and not a little controversy. Reference 203 lists twelve further references concerned with the microbial degradation of poly(vinyl alcohol). Misunderstandings have undoubtedly arisen through a failure to appreciate the need for an adequate digestion temperature and effective acclimatisation of the bacterium. There can be a drastic fall in efficiency of degradation at temperatures lower than 10–12 °C, since the desorption rate of the degrading micro-organisms at such temperatures exceeds the growth rate [203,219] and bioactivity is lower in any case. The fluctuations are influenced by variations in the composition of commercial size formulations, including the presence of organic chemicals such as methanol and acetic acid remaining from the polymerisation process, which may increase or decrease the biodegradability. In general, poly(vinyl alcohol) sizes can be degraded *or* eliminated by an optimally adapted inoculum in an appropriate sewage sludge phase, giving decomposition rates of 57–65% within seven days but with a potential for up to 100% elimination [211,212]. Trials have been carried out at a low temperature (8 °C) to demonstrate that even in winter poly(vinyl alcohol) can be eliminated by more than 90%, admittedly at a slower rate [211,212].

Acrylic size polymers generally show poor biodegradability (typically 3–10%), although recent research [211] has achieved up to 37% decomposition in special anaerobic cultures. However, these anionic polyelectrolytes can be readily eliminated from effluents by adsorption on sludge [220]. Acrylic size polymers may be precipitated in the third stage now included in many water treatment plants for the removal of phosphates, using a conventional inorganic precipitant such as iron(III) chloride. Some size formulations may require the addition of a specific precipitant of this kind, whilst others may be removed by bioelimination in the sludge. Polyester sizes may be disposed of by similar bioelimination methods [220]. Deliberate precipitation creates a need for subsequent disposal, but with acrylic size polymers this solid waste has high calorific value and is suitable for disposal by incineration. An advantage of acrylic size polymers arising from their ease of removal by precipitation is that they can be readily recycled, so that they need not enter the sewage system. Ultrafiltration is the preferred method of recycling [220,221].

10.5.3 Bleaching

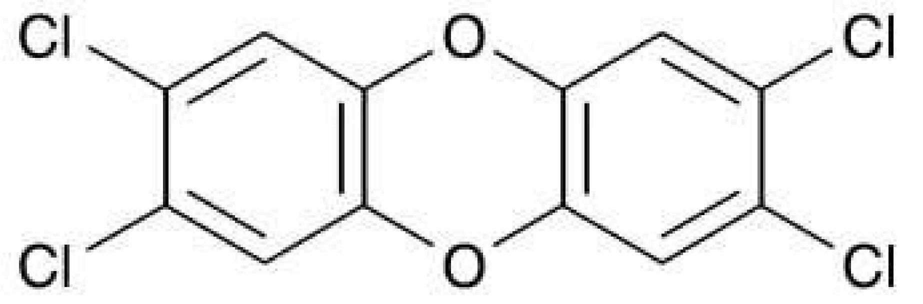
The three primary oxidants associated with textile bleaching are hydrogen peroxide (H_2O_2), sodium hypochlorite ($NaOC1$) and sodium chlorite ($NaClO_2$). There are other oxidising and reducing agents occasionally used (or proposed for use) in bleaching; these will be dealt with later. For the present, general factors affecting the use of the above three oxidising agents will be discussed. Many technical factors govern the selection of one bleaching agent over another:

- generic type of fibre (cellulosic, wool, synthetic)
- physical form of fibre (yarn, woven or knitted fabric)
- product and process costs
- stability, and therefore reliability
- versatility of process (batchwise or continuous)
- degree of whiteness obtained
- extent of any fibre damage.

Environmental factors have now become important in bleaching and are having far-reaching effects on the choice of bleaching agent. A particularly important parameter is the absorbable organic halogen value, commonly referred to as AOX. This is generally expressed as the mass of organohalogen compounds absorbed per unit mass of activated charcoal, there being three main steps in the analytical procedure [222]:

(1) Absorption of all organic halogen compounds by activated charcoal, taking care to avoid misleading results by uptake of inorganic salts such as sodium chloride
(2) Combustion of the activated charcoal and collection of the halogens thus released
(3) Quantitative determination of the halogens.

This aspect came to the fore with the well-known and much publicised discovery of the potent toxin and carcinogen 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (10.77), commonly but erroneously referred to simply as 'dioxin', in effluent from chlorine-based bleaching processes for wood pulp in papermaking. Although legislative requirements vary considerably worldwide the trend has been to ban or severely restrict the discharge of AOX-containing liquors. Typically, an AOX value of 0.5 mg/l must not be exceeded in waste water released from a textile wet processing works. This compares with a typical limit for drinking water of not more than 0.01 mg/l. In some legislative criteria there are limits on discharge from each processing line in a works, as well as on overall discharge. Typical values for three oxidising agents in cotton bleaching processes where no attempt has been made to minimise the AOX value are listed in Table 10.12.



10.77

Table 10.12 AOX values for cotton bleached with various oxidising agents [223]

Oxidising agent	AOX (mg/l)
Sodium hypochlorite	27.00
Sodium chlorite	2.40
Hydrogen peroxide	0.92

The seriousness of the AOX problem is highlighted by the fact that there is currently no economically acceptable solution for the specific removal of halogenated organic compounds from effluents [224]. There are important technical reasons why, over the years, hydrogen peroxide has progressively gained ascendancy over sodium hypochlorite as a bleaching agent. In view of the AOX values in Table 10.12 it is clear that there will be additional pressure, this time on ecological grounds, to continue the phasing out of hypochlorite bleaching in favour of peroxide. This is in spite of the fact that there are some steps (to be mentioned later) that can be taken to reduce the AOX values of effluent from hypochlorite bleaching. The intention here is to concentrate discussion on the chemistry of the products used. Hydrogen peroxide, because of its pre-eminence in bleaching technology, will be dealt with first, followed by sodium hypochlorite, sodium chlorite and other bleaching agents. The initial discussion is concerned mainly with cellulosic fibres, with some reference to synthetic fibres; wool and silk are then dealt with separately. The processing details of bleaching and the machinery used are dealt with elsewhere [11,143,225,226]. Excellent historical accounts are also available [227,228].

Peroxide bleaching

The advantages favouring the pre-eminence of hydrogen peroxide (over 90% of cotton goods are bleached with peroxide) include [143,225]:

(1) *Stability and consistency of supply*
Most of the hydrogen peroxide solution supplied for textile bleaching is acidic (pH 4.5–5.0) because it shows maximum stability under these conditions. Additives are present to increase its stability further at this pH.

(2) *Environmentally friendly*
As indicated above, peroxide does not contribute to AOX values and potentially decomposes completely into water and oxygen during effluent treatment.

(3) *Versatility of application*
Peroxide can be used over a wide range of application conditions in batchwise and continuous methods, the latter being predominant. The success of continuous peroxide bleaching is attributable to the relatively rapid rate at which bleaching takes place, although long-dwell processes are also established. Peroxide baths do not cause significant corrosion of machinery. Peroxide gives a good white and can be used even without prior scouring of the material. It is particularly suitable for combining with other processes, e.g. scouring, desizing, application of fluorescent brighteners, as well as the bleaching of many blends.

The technical disadvantages of hydrogen peroxide are relatively minor compared with the process costs:

(1) *Fibre damage*
This may occur by free-radical formation, especially in the presence of transition-metal ions such as those of iron or copper. Similar mechanisms can result in the decomposition of peroxide but there are means of controlling or avoiding this problem.

(2) *Quality of whiteness*
Higher levels of whiteness and more attractive tones (i.e. neutral or bluish rather than yellowish or reddish whites) are attainable with hypochlorite, although whites of the highest quality are produced using the two bleaching agents sequentially.

(3) *Cost-effectiveness*
If the costs for treating AOX-containing effluent are omitted, peroxide bleaching is more costly than hypochlorite bleaching. Data has been presented [222] showing that the chemical costs of a continuous bleaching process with alkaline hydrogen peroxide are on average about six times higher than those from sodium hypochlorite. In batchwise processing, peroxide can be twice as expensive as hypochlorite [222].

As mentioned above, hydrogen peroxide is available commercially as a stabilised liquid of pH 4.5–5.5. Solid peroxides have been proposed, with claims of bleached fabrics with greater strength and more stable whites [229], but it is difficult to foresee such solid peroxides gaining a commercial foothold at the expense of liquid hydrogen peroxide. Hydrogen peroxide exerts little bleaching action at pH 4.5–5.5 and requires activation to produce a bleaching effect. The principal means of activation is alkali addition. Given the required degree of alkalinity, temperature provides a further means of controlling the bleaching action, such as an overnight dwell at ambient temperature or from 3 to 20 minutes at 100 °C. Figure 10.20 shows the degree of whiteness attained at various pH [226], together with the corresponding curve for the amount of peroxide remaining in the treatment bath. This classic activation curve for hydrogen peroxide shows that bleaching is generally best carried out at pH 10.5–11.0. The amount of alkali required to give this pH will vary with the type of process, sodium hydroxide being the alkali most commonly added, although sodium carbonate or phosphate may be used.

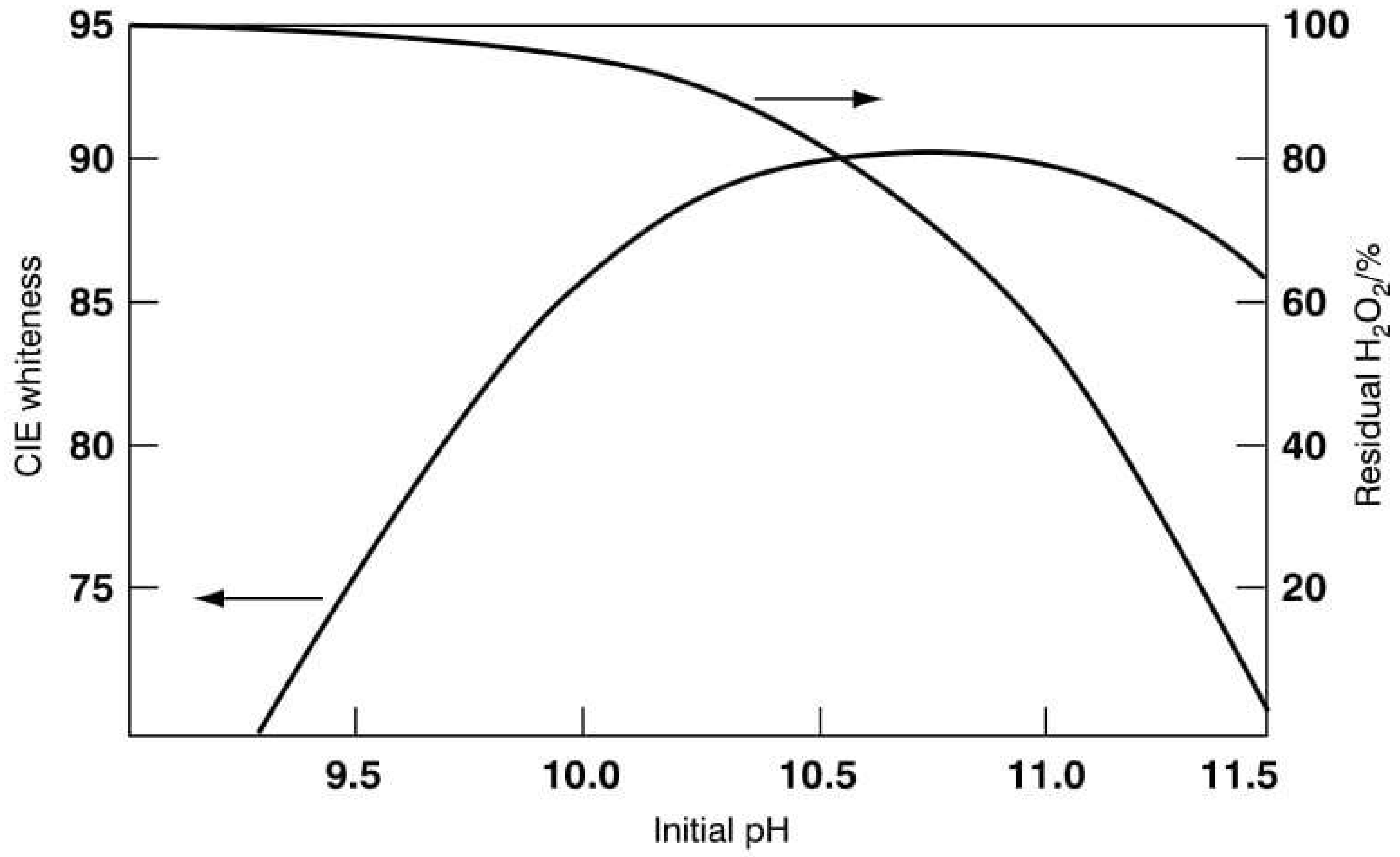


Figure 10.20 Optimisation of pH in hydrogen peroxide bleaching [226]

Under alkaline conditions an additive is required for stabilisation of the peroxide, which is necessary to avoid undesirably rapid decomposition with loss of bleaching efficiency and/or damage to the fibre. Traditionally, the most common stabilising agents have been the colloidal sodium silicates. The formulae of sodium silicates are best represented in terms of the ratio of sodium oxide to silica, which is 1 in sodium metasilicate (Na_2O:SiO_2) and 2 in the orthosilicate ($2Na_2O$:SiO_2). These silicates, however, are crystalline forms in which this ratio is 1 or greater. In the colloidal forms originally preferred for peroxide bleaching the ratio is less than 1. For example, in the so-called 'alkaline glass' form the ratio is 1:2, whilst in the so-called 'water glass' form it varies from 1:1.6 to 1:1.38. The colloidal silicates are efficient and economical stabilisers but care is needed to ensure efficient washing-off in order to avoid silicaceous deposits on the fabric and equipment. A simple and rapid test procedure has been developed to determine the relative suitability of stabilisers, with a view to keeping the running surfaces of a continuous bleaching range free from deposits [230]. Although such colloidal forms have been preferred, the crystalline meta- and orthosilicates can also be used and may provide easier washing-off.

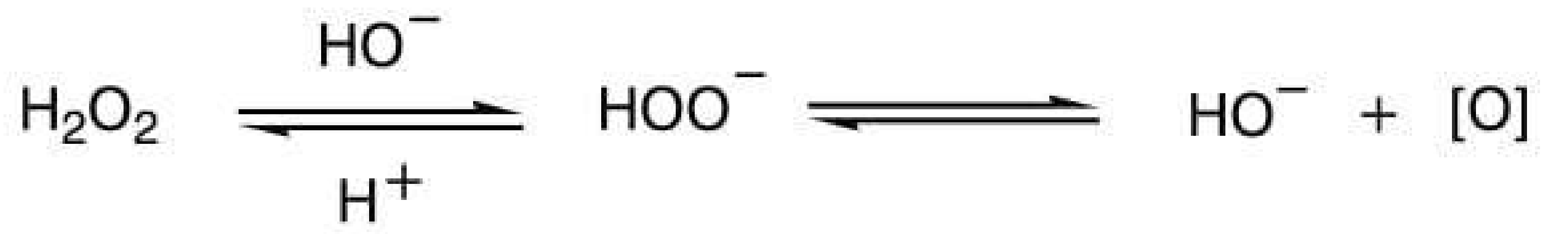
The required degree of alkalinity is generally obtained by the addition of sodium hydroxide, sodium carbonate or a phosphate, the amount of alkali varying with the type and quantity of silicate used. Since the bleaching action yields acid, sufficient alkali is required for neutralisation as well as absorption by the cellulose. The mechanism by which these stabilisers act is complex, although the elements of buffering action and sequestering of transition-metal ions, such as those of iron(III) and copper(II), undoubtedly contribute. Magnesium ions also play an essential part in the mechanism and must be added (as the sulphate, for example) if sufficient are not already present in the system. It is important to recognise that whilst transition-metal ions catalyse the decomposition of peroxide, the alkaline earth elements stabilise it. In the absence of calcium and magnesium even silicates can act as bleach activators [19].

The problems associated with silicaceous deposits have led to the adoption of more costly organic stabilising agents that also aid in plant cleaning and reduce the incidence of reprocessing. These organic stabilisers are often commercially blended products which may or may not contain magnesium salts [143], the three main types being aminopolycarboxylate sequestering agents, protein degradation products and selected surfactants. The preferred sequestering agents, in terms of both sequestering ability and stability to oxidation, are DTPA (10.6), either as its sodium or its magnesium salt, and its hydroxy derivatives [18]. Relatively simple methods of evaluating the efficiency of stabilisers have been used, but more reliable results are obtained with statistical experimental methods involving a realistic simulation of the bleaching process [231,232].

The mechanism of peroxide bleaching

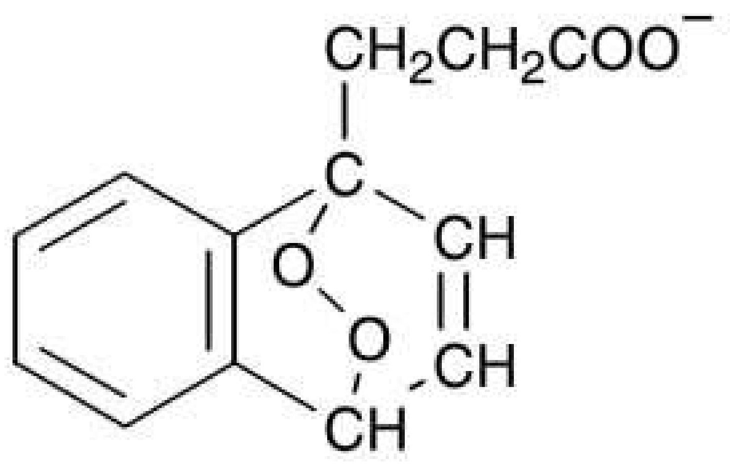
The details of this mechanism have been the subject of much debate over the years. Dannacher and Schlenker [233] have reviewed the various hypotheses and applied experimental criteria to establish the most likely mechanism. The fact that the bleaching effect varies widely with reaction conditions suggests that the actual bleaching agent is not hydrogen peroxide itself but another species liberated from the peroxide under the influence of pH and temperature. This much is generally agreed; there is, however, much debate regarding the liberated species. Since molecular oxygen has no bleaching effect, nascent or atomic oxygen has been proposed as the active species on the basis that it is readily liberated from the perhydroxide anion (HOO^-), according to Scheme 10.21. Dannacher and Schlenker reject this, since calculations show that the formation of oxygen atoms is energetically highly unfavourable and is not expected to occur under bleaching conditions.

Singlet oxygen has also been proposed and this can indeed be formed, particularly in mixtures of hydrogen peroxide and sodium hypochlorite. However, carefully designed experiments showed that under these conditions sodium hypochlorite has neither a direct



$$H_2O_2 \underset{H^+}{\overset{HO^-}{\rightleftharpoons}} HOO^- \rightleftharpoons HO^- + [O]$$

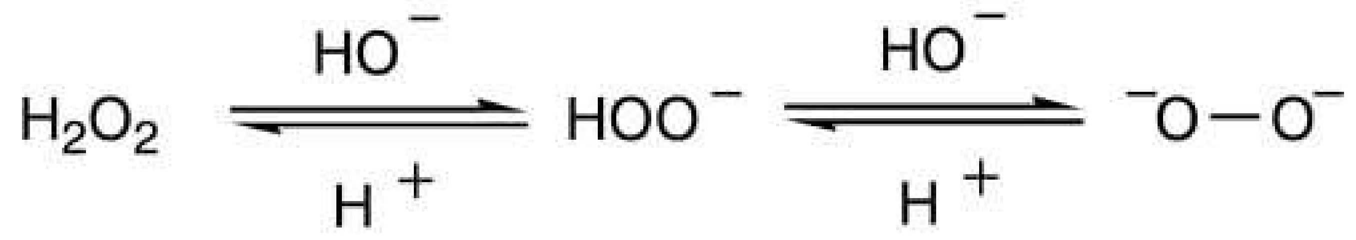
Scheme 10.21



10.78

bleaching effect (because it is consumed in the reaction with peroxide) nor an indirect bleaching effect via singlet oxygen. Dannacher and Schlenker also examined the effect of singlet oxygen derived from the thermal decomposition of an endoperoxide (10.78). They concluded that singlet oxygen has no bleaching effect when homogeneously dispersed in a liquor and that alkaline hydrogen peroxide solution contains no singlet oxygen.

The active species most often cited in recent times has been the perhydroxide anion mentioned previously (Scheme 10.21), even though it shows a decrease in redox potential with increasing pH. Hydrogen peroxide exists in aqueous solution in a dissociated equilibrium with the perhydroxide anion (HOO^-) and the peroxo dianion ($^-O\text{-}O^-$), as in Scheme 10.22. In view of the predominance of this hypothesis, Dannacher and Schlenker subjected it to a thorough investigation, studying the bleaching effect of hydrogen peroxide at 60 °C over the range of pH 2 to 13 and obtaining the results shown in Figure 10.21. If the



$$H_2O_2 \underset{H^+}{\overset{HO^-}{\rightleftharpoons}} HOO^- \underset{H^+}{\overset{HO^-}{\rightleftharpoons}} {}^-O{-}O^-$$

Scheme 10.22

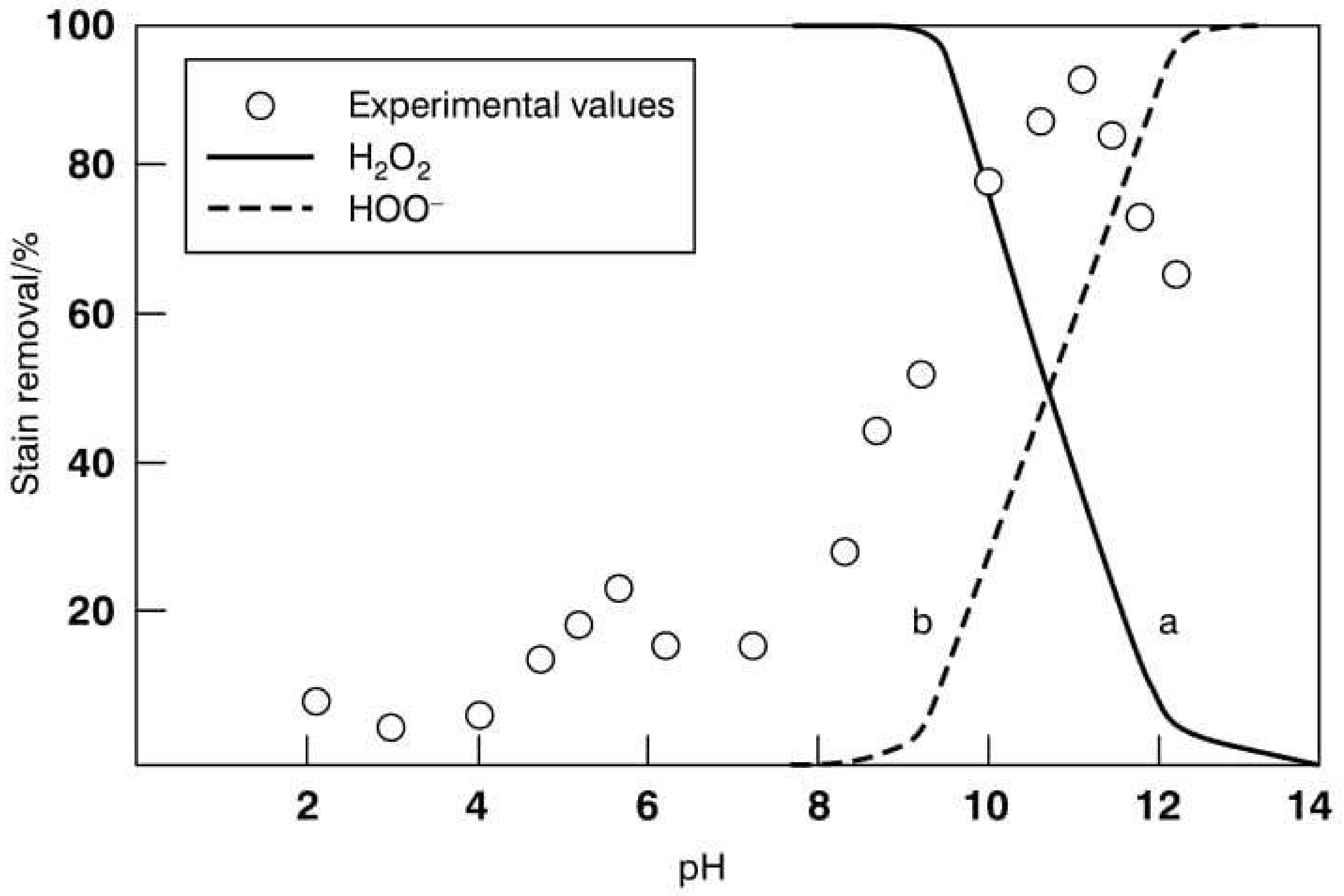
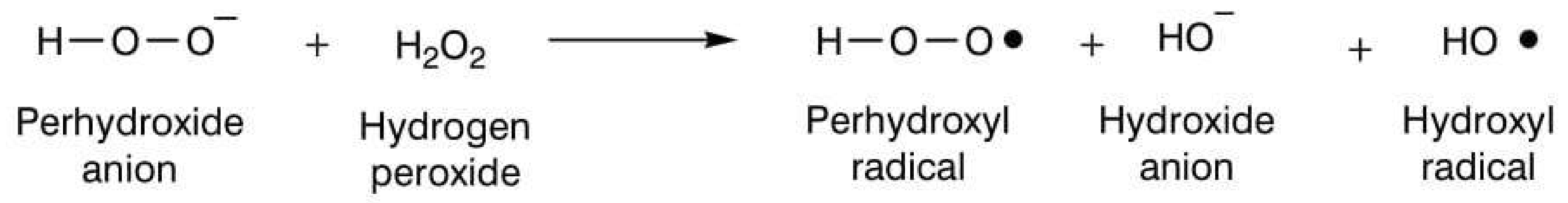


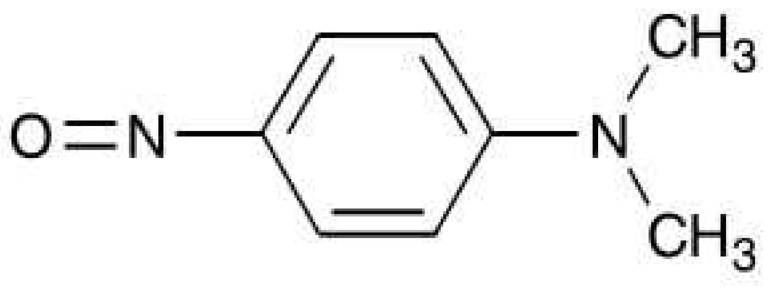
Figure 10.21 Relative stain removal after 60 min bleaching at 60 °C [233] 6.5×10^{-3} mol/l hydrogen peroxide in buffer solution. Relative share (%) of the protolytic forms of hydrogen peroxide in the total amount at 60 °C ($^-O{-}O^-$ negligible in this range)

perhydroxide anion were the effective agent one would expect the bleaching effect to increase with concentration and thus with increase in pH beyond the equilibrium point of pH 11. Figure 10.21, however, shows that at the point where the concentration of perhydroxide anions begins to exceed that of undissociated hydrogen peroxide, the bleaching effect decreases considerably, indicating that the perhydroxide anion is clearly not the effective bleaching agent [233].

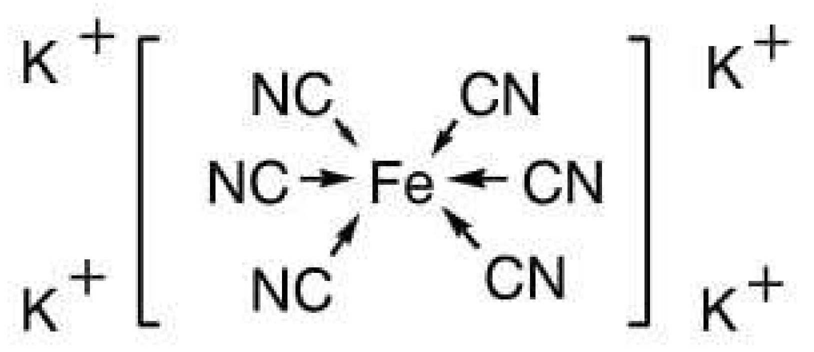
As shown in Scheme 10.23, the perhydroxide anion can give rise to both perhydroxyl and hydroxyl free radicals. These free radicals have been proposed as the active bleaching agents. Dannacher and Schlenker carried out bleaching tests in the presence of scavengers for the hydroxyl free radical, 4-nitroso-*N*,*N*-dimethylaniline (10.79) and potassium hexacyanoferrate(II) (10.80) separately at a concentration of 10^{-3} mol/l [233]. The bleaching effect was just as powerful in the presence of the scavengers as in their absence. It was concluded that the hydroxyl free radical has no bearing on the bleaching effect of hydrogen peroxide.



Scheme 10.23

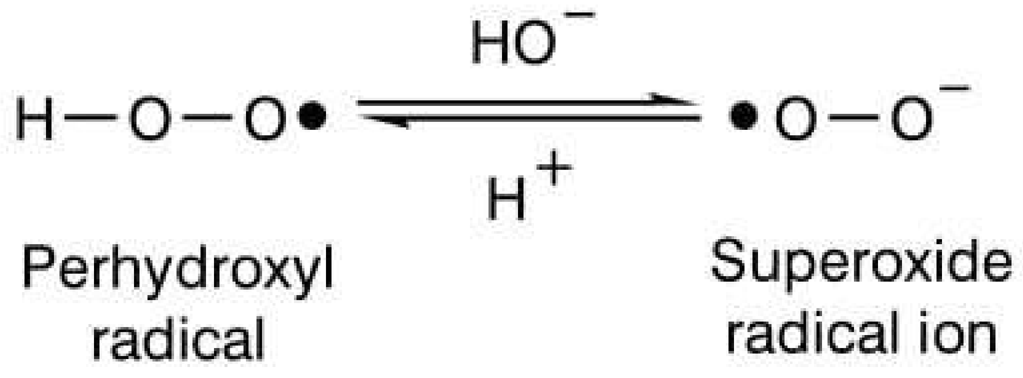


10.79

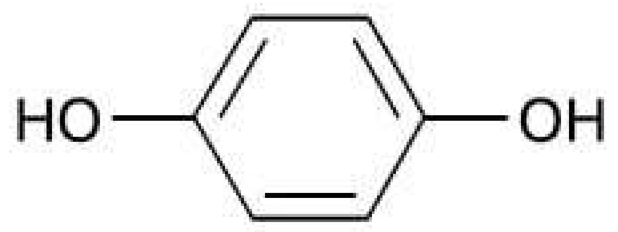


10.80

Consideration of pK_a values suggests that the perhydroxyl radical is dissociated almost quantitatively in the optimum pH range for peroxide bleaching, giving rise to the conjugate base ·O–O⁻ known as the superoxide radical ion (Scheme 10.24). When Dannacher and Schlenker carried out tests using hydroquinone (10.81) as a scavenger for the superoxide radical ion, it was found that the bleaching effect decreased with increasing concentration of scavenger (Figure 10.22). These results suggested that the effective species in hydrogen peroxide bleaching is the superoxide radical. The agreement between experimental and calculated results for superoxide concentration at different pH values was taken as further support for this mechanism [233].



Scheme 10.24



10.81

Hydroquinone

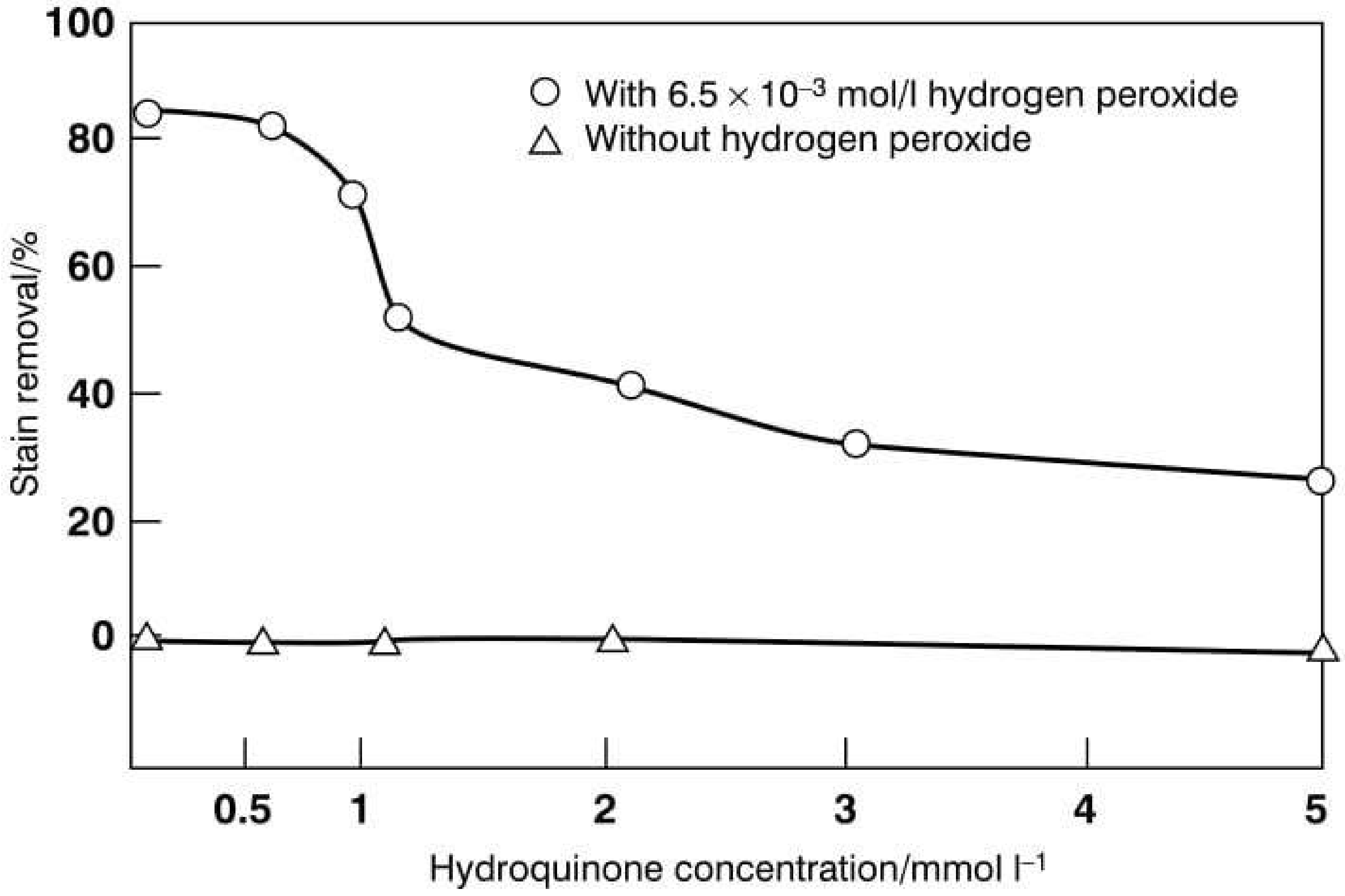
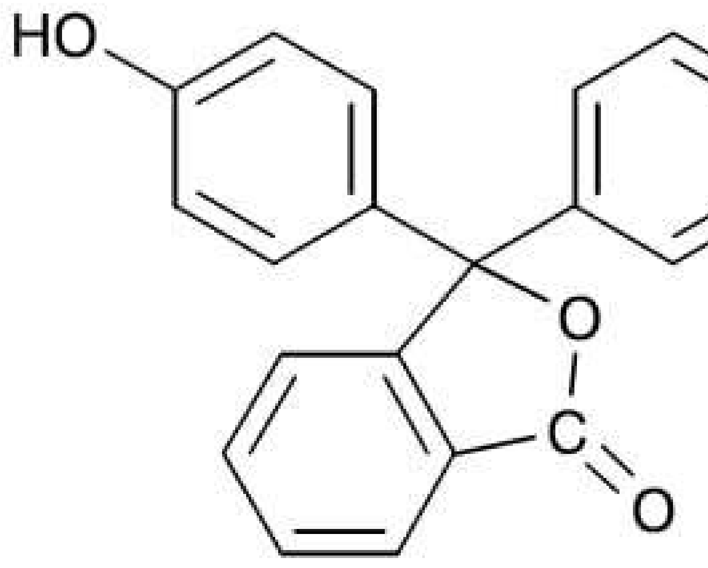


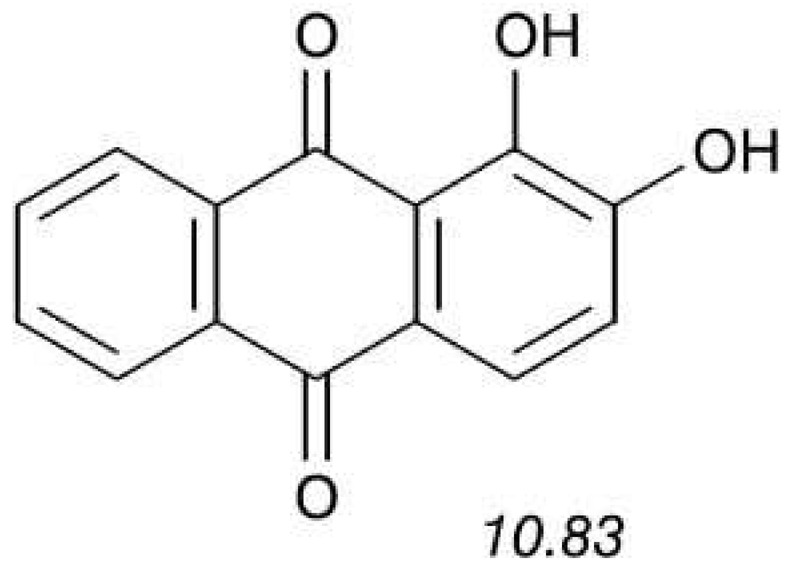
Figure 10.22 Effect of increasing hydroquinone concentration on the relative stain removal after 60 min at pH 10.5 [233]

However, these conclusions have been vigorously challenged by Spiro and Griffith [234]. The bleaching tests of Dannacher and Schlenker were carried out on cotton stained with tea. Spiro and Griffith pointed out that tea stains are complex mixtures of coloured polyphenolic compounds with unknown protonation constants. They claimed that kinetic studies of peroxide bleaching are more easily interpreted using individual coloured compounds with known properties such as phenolphthalein (10.82), alizarin (10.83) or crocetin (10.84), a yellow polymethine colorant isolated from saffron. Spectrophotometric studies by Spiro and Griffith of the bleaching of these compounds with hydrogen peroxide demonstrated that none of these reaction rates was affected by addition of a scavenger for hydroxyl and perhydroxyl radicals, which were therefore ruled out as effective species. They do concur with Dannacher and Schlenker, however, that singlet oxygen can also be ruled out on the basis of scavenging experiments. Offering a radically different interpretation, Spiro and Griffith claimed that all the kinetic data can be explained quantitatively on the assumption that the perhydroxide anion (at higher pH values) and hydrogen peroxide itself (at lower pH values) are the only active oxidising species. Further studies of the bleaching of malvidine chloride (10.85) at pH 1.5–4.0 showed that the only significant oxidant was the hydrogen peroxide molecule, which was thus not as inert as Dannacher and Schlenker apparently believed. Spiro and Griffith concluded that in the peroxide bleaching of a wide range of colorants there is no need to invoke any oxidising species other than the perhydroxide anion and molecular hydrogen peroxide.



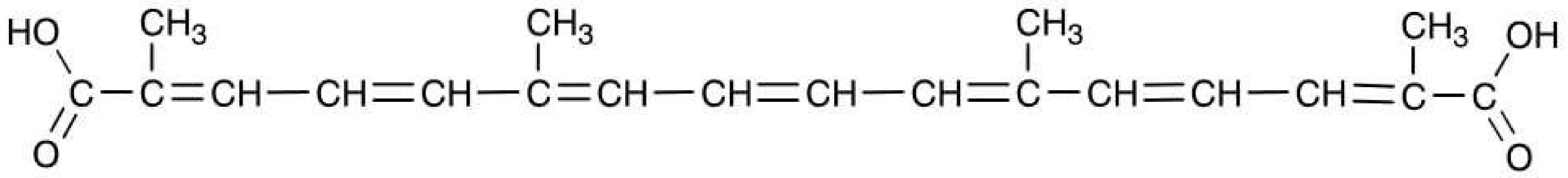
10.82

Phenolphthalein



10.83

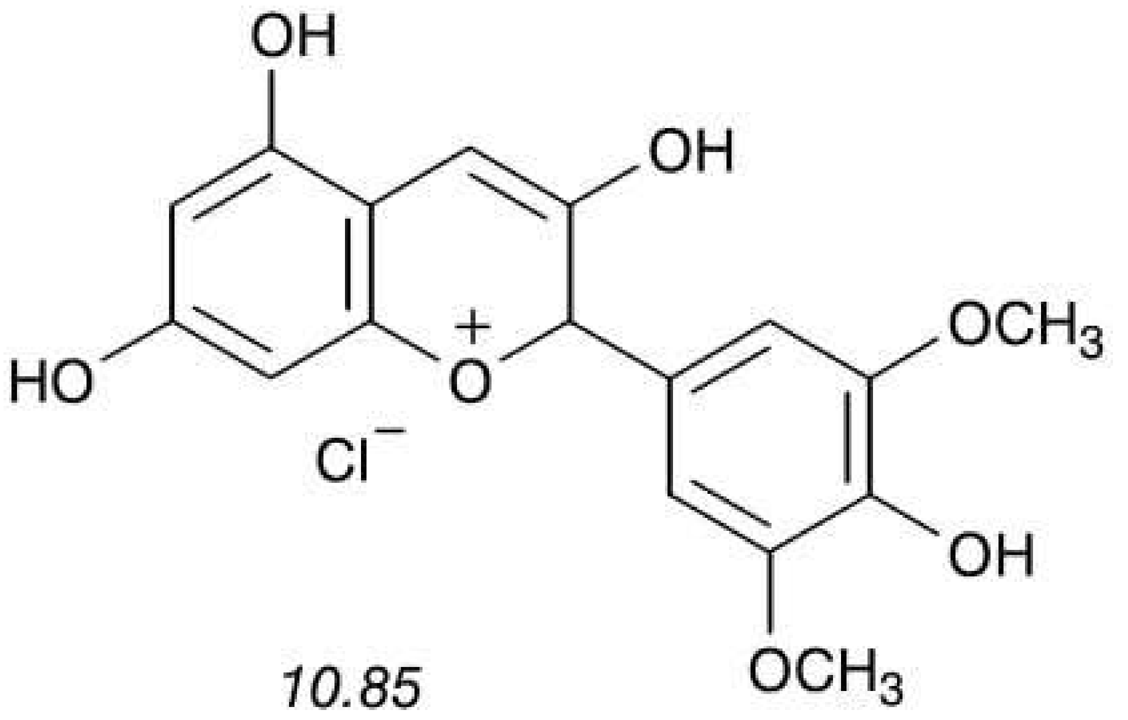
Alizarin



$$HO\!-\!\underset{\underset{O}{\|}}{C}\!-\!\overset{\overset{CH_3}{|}}{C}\!=\!CH\!-\!CH\!=\!CH\!-\!\overset{\overset{CH_3}{|}}{C}\!=\!CH\!-\!CH\!=\!CH\!-\!CH\!=\!\overset{\overset{CH_3}{|}}{C}\!-\!CH\!=\!CH\!-\!CH\!=\!\overset{\overset{CH_3}{|}}{C}\!-\!\underset{\underset{O}{\|}}{C}\!-\!OH$$

10.84

Crocetin



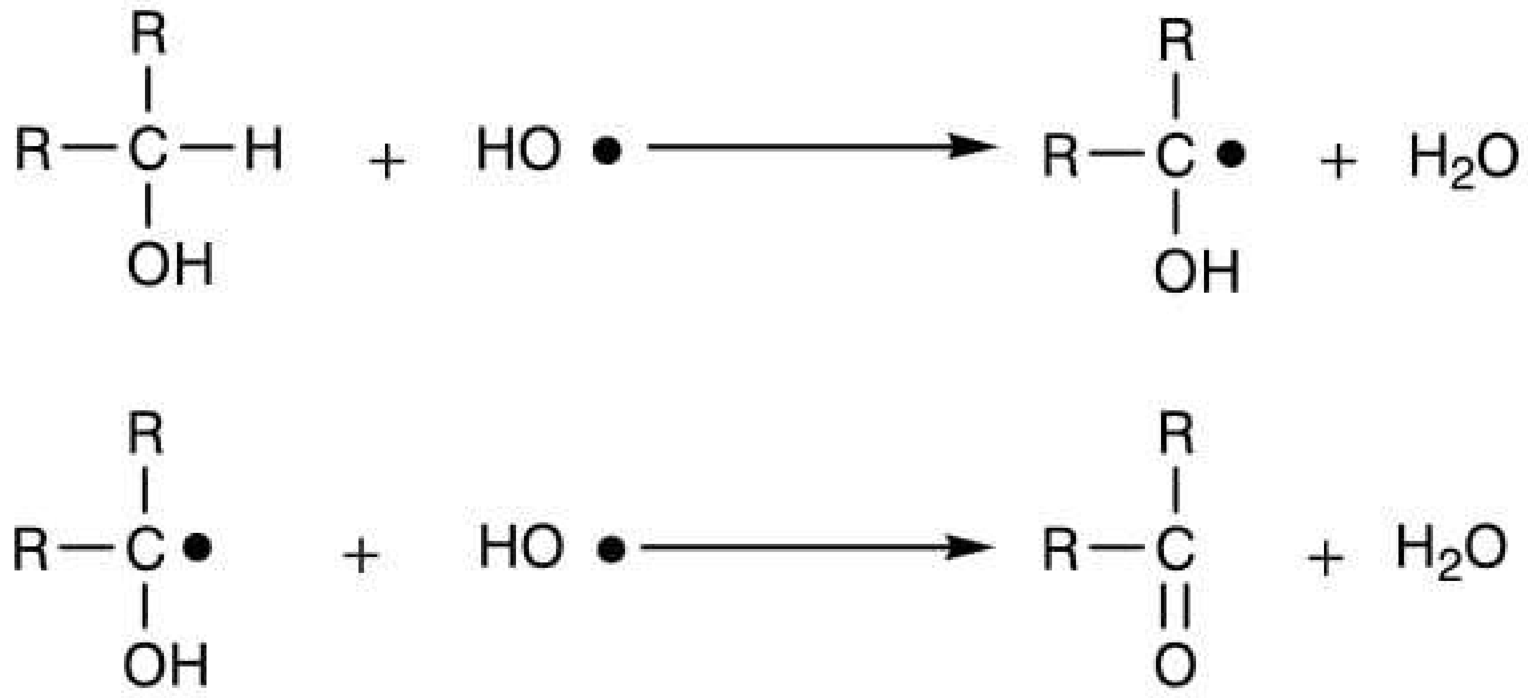
10.85

Thus the detailed mechanism of peroxide bleaching is not yet finally resolved. It should be borne in mind, however, that the work of Dannacher and Schlenker was carried out at 60 °C on tea-stained cotton, whereas Spiro and Griffith studied the decolorisation of individual colorants at 21–25 °C in the absence of a textile substrate.

Fibre tendering and process control

In an optimally controlled process free from transition-metal ions hydrogen peroxide bleaching is remarkably safe, there being no reported detrimental effects of bleaching at around 100 °C or for more than several hours [143]. Under such conditions, most of the peroxide appears to be consumed in the oxidation of chain end units of the cellulose macromolecule. The other major effect on the substrate is oxidation of secondary hydroxy to keto groups, accompanied by the formation of very few aldehyde or carboxyl groups [235].

Owing to the relative inactivity of keto groups in cellulose, the bleached effect is stable and is not susceptible to yellowing. This action of hydrogen peroxide is not entirely random amongst all cellulosic hydroxy groups but is directed mainly towards the C3 hydroxy group on randomly located glucose units in the amorphous regions of cellulose, as many as 8–17 keto groups being formed per macromolecule. The formation of keto groups is thought to occur as a result of transient generation of the free radical form of the C3 hydroxy group, as in Scheme 10.25. Free radicals can be formed from the C3 hydroxy groups following reaction between hydrogen peroxide and perhydroxide anions (Scheme 10.23) although other factors may be involved, such as a localised concentration of radicals in the amorphous regions of the fibre. A supply of free radicals can be generated by heat treatment, without requiring the presence of transition-metal ions as a catalyst. The number of oxygen atoms consumed per chain scission exceeds 100, compared with 26 for hypochlorite bleaching. The yield of oxidised hydroxy groups is less than 10%, whereas it is about 40% for hypochlorite treatment. Under these circumstances, the decomposition of hydrogen peroxide and its oxidative modification of cellulose can be adequately regulated by a well-formulated stabiliser, so that an unacceptable degree of fibre damage is avoided.



Scheme 10.25

In the presence of certain transition-metal ions, however, notably Fe(II) or Fe(III), the decomposition of hydrogen peroxide and its oxidative attack on cellulose are accelerated. This results in uncontrolled damage, even to the extent in some cases of forming holes in a fabric. Although sequestering agents and other stabilisers, such as silicates, can decrease such severe degradation, in practice they cannot be relied upon to give consistent total protection in the presence of catalysing metals. In such cases, a pretreatment specifically to remove such metals before bleaching is recommended [143].

Various metals can be present in raw cotton, the amounts varying with source and treatment (Table 10.13). There has been a trend in recent years towards increased metal contamination of textiles, giving rise to a great deal of research in this area. Indeed, Reicher [236] cites 29 other references in the period 1987–91 alone. Rotor spinning has become more prevalent in recent years and this is known to give an increased incidence of localised critical concentrations of metal contamination. Despite the overall complexity of metallic contamination in cotton fibres, iron is the main culprit with regard to catalytic damage in peroxide bleaching [236,237] and hence is the only one considered here.

Metal-ion catalysis of hydrogen peroxide decomposition can generate perhydroxyl and hydroxyl free radicals as in Scheme 10.26 [235]. The catalytic effects of Fe^{2+} and Fe^{3+} ions are found to be similar [235]. It is not necessary for the active catalyst to be dissolved [237], as rust particles can be a prime cause of local damage. The degradative free-radical reaction competes with the bleaching reaction, as illustrated in Scheme 10.27 [237]. Two adverse consequences arise from the presence of free radicals:

- fibre damage
- rapid decomposition of hydrogen peroxide, leading to a corresponding loss of bleaching action.

Table 10.13 Metal ion content of six different cotton samples obtained by atomic absorption studies [236]

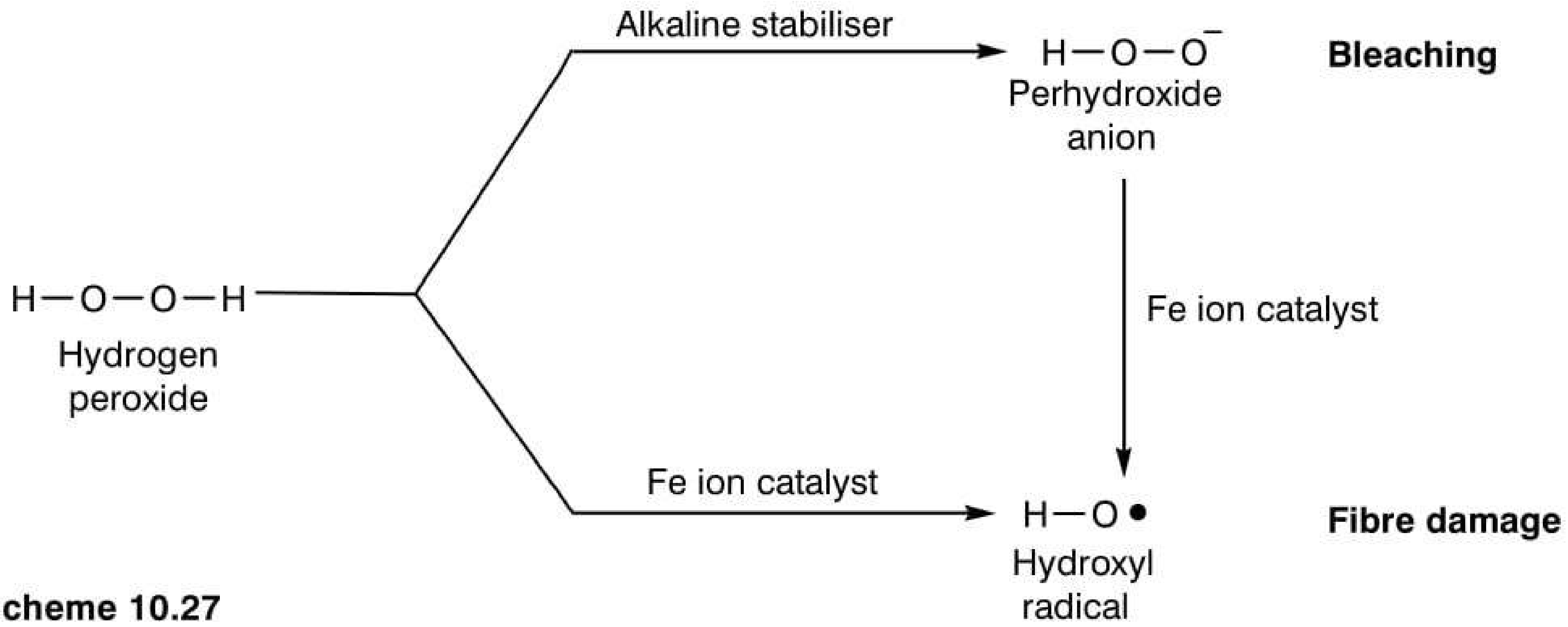
Sample: Metal (mg/kg)	1	2	3	4	5	6
Al	23	21	32	47	25	22
Ba	1.5	1.5	1.6	1.2	2.0	1.5
Ca	580	600	840	830	580	630
Cu	3	4	2	5	3	2
Fe	34	100	110	790	36	94
K	4500	4600	4500	5300	4700	4700
Mg	490	510	520	530	520	550
Mn	3.2	3.5	4.0	6.7	3.3	3.7
Na	220	230	230	330	330	320
Ni	nd	1.2	nd	2.1	nd	1.0
P	240	270	260	330	270	270
Pb	nd	nd	nd	7.6	nd	nd
S	340	360	360	430	380	380
Sr	5.4	5.6	5.6	5.9	5.7	6.0
Ti	0.3	0.25	0.7	1.4	0.8	0.7
Zn	4.5	7.3	5.3	35	4.9	13

nd Not detected in practice (Ni < 1 mg/kg; Pb < 3 mg/kg)

$$\mathrm{H{-}O{-}O{-}H} + \mathrm{Fe^{2+}} \longrightarrow \mathrm{HO}\bullet + \mathrm{HO^{-}} + \mathrm{Fe^{3+}}$$

$$\mathrm{H{-}O{-}O^{-}} + \mathrm{Fe^{3+}} \longrightarrow \mathrm{H{-}O{-}O}\bullet + \mathrm{Fe^{2+}}$$

Scheme 10.26



Scheme 10.27

This is an important but very difficult area for research, particularly regarding the formulation and evaluation of stabiliser systems. Non-reproducibility of results is a serious problem and in commercial practice a single batch can unexpectedly give rise to damage despite using the same protective measures that had been successful with apparently similar batches. In research, it is difficult to obtain consistent metal-containing samples direct from nature, whilst artificially contaminated specimens do not always give results directly comparable with substrates contaminated naturally.

In both research and practice, critical localised concentrations of metal contamination can be difficult to detect. Potassium hexacyanoferrate(II) (10.80) gives an intense deep blue coloration with iron(III), permitting extremely sensitive detection of tiny iron spots even by visual inspection. It is recommended as a quality control measure on batches of cotton destined for bleaching [237]. However, in view of the random distribution of metal traces, even the most sensitive test cannot guarantee freedom from contamination throughout a batch of goods to be bleached.

Certain researchers have preferred soluble salts such as iron(III) nitrate [236] to represent deliberate contamination, whilst others have used insoluble forms. However, even iron(III) oxide in the form of rust is found to vary in catalytic activity depending on physical form. Although uniform distribution of the contamination, at least below a relatively low concentration, has been claimed to be less troublesome than localised concentrations, there is not even agreement on this. A further complication is that different studies have been carried out in either the absence or the presence of a cellulosic substrate. With these provisos in mind, the catalytic behaviour of trace metals and the effects of some preventive agents will be outlined.

The parameter most commonly monitored in this research is the extent of hydrogen peroxide decomposition. Measurement of tensile strength and/or the degree of polymerisation can be useful indicators of fibre damage. The effect of iron(III) ion concentration in accelerating the rate of peroxide decomposition is shown in Figure 10.23, using a system comprising hydrogen peroxide, sodium silicate and magnesium sulphate at 95 °C and pH 12. The effects of pH and Fe(III) concentration on decomposition are indicated in Figure 10.24. Only slight changes in these variables can greatly influence the degree of decomposition.

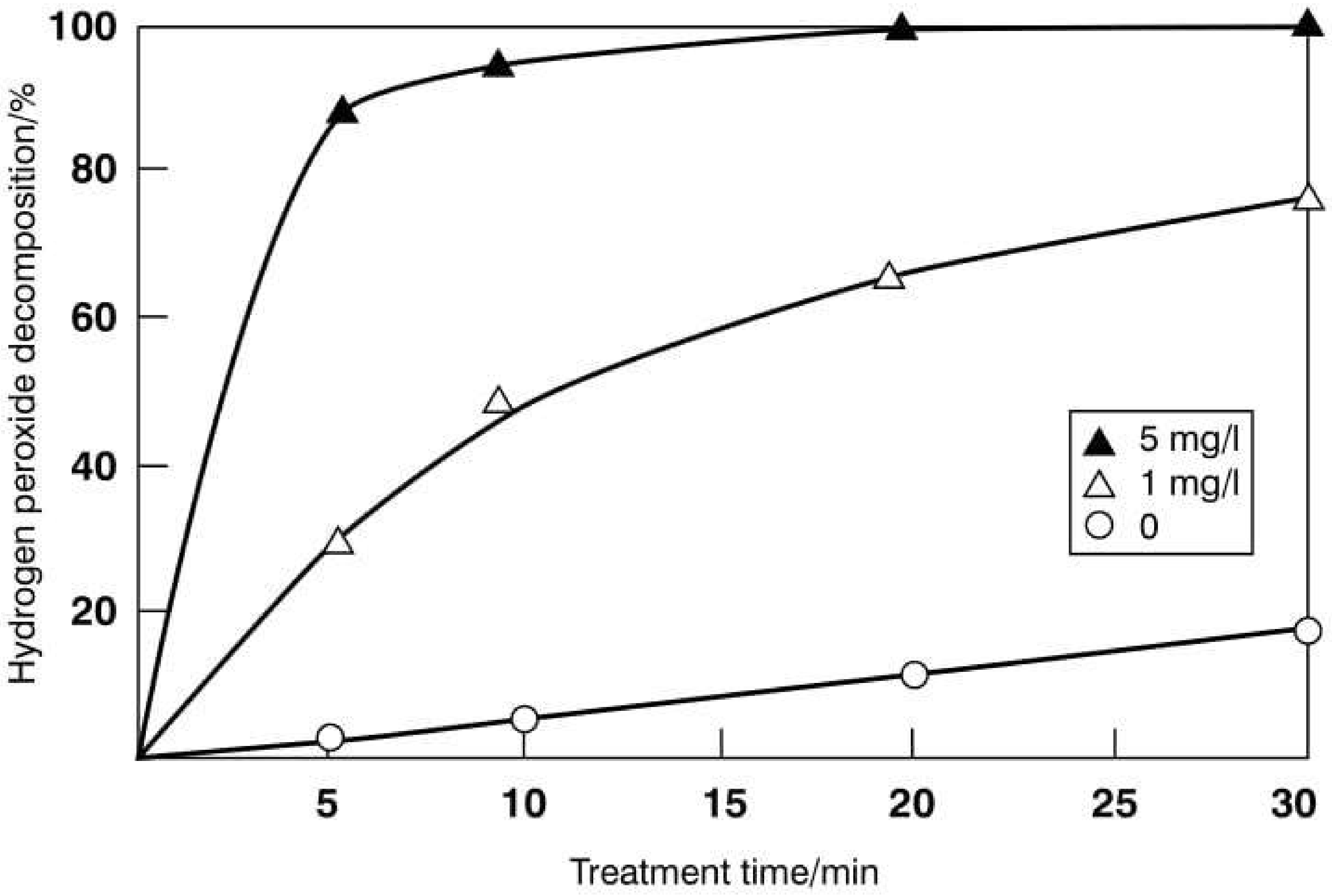


Figure 10.23 Effect of Fe(III) ion concentration on rate of hydrogen peroxide decomposition in absence of substrate [237]. Initial concentration 2.9 g/l H_2O_2, Sodium silicate 5 g/l, Magnesium sulphate 0.2 g/l, 95 °C, pH 12

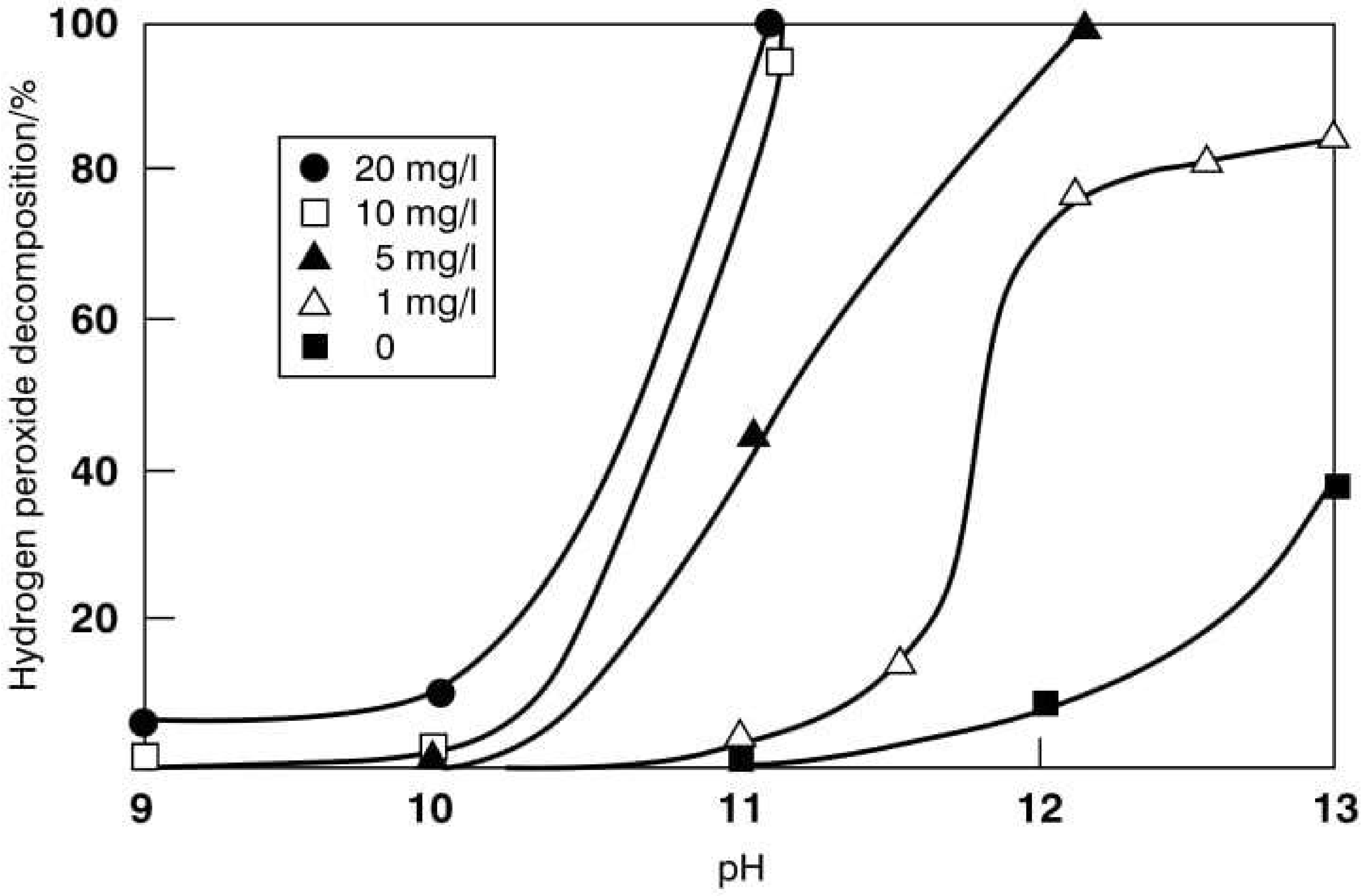


Figure 10.24 Effects of pH and Fe(III) ion concentration on hydrogen peroxide decomposition in absence of substrate [237]. Initial concentration 2.9 g/l H_2O_2, Sodium silicate 5 g/l, Magnesium sulphate 0.2 g/l, 95 °C, 30 min

The effect on the decomposition rate of replacing sodium silicate and magnesium sulphate by a phosphonate stabiliser is shown in Figure 10.25. In this case, at a concentration of 2 g/l of the specific phosphonate used proved more effective in retarding Fe(III)-catalysed peroxide decomposition than the combination of 5 g/l sodium silicate and 0.2 g/l magnesium sulphate represented by Figure 10.23. However, doubling the concentration of silicate and magnesium sulphate also brought about a considerable improvement in stability (compare Figures 10.23 and 10.26).

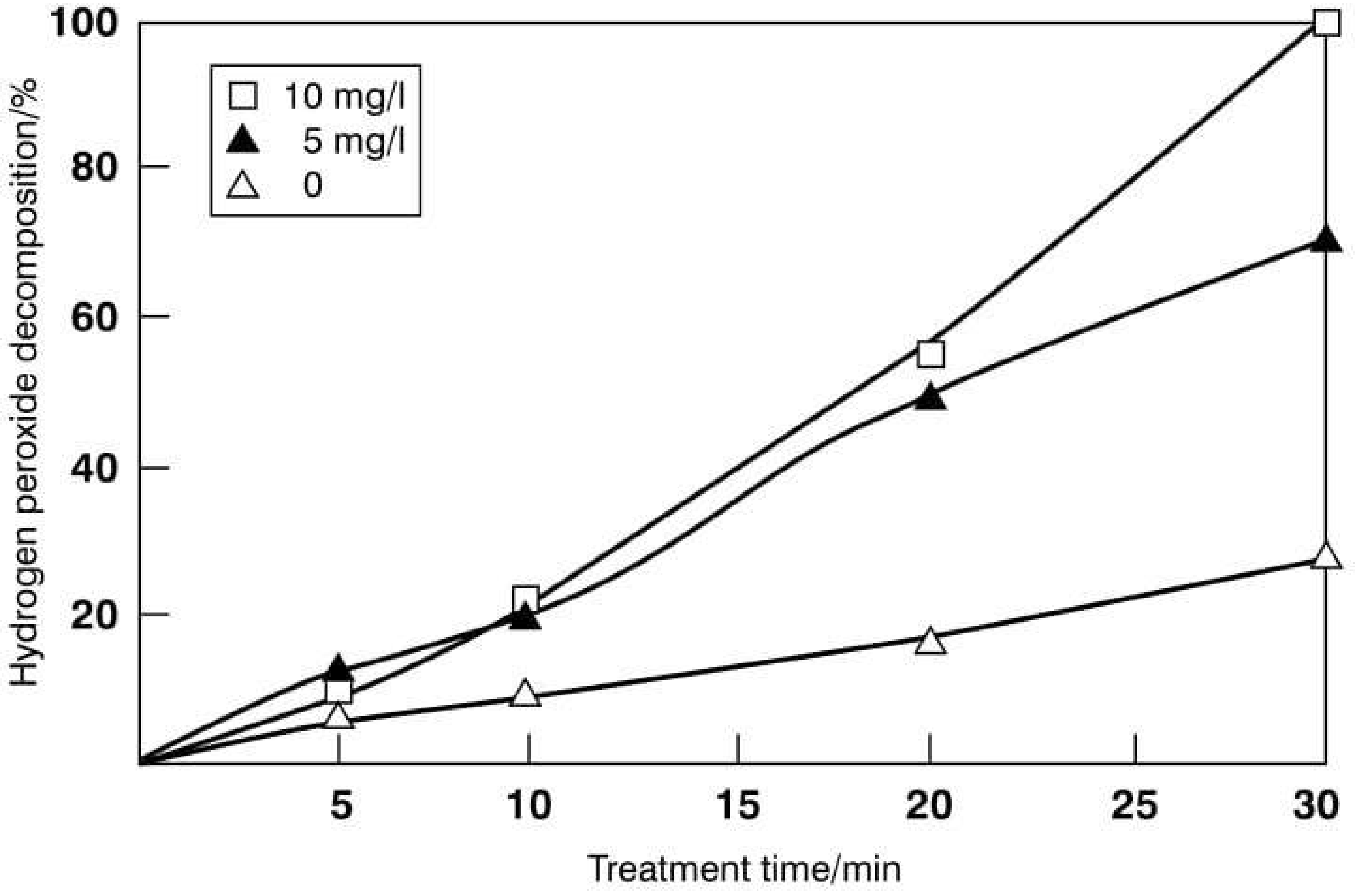


Figure 10.25 Effect of phosphate stabiliser on Fe(III)-catalysed decomposition of hydrogen peroxide in absence of substrate [237]. Initial concentration 2.9 g/l H_2O_2, Phosphonate stabiliser 2 g/l, 95 °C, pH 12

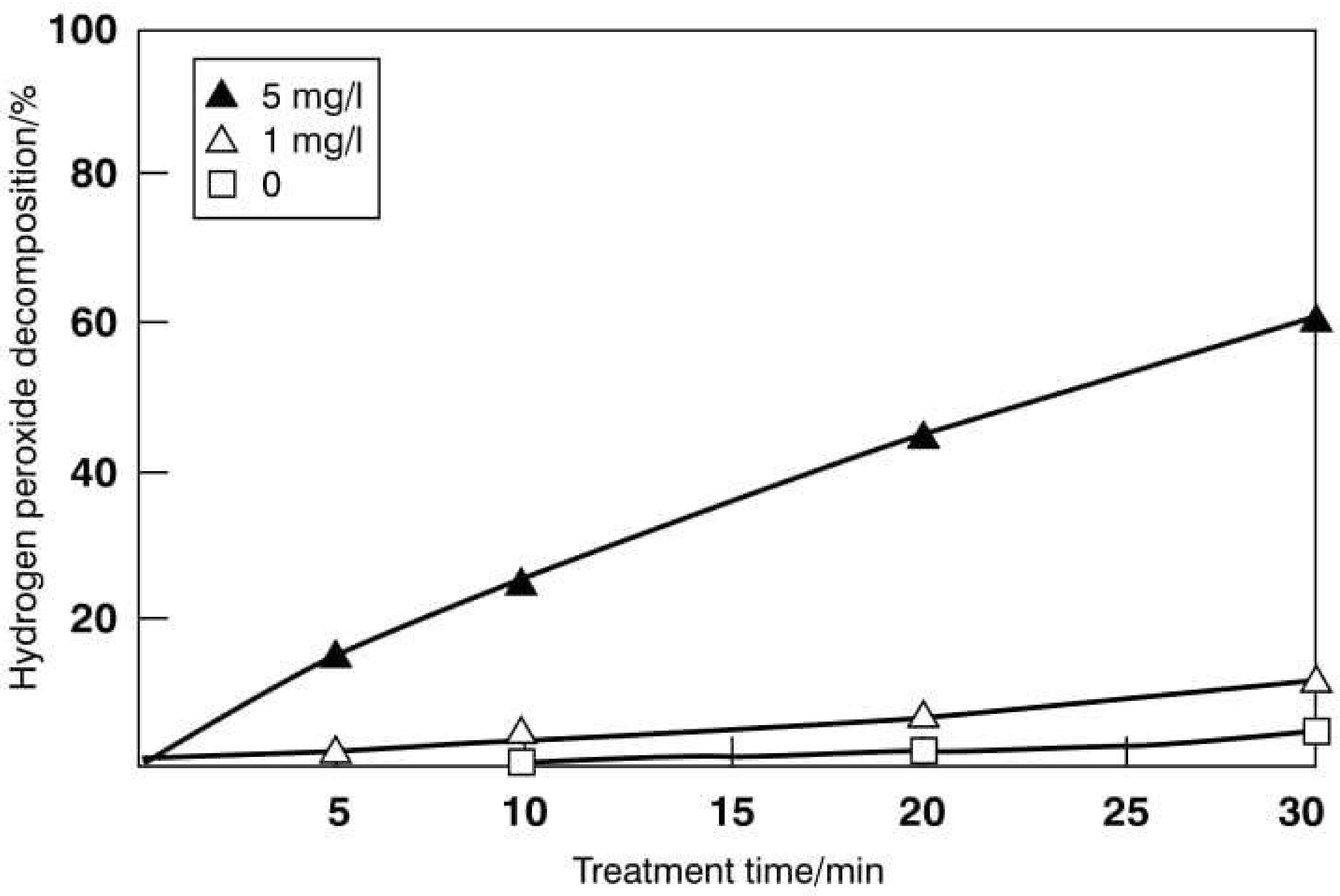


Figure 10.26 Effect of magnesium silicate stabiliser on Fe(III)-catalysed decomposition of hydrogen peroxide in absence of substrate [237]. Initial concentration 2.9 g/l H_2O_2, Sodium silicate 10 g/l, Magnesium sulphate 0.4 g/l, 95 °C, pH 12

The results shown in Figures 10.23 to 10.26 were obtained in the absence of a textile substrate. Those in Figure 10.27 were determined in the presence of cotton and involved measurement of the degree of polymerisation of the cellulose [236]. These curves show the effects of increasing the concentration (up to 40 g/l) of an unspecified commercial sequestering agent on both peroxide decomposition and the degree of polymerisation of the cellulose. The contaminant present on the cotton was iron(III) nitrate applied artificially. The initial concentration (3 g/l) of sequestering agent present was that recommended by the manufacturer. Under these conditions the loss of peroxide was 80%, accompanied by an unacceptable lowering of the degree of polymerisation to less than 1000. It was necessary to increase the concentration of complexing agent by several times the recommended amount in order to obtain acceptable protection. Such an increase may be impossible to justify, however.

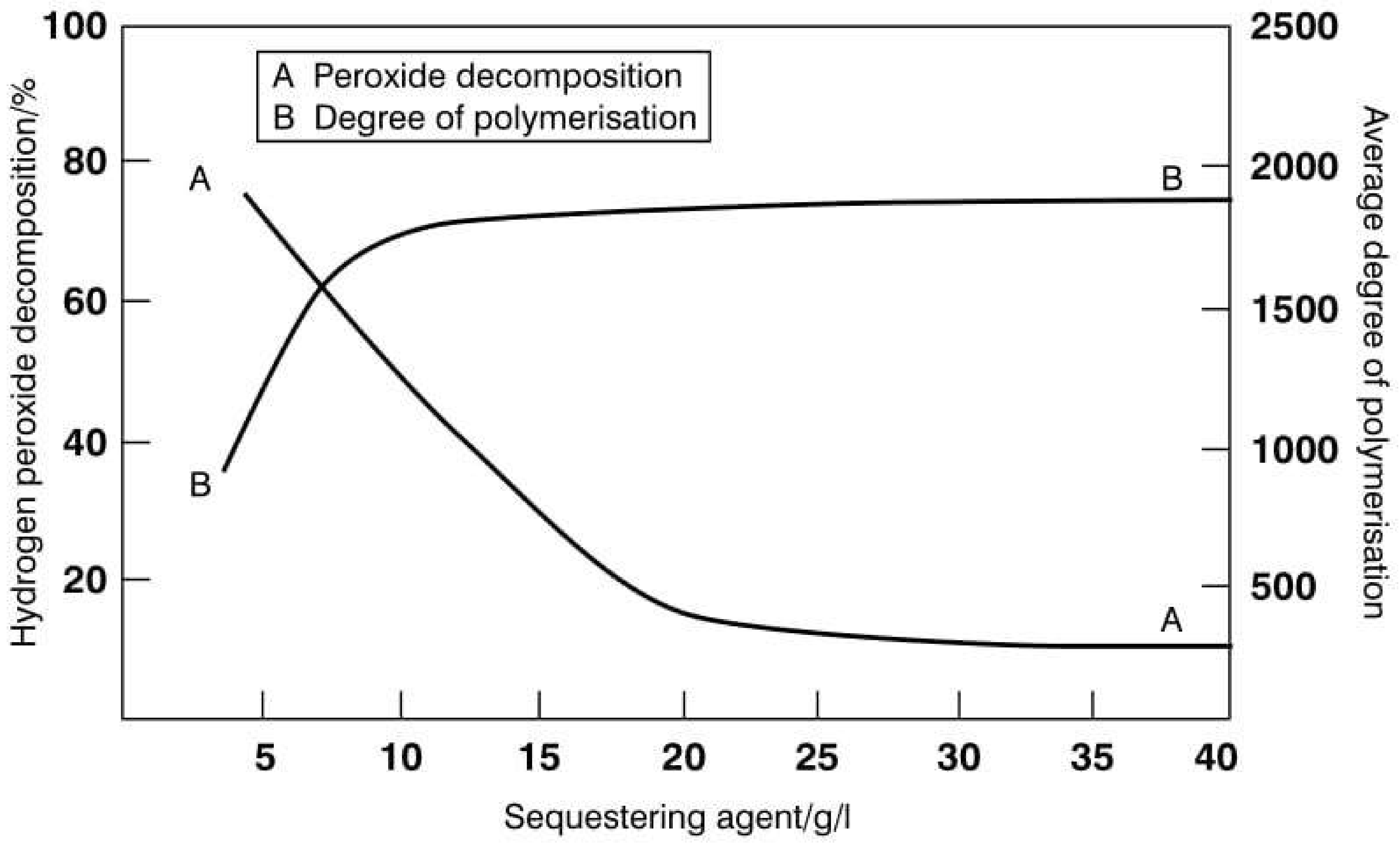


Figure 10.27 Effect of sequestering agent concentration on the decomposition of hydrogen peroxide and degree of polymerisation of cotton cellulose [236]

It is evident that careful optimisation of all the parameters involved is essential for efficient bleaching with minimal fibre damage. The need for close control of pH, minimisation of liquor ratio and coordination of the component concentrations with treatment time and temperature is critical [226]. Titration of samples of the liquor taken at regular intervals has been the traditional method of analysis. An obvious disadvantage is the unavoidable delay after sampling before corrective action can be taken. Hence the trend has been towards continuous monitoring. A method of continuous on-line monitoring and control of a continuous bleaching range, using measurement of pH, conductivity and temperature, has been described [238].

The use of biosensors and chemosensors to monitor peroxide in continuous ranges has been examined [239]. Biosensors incorporate electrochemical/enzymatic features with oxygen detectors. Chemosensors depend on anodic or electrolytic oxidation and are more robust under the conditions prevailing in the textile industry. This technique is limited to peroxide concentrations from 0.01 to 100 mg/l, so dilution of the test sample from an operating level of 10–50 g/l is necessary. Chemosensors offer a rapid means of determining the concentration of peroxide. Being small, they can be fitted quite close to the point of measurement with a direct link to the bleach liquor dispenser. In continuous flow measurement, where liquor is transported continuously through the measuring instrument, continual monitoring of the prevailing concentration is provided. By means of suitable electronic control equipment connected to the sensor system, automatic logging of measured values is possible and, if necessary, appropriate adjustment of the liquor can take place immediately [239].

An alternative electrochemical method is based on the detection of hydrogen peroxide at an electrode supplied with a reference voltage [240]. Many electrode materials, however, give proportional measurements only up to 0.02 mol/l but a special electrode material of the glassy carbon type provides linearity between current signal and peroxide concentration up to 50 g/l. The measuring cell has five components: the measuring, reference and back electrodes determine the current signal, whilst a pH and temperature probe provides compensation for the pH- and temperature-dependence of the current signal. In spite of the advantages offered by these systems most monitoring still depends on manual titration, with manual intervention at the dispensing stage where necessary [240].

Typical peroxide bleaching bath formulations

The composition of bleaching formulations varies widely with the machinery available and the condition of the substrate. Typical formulations and conditions have been given [143] for batchwise processing (Table 10.14) and for continuous processing (Table 10.15). The need to conserve energy in recent years has led to growing interest in cold pad–batch peroxide bleaching, in which padded fabric is batched without uneven drainage or surface drying for 15–24 hours at ambient temperature. Table 10.16 gives typical pad liquor formulations [143,225,241]. A good wetting agent is required to ensure rapid and thorough wetting of grey fabrics at 25–35 °C, together with an efficient detergent to assist in removal of fats and waxes. A persulphate (up to 5 g/l) may also be added to assist desizing [143]. The addition of a peroxide activator based on 1,2,4-triazole has been suggested as a means of accelerating bleaching at about 30 °C [242].

Table 10.14 Recommended conditions for batchwise peroxide bleaching [143]

Additives	Kier (% owf)	Jig (% owf)	Winch or jet (g/l)	Package machine (g/l)
Magnesium sulphate heptahydrate			0.1	0.1
Wetting agent			0.5–2	0.5–2
Sodium silicate (79Tw)	2–3	3–5	7	2–7
Organic stabiliser		1–1.5	1–2	0.5–2
Caustic soda (100%)	0.6–1.4	0.25–0.8	5–15	5–15
Hydrogen peroxide (35% solution)	3–5	2–5	5–15	5–15
Liquor ratio	4:1	3:1	15–20:1	8–10:1
Temperature (°C)	95	95	95	90
Time (min)	60–120	60–120	60–120	60–120

Table 10.15 Recommended conditions for continuous peroxide bleaching [143]

Additives (g/l)	J-box conveyor (woven goods in rope form)	Roller-bed steamer	Pressure steamer	Jemco machine	J-box (knitgoods)
Magnesium sulphate heptahydrate	0.1	0.1	0.1	0.1	0.1
Wetting agent	2–5	2–5	2–5	0.5	5
Sodium silicate (79Tw) or organic stabiliser	5–10	10–20	5–10	1.5	10
Caustic soda (100%)	2–5	5–15	2–5	4	5
Hydrogen peroxide (35% solution)	15–30	45–60	30–45	2	45
Liquor ratio	1:1	1:1	1:1	10:1	1:1
Temperature (°C)	95–98	95–98	120–140	95–100	95–98
Time (min)	60–120	10–30	1–2	40–60	60–90

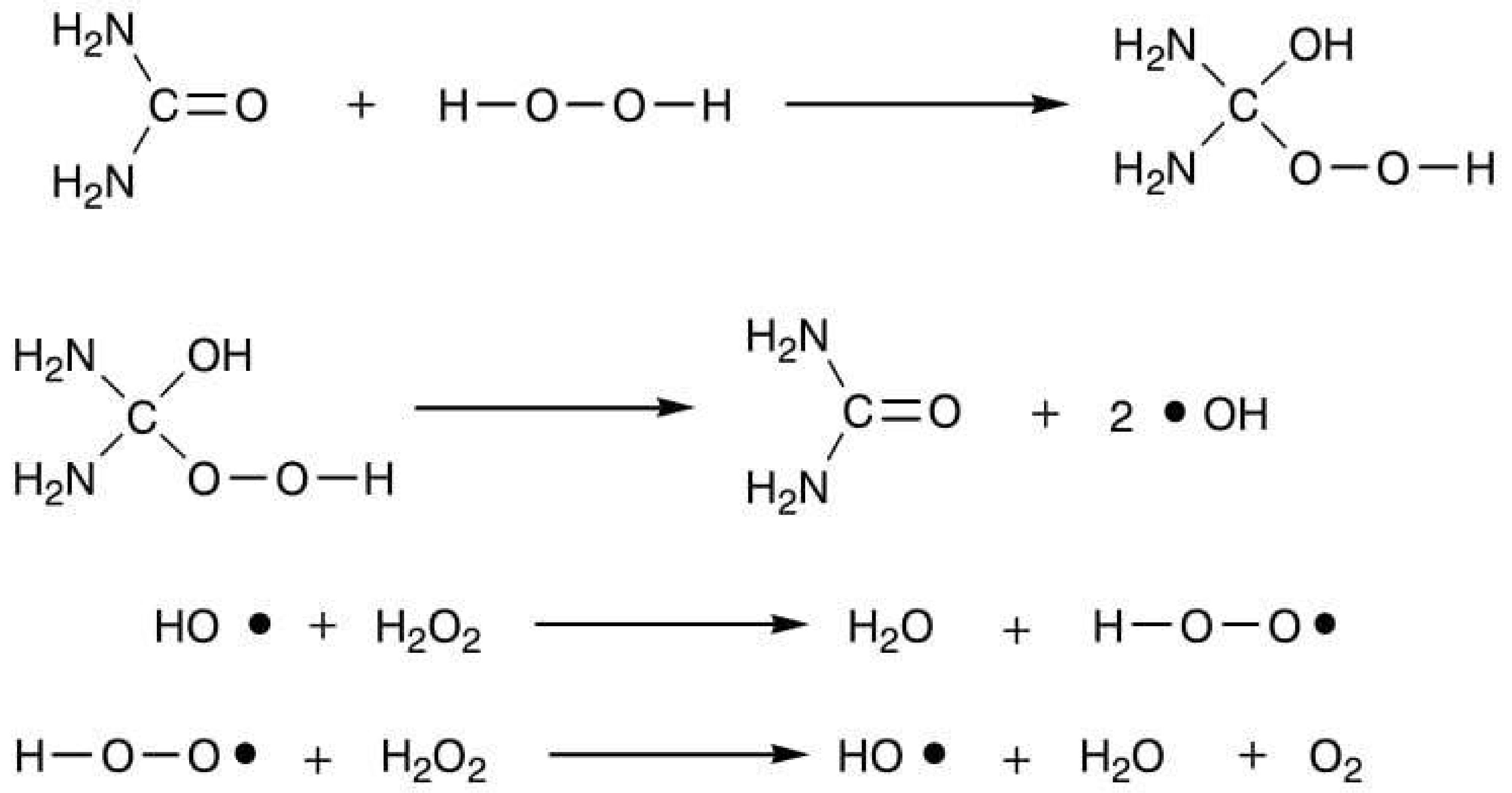
The above recommendations are for caustic scoured or peroxide desized fabrics. For fabrics not so treated, the amounts of caustic and peroxide should be increased by 50% [143]

Table 10.16 Recommended conditions for cold pad-batch peroxide bleaching

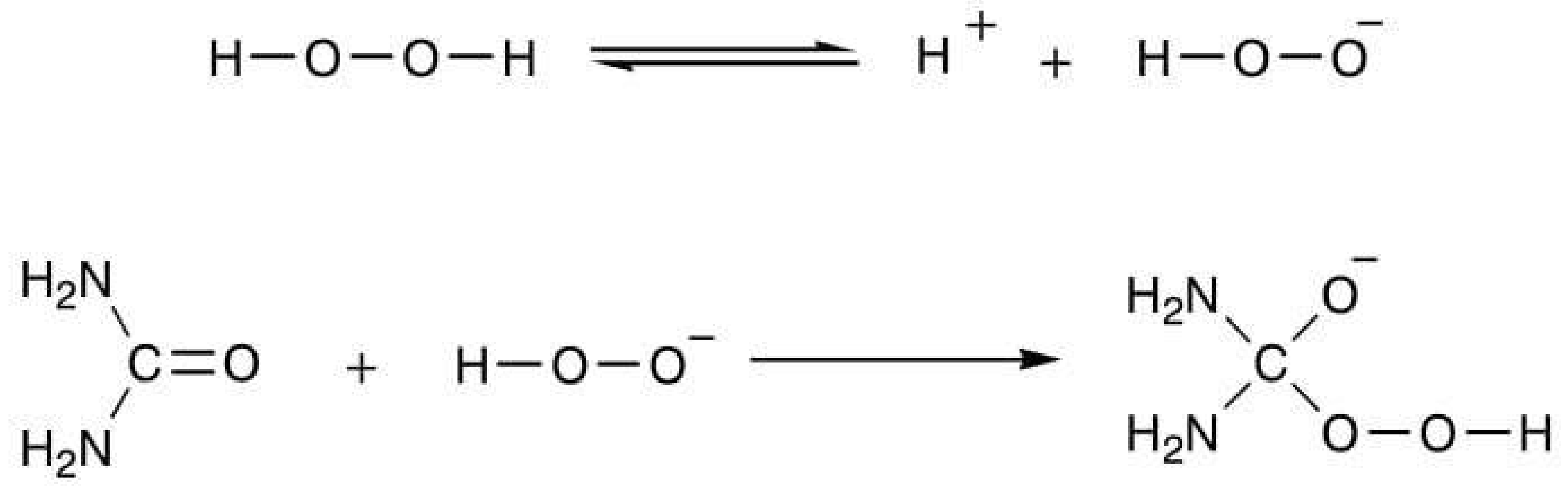
	References	
Additives (g/l)	225	143,241
Magnesium sulphate heptahydrate	0.1	
DTPA (10.6) (40%)	0.1	
Wetting agent	2–5	
Organic stabiliser	0–15	6–10
Sodium silicate (79Tw)	10–15	8–12
Sodium hydroxide (100%)	10–20	8–15
Hydrogen peroxide (35%)	40–60	40–50

In some circumstances, hydrogen peroxide can be combined with an organic activator. One such process suggests the use of hydrogen peroxide and urea for the bleaching of linen [243]. Recommended additions are 7 g/l hydrogen peroxide, 8 g/l urea and 1 g/l nonionic wetting agent for 2.5 hours at pH 6, 95 °C and 50:1 liquor ratio. Under these conditions urea accelerates the decomposition of peroxide, which is normally slow at pH 6. In the presence of urea, peroxide decomposition is believed to proceed according to Scheme 10.28 [243]. In this scheme, hydrogen peroxide and urea interact to form an unstable complex which then decomposes to yield hydroxyl radicals. These attack more of the peroxide molecules to yield perhydroxyl radicals, hydroxyl radicals and molecular oxygen. It is also likely that urea interacts with perhydroxide anions from hydrogen peroxide according to Scheme 10.29. This anionic complex of urea can be a further source of hydroxyl radicals. The influence of temperature on the whiteness index of linen subjected to this process is shown in Figure 10.28. The process may be applied to scoured or unscoured linen [243].

The success of peroxy bleach activators such as tetra-acetylethylenediamine (10.86) in detergent formulations for low-temperature laundering has encouraged trials of this approach in peroxide bleaching [244,245]. TAED is colourless, odourless, non-toxic, non-sensitising, non-mutagenic and stable on storage. During biological treatment it is degraded to carbon dioxide, water, ammonia and nitrate; ethylenediamine is not detected on biodegradation [245]. TAED seems to be an ideal peroxide activator in the neutral to weakly alkaline range in textile bleaching, being entirely benign environmentally. Such an



Scheme 10.28



Scheme 10.29

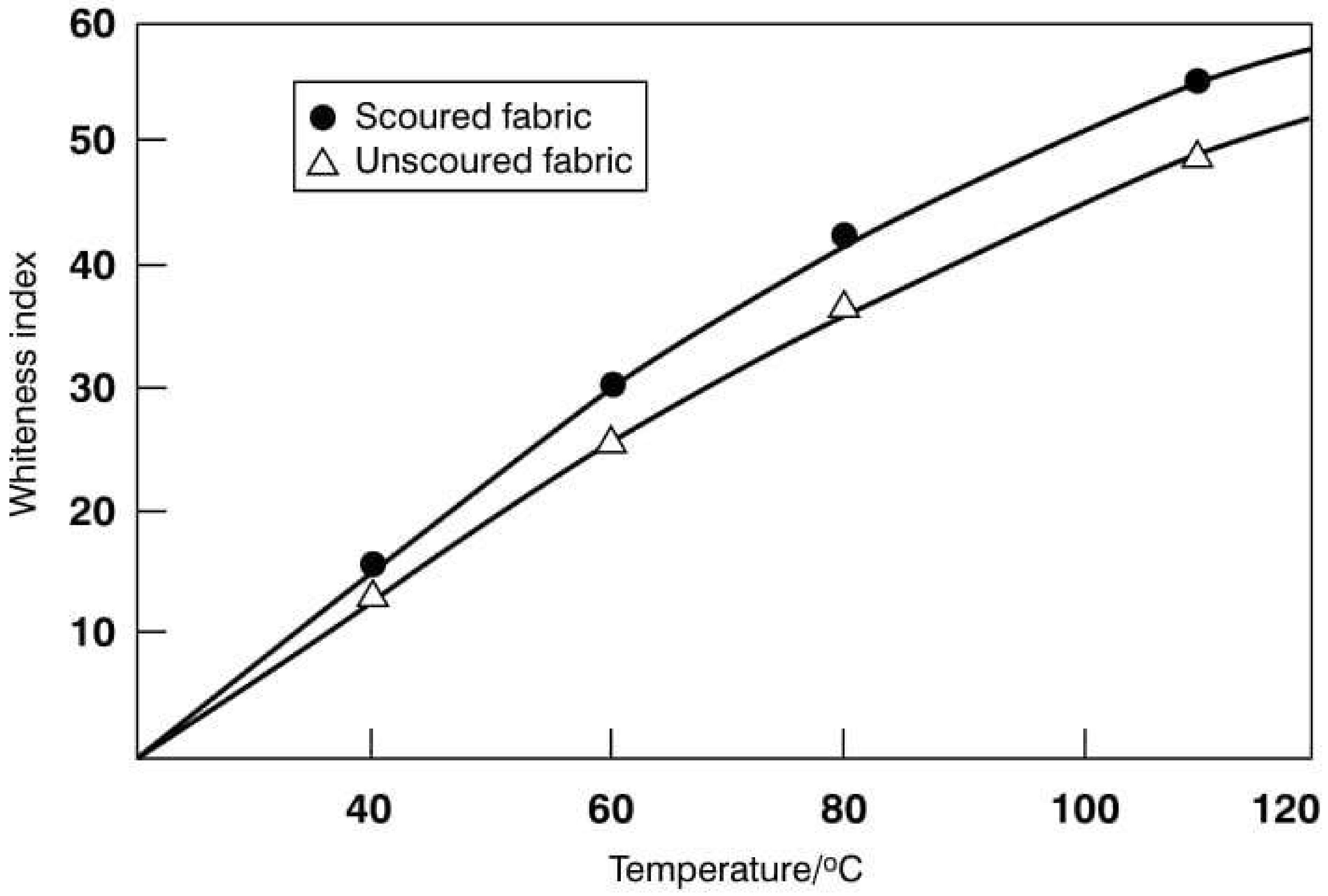


Figure 10.28 Effect of temperature on the whiteness index of linen bleached using urea-activated hydrogen peroxide [243]. Treated with 7 g/l hydrogen peroxide and 8 g/l urea for 150 min at pH 6 and 50:1 liquor ratio

approach permits bleaching at lower temperatures and near-neutral pH values. Advantages of this process over hot alkaline peroxide bleaching include:

- at neutral or weakly alkaline pH fibre damage is only slight and catalytic fibre damage is almost unknown
- low temperatures (60 °C or lower) permit energy savings
- handle is improved, since cotton waxes remain on the fibre
- the process can be used for coloured goods, since colour bleeding is minimal at low temperatures
- the process is suitable for regenerated cellulosic fibres, giving less swelling of cellulose
- the process is less sensitive to hard water.

The disadvantages include:

- TAED powder is difficult to dissolve in water
- disintegration of cotton husks is not as good as in alkaline bleaching.

The formulations listed in Table 10.17 have been suggested [244].

The mechanism of activation is believed to be as follows. In an alkaline medium, hydrogen peroxide yields the perhydroxide anion (Scheme 10.22), which reacts with TAED (10.86) to form diacetylethylenediamine (10.87) and the peracetate anion (10.88) as in Scheme 10.30 [244]. At pH 8–9, the peracetate anion is in equilibrium with free peracetic acid, as in Scheme 10.31 [244]. The peracetic acid reacts with the peracetate anion to form nascent oxygen which is the active bleaching agent, as in Scheme 10.32 [244]. Further possible activators suggested by Kleber [244] include:

PAG	penta-acetylglucose
BOBS	sodium *p*-benzoyloxybenzenesulphonate
NOBS	sodium *n*-nonanoyloxybenzenesulphonate
TAGU	tetra-acetylglycoluril

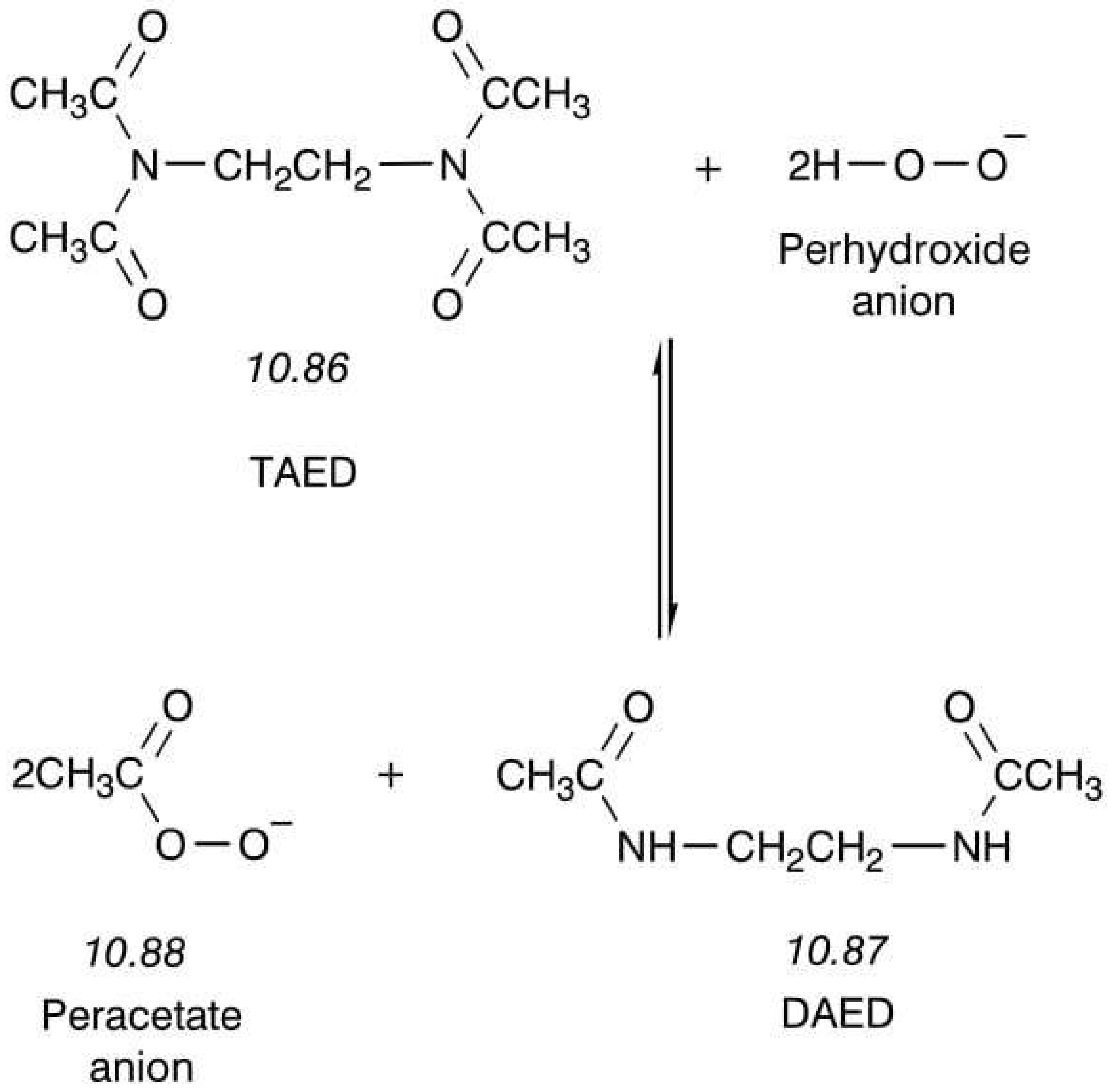
DADHT	diacetyldioxohexahydrotriazine
PAP	phthaloylaminoperoxycaproic acid.

Certain activated peroxide systems are specifically designed for bleaching wool and these will be mentioned later.

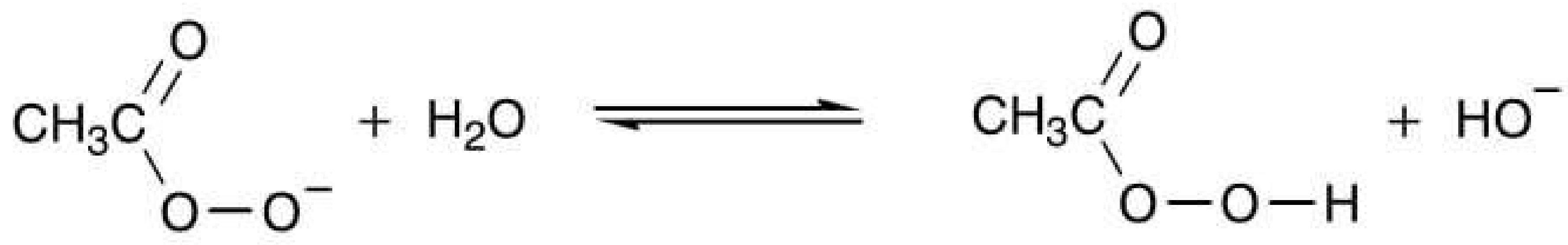
The final step after peroxide bleaching is to ensure that the goods do not contain residual peroxide. Reducing agents have been used traditionally for this purpose. However, the possibility of using environmentally friendly catalase enzymes should not be overlooked [87–89].

Table 10.17 Recommended conditions for TAED-activated peroxide bleaching [244]

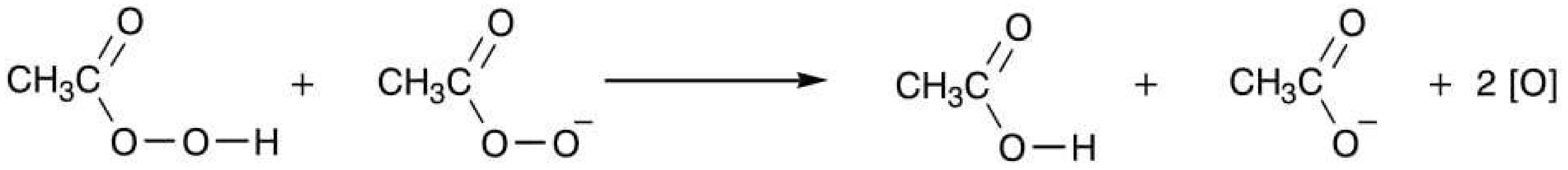
Pad-steam	
Hydrogen peroxide (35%)	5.16 ml/l
Sodium carbonate	6.36 g/l
TAED	3.42 g/l
Stabiliser	3 g/l
Wetting agent	2 g/l
Defoamer	1–2 drops
Pad to 100% liquor pick-up and steam for 30 min	
Cold pad–batch	
Hydrogen peroxide (35%)	8.6 ml/l
Sodium bicarbonate (10% w/v)	84 ml/l
TAED	5.7 g/l
Stabiliser	10 g/l
Wetting agent	4 g/l
Defoamer	1–2 drops
Pad to 100% liquor pick-up and batch for 2 hours at ambient temperature	



Scheme 10.30



Scheme 10.31



Scheme 10.32

Hypochlorite bleaching

As indicated in Table 10.12, bleaching with sodium hypochlorite is the most environmentally damaging of all bleaching processes with regard to AOX values. Consequently, despite the economical and technical benefits of this bleaching process, the use of hypochlorite will continue to decline and may even be banned in some countries.

The advantages of this bleaching agent include:

(1) economical attractiveness
(2) lower risk of catalytic fibre damage, although some chemical damage can occur depending on temperature and pH
(3) powerful bleaching action.

The disadvantages, in addition to the environmentally sensitive aspects already mentioned, include:

(1) hypochlorite bleaching does not compete effectively with the rapid peroxide bleaching process
(2) despite the intense whiteness that can be produced, hypochlorite bleached goods are prone to subsequent yellowing on storage
(3) the substrate must be scoured before hypochlorite bleaching
(4) many dyes and fluorescent brighteners are destroyed or degraded by hypochlorite bleaching
(5) stock solutions of sodium hypochlorite are unstable and must always be chemically analysed before use.

Sodium hypochlorite is commercially available as an alkaline solution, normally containing the equivalent of 12–14% available chlorine. However, this is so unstable that analytical testing of its strength is always necessary before use. Calcium hypochlorite (bleaching powder), stabilised by adding lime, has been used in the past but this product is no longer used in textile bleaching.

The mechanism of hypochlorite bleaching appears to be considerably less controversial than peroxide bleaching. The pH-related active species in sodium hypochlorite are shown in Figure 10.29 and Scheme 10.33. The pH range 9–11 is the most suitable for hypochlorite bleaching. The active bleaching species is the hypochlorite anion ClO^-. In fact bleaching can be accelerated by lowering the pH but the liberation of hypochlorous acid HClO dramatically increases damage to the fibre. This reaches a maximum at pH 6–8 and such processes have never been exploited commercially. Higher temperatures also increase the rate of bleaching and especially the extent of fibre damage, so that hypochlorite bleaching is usually carried out at ambient temperature for several hours. The effect on cellulose is mainly one of depolymerisation as a result of chain scission. Degradation includes the non-specific formation of a minor proportion of aldehyde, keto and carboxyl groups, the last-named predominating at the usual pH of bleaching (Figure 10.30). The formation of aldehyde groups, however, results in a tendency for the bleached fibre to yellow on storage. In the traditional process, the optimum pH of 10–11 is carefully controlled by addition of alkali, usually sodium carbonate. Typical bleach liquor formulations are given in Table 10.18.

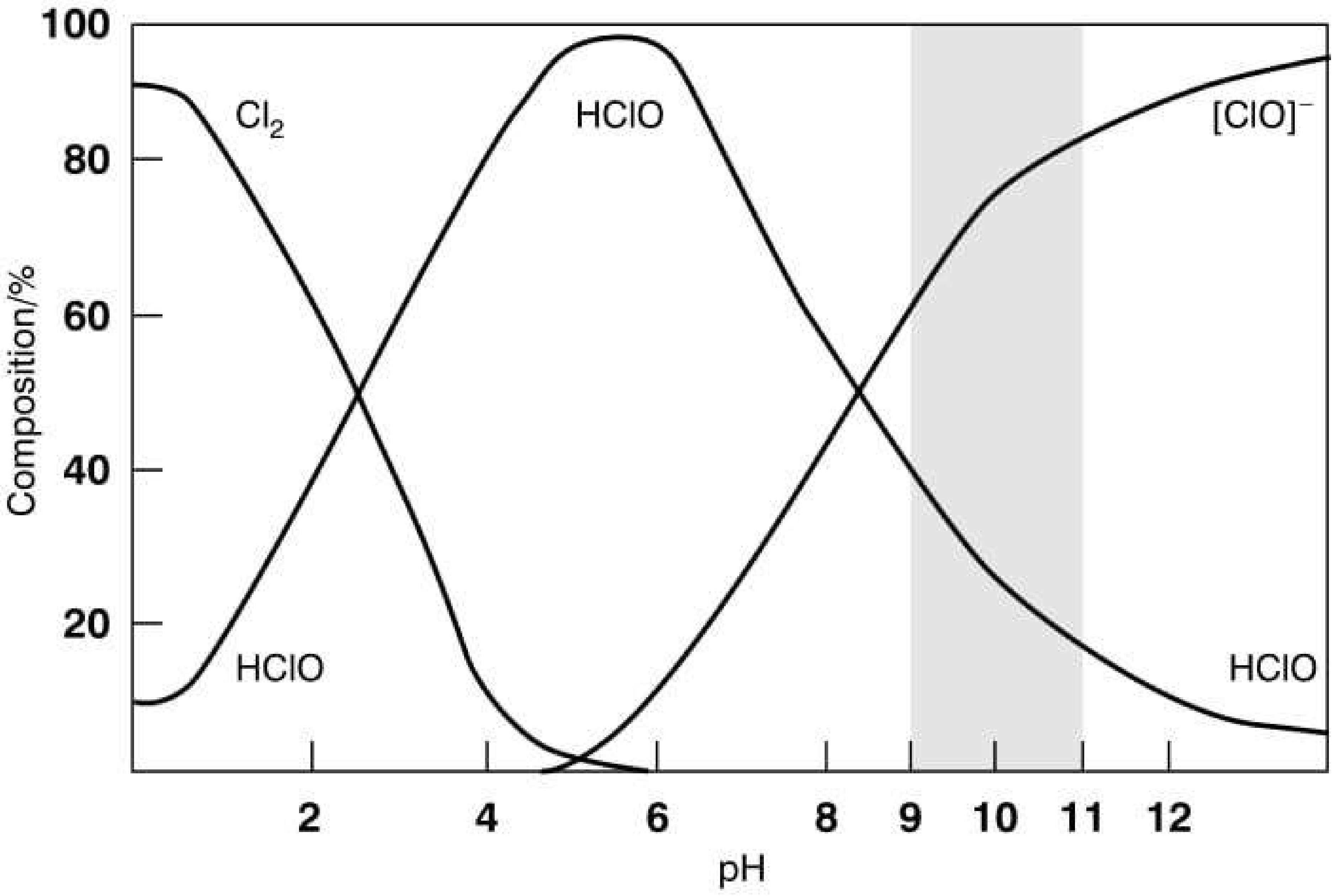


Figure 10.29 Effect of pH on the composition of sodium hypochlorite solutions [246]

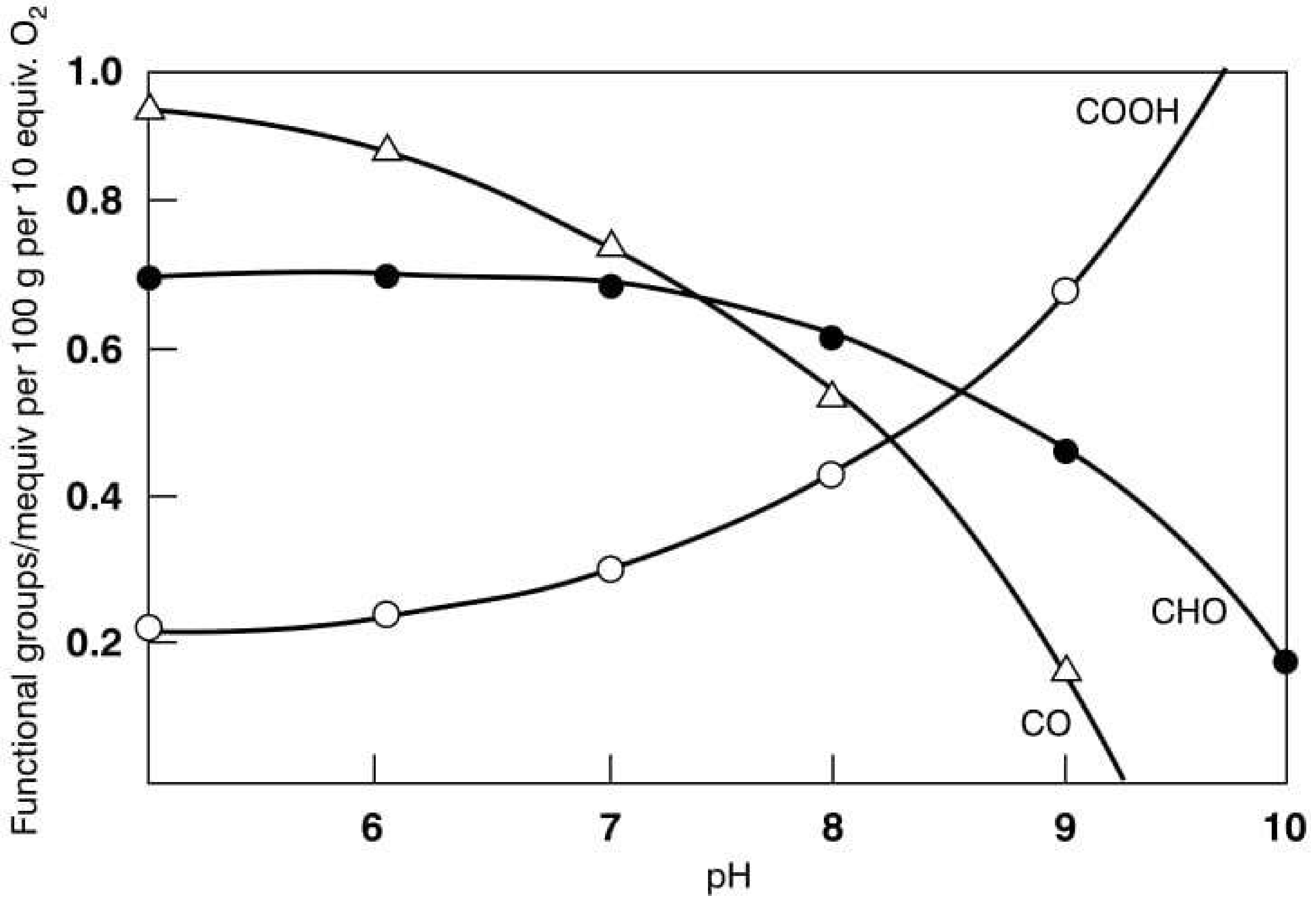
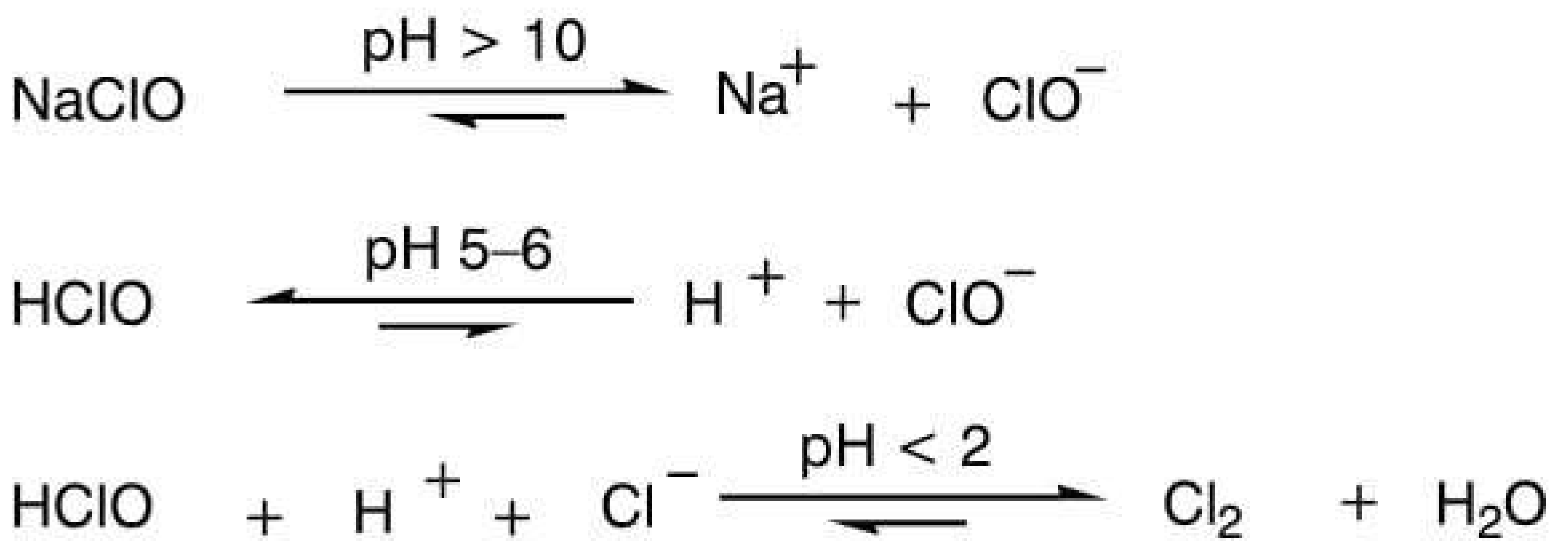


Figure 10.30 Functional groups formed by oxidising cotton cellulose with sodium hypochlorite over the pH range 5–10 [235]



$$\mathrm{NaClO} \xrightleftharpoons{\mathrm{pH} > 10} \mathrm{Na^+} + \mathrm{ClO^-}$$

$$\mathrm{HClO} \xrightleftharpoons{\mathrm{pH}\ 5\text{–}6} \mathrm{H^+} + \mathrm{ClO^-}$$

$$\mathrm{HClO} + \mathrm{H^+} + \mathrm{Cl^-} \xrightleftharpoons{\mathrm{pH} < 2} \mathrm{Cl_2} + \mathrm{H_2O}$$

Scheme 10.33

Table 10.18 Recommended conditions for hypochlorite bleaching [143]

	Cistern	Jig	Winch	Package machine	J-box conveyor
Available Cl_2 (g/l)	2–4	2–4	1–2	1–2	2–5
Sodium carbonate (g/l)	2–4	2–4	1–2	1–2	2–4
Treatment time (h)	3–4	1–2	1–2	1–2	1–2

Despite its technical usefulness, hypochlorite bleaching faces severe environmental pressures because it yields AOX values well in excess of permitted levels. The AOX value observed increases with the active chlorine content of the bleach liquor (Figure 10.31) and with the time of treatment (Figure 10.32).

The state of the substrate, including the source of the cotton and its degree of purity, has a major influence on the AOX value. It has been shown [247] that under similar bleaching conditions pure cotton cellulose gives an AOX value of 8–9 ppm, scoured or desized cottons give intermediate values of 13–60 ppm and raw cotton 70 ppm or higher. Although pure cellulose already gives a measurable AOX value, much higher values arise from impurities in cotton. The concentration of hypochlorite applied and the treatment time can scarcely be

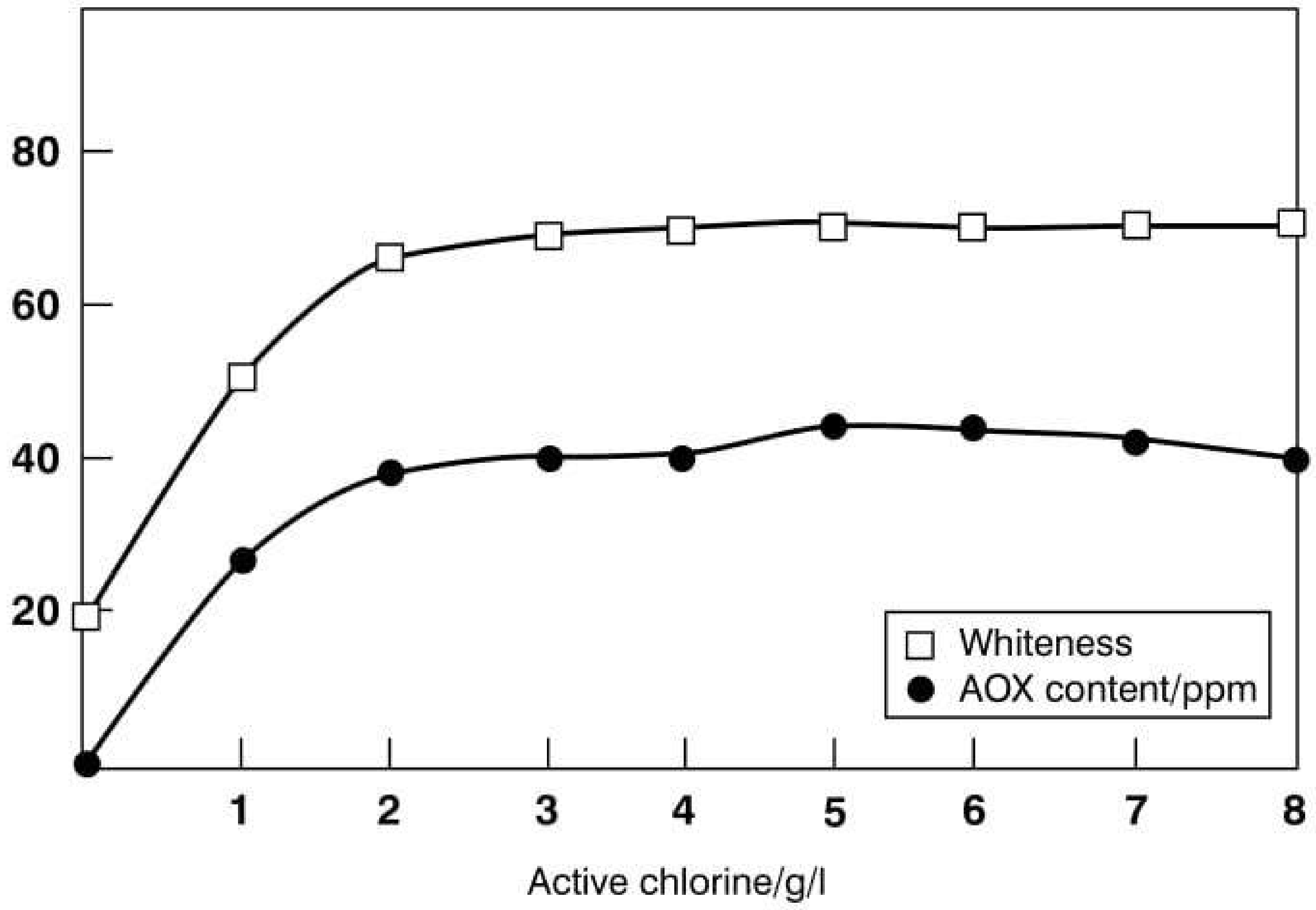


Figure 10.31 Influence of active chlorine concentration on AOX content and whiteness [247]

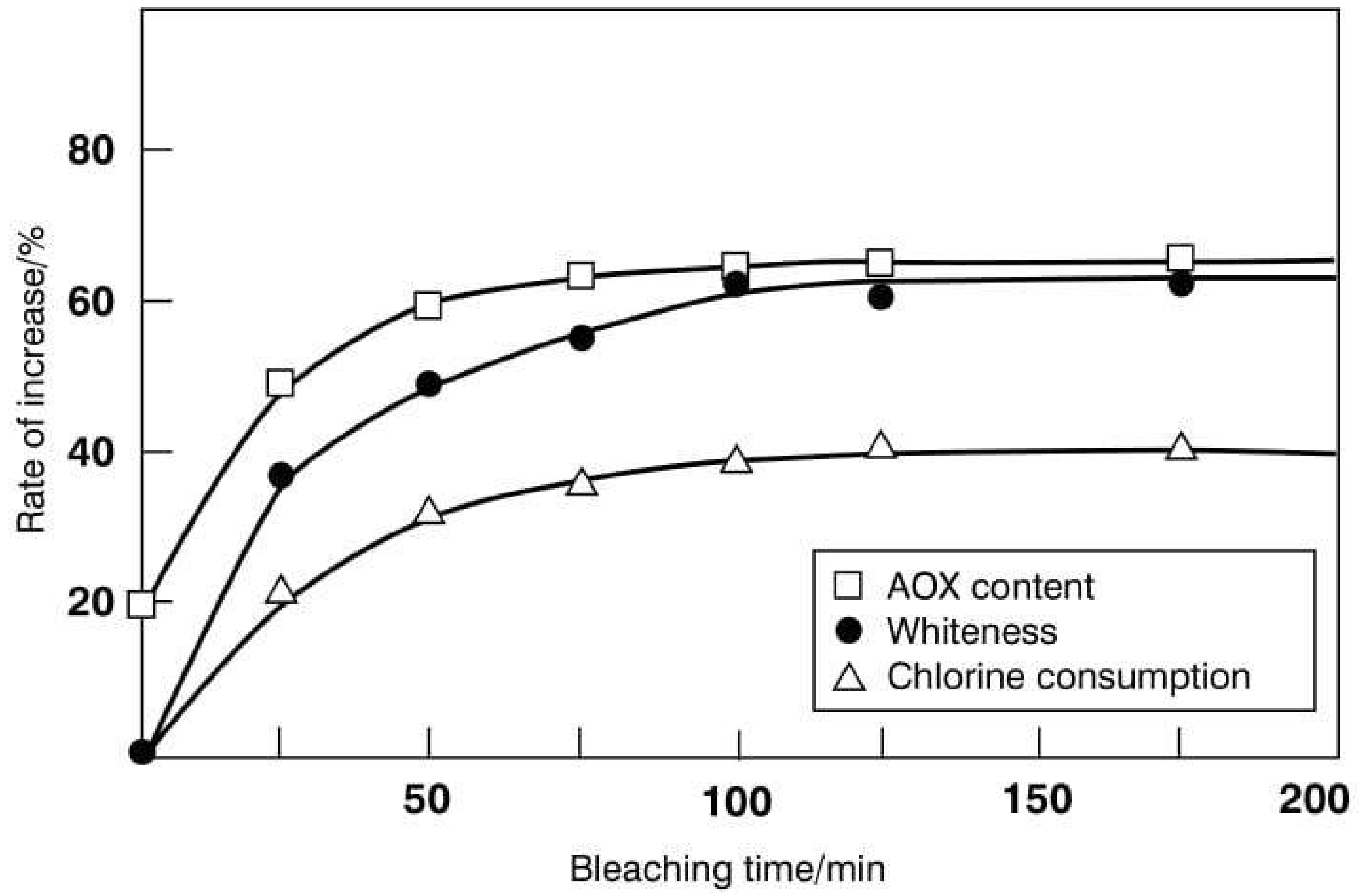


Figure 10.32 Rates of increase of whiteness, AOX content and chlorine consumption with time of bleaching [247]

varied widely in practice, since they have been adjusted already to minimum values determined by the degree of whiteness required and the economy of the process [222]. This implies that attempts to reduce the AOX value must concentrate on removing impurities as much as possible during the pretreatments (scouring, desizing and washing-off) before hypochlorite bleaching [222,247,248].

The purification of cotton can be improved considerably by pretreatment with hydrogen peroxide and this gives even lower AOX values after hypochlorite bleaching [222]. This double bleaching, however, considerably increases process and chemical costs and demands additional processing capacity. Würster and Conzelmann [222] have estimated that such measures can lead to a reduction in pollution levels by about 70% at justifiable cost, offering the possibility of bleaching cotton with hypochlorite without exceeding permissible AOX loading of the effluent. Nevertheless, it seems inevitable that hypochlorite bleaching will continue to decline on environmental grounds.

After bleaching with hypochlorite it is always necessary to remove or inactivate any residual chlorine present. The importance of this is highlighted by the fact that the concentration of undissociated hypochlorous acid reaches a maximum at pH 6, giving the greatest risk of damage to the fibre. Hence it is essential to avoid lowering the pH to neutral during washing off before an antichlor treatment has been given. The traditional antichlors have been sodium bisulphite, or less often the sulphite or dithionite, but the current trend is to use hydrogen peroxide (Scheme 10.34) on environmental grounds [143].

$$\mathrm{ClO^-} + \mathrm{HSO_3^-} \longrightarrow \mathrm{Cl^-} + \mathrm{HSO_4^-}$$

$$\mathrm{ClO^-} + \mathrm{H_2O_2} \longrightarrow \mathrm{Cl^-} + \mathrm{H_2O} + \mathrm{O_2}$$

Scheme 10.34

Chlorite bleaching

Sodium chlorite is commercially available as an alkaline powder (80%) or as an alkaline liquid (26%) of specific gravity 1.25. As indicated in Table 10.12, chlorite gives considerably lower AOX values than hypochlorite, although not as low as peroxide. Bleaching with chlorite differs significantly from peroxide or hypochlorite bleaching, as it is generally carried out under acidic conditions. The general advantages of chlorite bleaching include:

(1) no need for special cleaning treatments before bleaching, although such preparation does give rise to lower AOX values
(2) the risk of chemical damage is low
(3) minimal scouring action of the acidic bleach results in lower weight losses
(4) softer handle and good sewability due to low degree of removal of fats and waxes
(5) this oxidising bleach is the least sensitive to accelerated damage by metallic contamination
(6) washing off is easier than with alternative bleaching agents
(7) useful for synthetic fibres and particularly important for acrylic fibres.

The disadvantages include:

(1) toxic and unpleasant chlorine dioxide vapour can be liberated
(2) acidic chlorite solutions are highly corrosive and thus demand highly specialised and expensive equipment
(3) no rapid chlorite bleaching process is available
(4) residual fats and waxes can be advantageous (see above), but they can also be disadvantageous by giving lower absorbency
(5) many dyes and fluorescent brighteners are destroyed or degraded by chlorite bleaching.

As with hypochlorite, the mechanism of chlorite bleaching does not appear to be controversial. The pH-related active species in sodium chlorite solution are shown in Figure 10.33. Initially, sodium chlorite hydrolyses in solution, as indicated in Scheme 10.35. Chlorous acid, however, dissociates in water to a limited extent only. Acidic or acid-releasing agents, sometimes referred to as activators, are needed to lower the pH and raise the concentration of chlorous acid to a level suitable for bleaching. However, as demonstrated in Figure 10.33, the reactions in solution are complex. Evidently the chlorite anions formed undergo the various reactions shown in Scheme 10.36, producing chlorine dioxide vapour (ClO_2), chlorate anions (ClO_3^-), chloride anions (Cl^-) and oxygen. Figure 10.34 illustrates the amounts of chlorite anions, chlorine dioxide, chlorate anions (which have no bleaching action) and oxygen produced at various pH values from a sodium chlorite solution (1 g/l) after 1 hour at 95 °C in a stream of nitrogen [235]. This demonstrates very clearly that decomposition according to Scheme 10.36 is very slow at pH 5 and almost ceases above pH 6. Below pH 5 the decomposition products are mainly chlorine dioxide and chlorate anions. Oxygen accounts for less than 5% of the products formed by decomposition.

The rate of chlorite bleaching increases as pH decreases, but only between pH 2 and 9 is the rate proportional to the concentration of chlorous acid present in solution. At low pH values, evolution of the noxious and corrosive gas chlorine dioxide increases. In practice it is necessary to keep the pH above 3 in order to minimise the formation of chlorine dioxide. It is necessary to monitor the pH during chlorite bleaching because acid is liberated by the

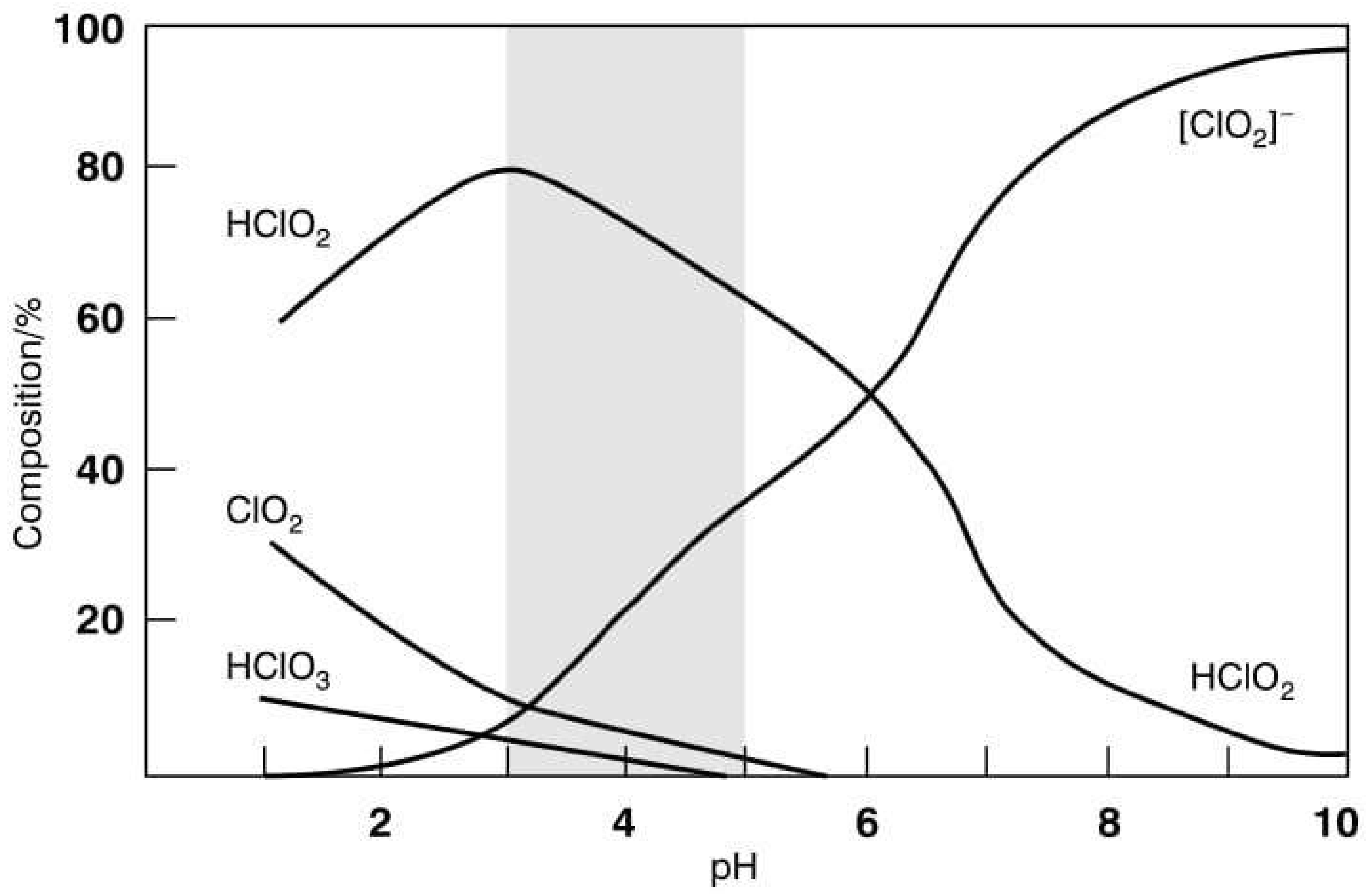


Figure 10.33 Effect of pH on the composition of sodium chlorite solutions [249]

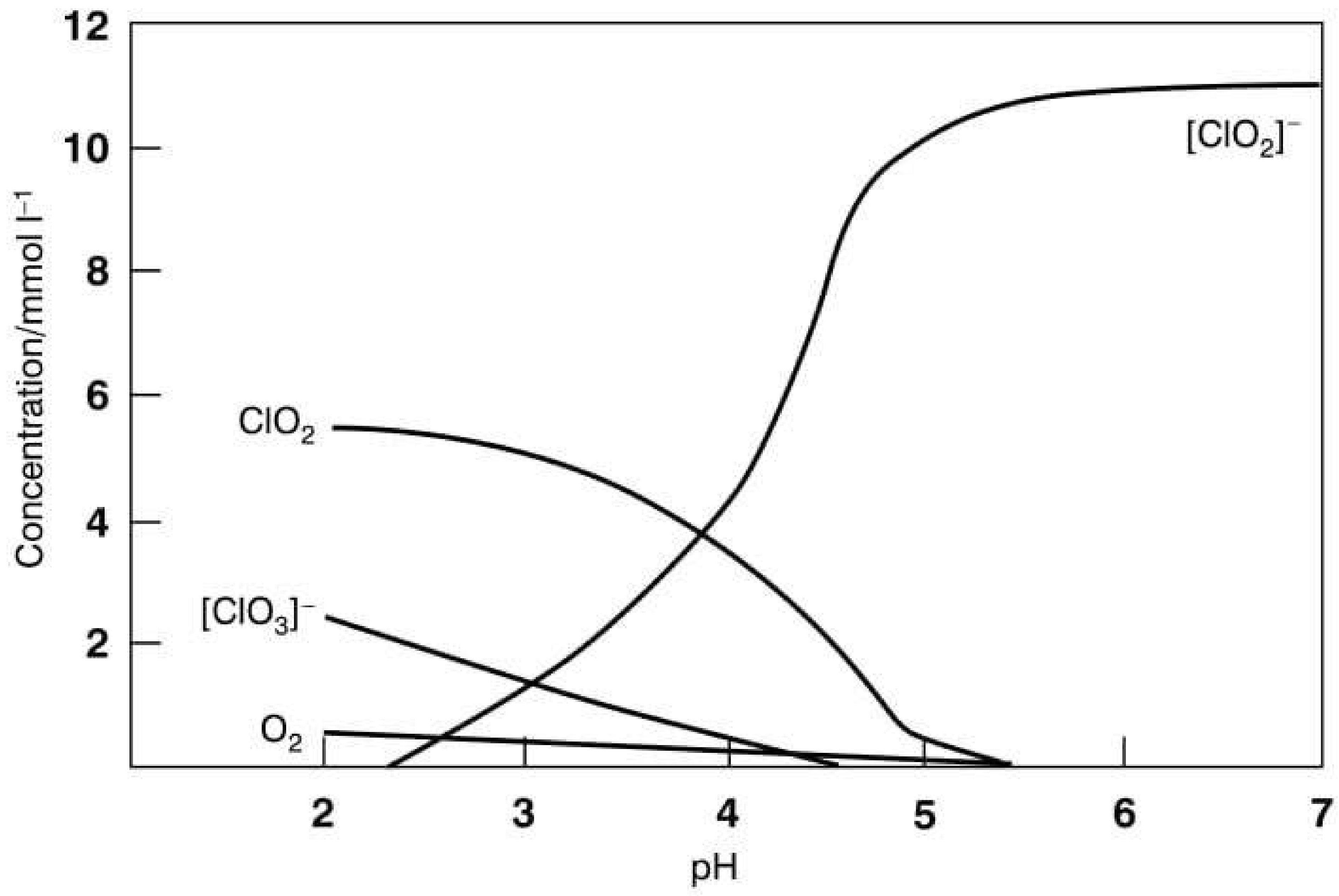


Figure 10.34 Decomposition of sodium chlorite solution as a function of pH [235]

$$\underset{\text{Sodium chlorite}}{NaClO_2} + H_2O \rightleftharpoons NaOH + \underset{\text{Chlorous acid}}{HClO_2}$$

Scheme 10.35

$$5\ ClO_2^- + 2\,H^+ \longrightarrow 4\ ClO_2 + Cl^- + 2\ HO^-$$

$$3\ ClO_2^- \longrightarrow 2\ ClO_3^- + Cl^-$$

$$ClO_2^- \longrightarrow Cl^- + 2\,[O]$$

Scheme 10.36

reactions, creating a need for careful adjustment or compensation. Bleaching is generally carried out at about pH 4. In some processes, particularly continuous or short liquor methods, this pH shift is allowed for by setting the initial pH somewhat higher (pH 4.5–6.5). Sodium nitrate is sometimes added to inhibit corrosion of stainless steel vessels to some extent. Sodium dihydrogen phosphate is a useful pH buffer able to act as an activator for sodium chlorite to improve the bleaching performance. Table 10.19 gives some typical processing conditions.

Table 10.19 Recommended conditions for chlorite bleaching [143]

Additives (g/l)	Cistern	Jig	Winch or jet	Package machine	J-box conveyor	Cold bleach
Sodium chlorite (80%)	2–4	2–6	1–3	2–4	20	20–25
Sodium dihydrogen phosphate	0.5–2	0.5–2	1	0.5–1		
Sodium nitrate		1–2	1–3	1–2		
pH	3.8–4.2	3.8–4.2	3.8–4.2	3.8–4.2	6–6.5	6–6.5
Temperature (°C)	80–85	80–85	80	80	80–85	20
Time (h)	3–4	1–2	1–2	1–2	1–4	16–18

Aftertreatment with detergent (2–5 g/l) and sodium carbonate (2–5 g/l) often enhances whiteness and may improve fabric absorbency, particularly if the goods have not been scoured before bleaching. Antichlor treatment is unnecessary for white goods but may be required before coloration. A convenient antichlor treatment involves combining the detergent aftertreatment with sodium perborate, percarbonate or thiosulphate [143]. Traditional reductive antichlors such as sodium bisulphite are not recommended, since their residues can be just as troublesome as chlorite residues.

Under optimum bleaching conditions, chlorite does not degrade cellulose but degradation can occur from excessive oxidant concentration, prolonged treatment time or non-optimum pH conditions, the main effect being depolymerisation. Formation of some aldehyde groups is suspected, since the bleached goods can be susceptible to yellowing on storage.

The popularity of chlorite bleaching has always been restricted by the toxic and highly corrosive nature of chlorine dioxide, which even attacks stainless steel. Hence equipment costs for chlorite bleaching are high. Environmental aspects, in particular AOX values and the toxicity of chlorine dioxide, will increasingly mitigate against the process in future. As already noted (Table 10.12), chlorite bleaching reaches a significant AOX level, although this is only about one-tenth of that produced by hypochlorite bleaching of the same sample. It should also be borne in mind that chlorite bleaching is recommended for some synthetic fibres as well as cellulosics. Kleber [224] considers that consent levels for AOX can easily be met in practice and that chlorite bleaching will continue.

It is important to examine the influence of impurities or additives, such as sizes and lubricants, since these are often prime sources of higher AOX values rather than the substrate itself. It is equally important to assess the contribution of auxiliaries in the bleaching bath to the total AOX value. Kleber [224] has reported several studies of systems requiring compliance with an AOX consent of 3 ppm. Table 10.20 shows that: (a) synthetic

Table 10.20 Effect of surfactant addition on AOX values after chlorite bleaching of synthetic fibres [224]

	AOX value (ppm) after chlorite bleaching	
Fibre	Without surfactant	With surfactant
Polyester	0.6	2.8
Polyamide	0.6	2.6
Acrylic	1.2	2.8

fibres are negligible contributors to AOX values; and (b) the inappropriate choice of an auxiliary (in this case a surfactant) can have an adverse effect. Similarly, the fibre manufacturer's yarn finish may have a positive or negative influence on the AOX value. Thus careful attention should be given to all yarn additives and to the auxiliaries used in bleaching.

The possible benefits of prescouring to remove such contaminants should also be considered. Alkaline pretreatments, including boiling off of cotton, have a profound effect on AOX values after chlorite bleaching (Tables 10.21 and 10.22). It can be beneficial, from the viewpoint of both AOX and whiteness, to follow a chlorite bleach with a peroxide treatment. Linen yarns after an alkaline scour and chlorite bleach gave a whiteness value of 63.9 with an unacceptably high AOX value of 8.0 ppm. These results were improved to 78.5 and 1.2 ppm respectively after peroxide treatment [224].

Peracetic acid bleaching

In traditional peroxide bleaching, hydrogen peroxide is activated by alkali. Acids, both inorganic and organic, can also be used to activate peroxide by the formation of a peracid. Peracids can be effective oxidative bleaching agents and, at least potentially, offer an alternative to the environmentally sensitive chlorine bleaches. Although known for quite

Table 10.21 Effect of washing on AOX and whiteness values before and after chlorite bleaching [224]

Substrate		Residual fat (%)	AOX (ppm)	Whiteness (460 nm) Before bleach	Whiteness (460 nm) After bleach
Cotton:	untreated		3.8	54.6	81.3
	washed	2.2	2.4	61.5	87.7
Viscose:	untreated		6.2	68.7	81.1
	washed	0.1	2.8	72.0	84.1
Nylon:	untreated		2.6	82.3	80.6
	washed	0.9	1.2	81.6	84.9
Acrylic:	untreated		2.8	70.9	75.5
	washed	0.7	1.5	72.5	78.5

Table 10.22 Effect of desize and boil-off of cotton on AOX and whiteness values before and after chlorite bleaching [224]

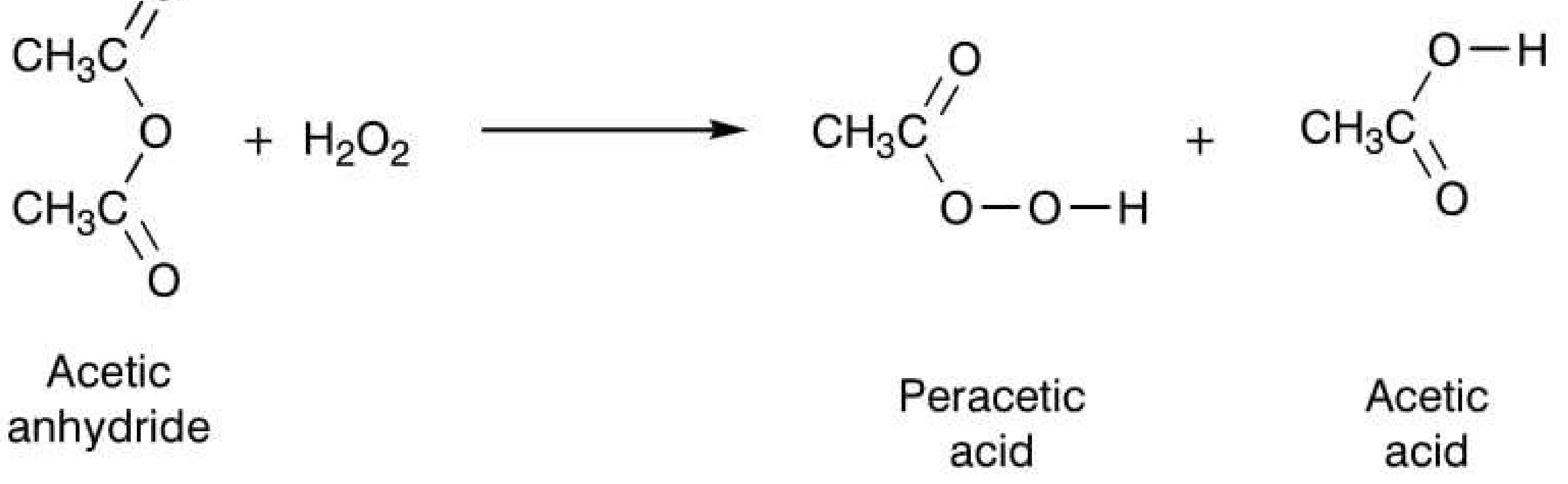
Pretreatment	AOX (ppm)	Whiteness (460 nm)		Chlorite consumption
		Before bleach	After bleach	
Bleach only	4.4	58.0	87.9	51.4
Desize* and bleach	7.2	61.2	89.1	57.3
Desize*, boil-off & bleach	2.8	62.7	89.9	55.0

* Starch sized and enzyme desized

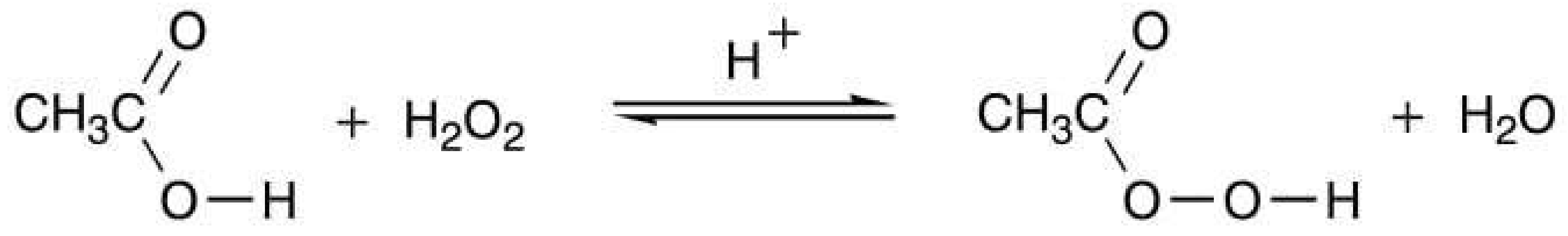
some time, they have not achieved much use in practice, mainly because of their high cost and difficulties in preparing and handling them. Recent environmental concerns, however, have revived interest in their potential. Comparison with chlorine bleaches is one aspect often highlighted, but ultimately they will have to compete both technically and economically with peroxide bleaching. Peracetic acid is undoubtedly the peracid of greatest interest for textile bleaching, although persulphate and others have also been evaluated.

Peracetic acid is produced in equilibrium with acetic acid by the reaction of acetic anhydride with hydrogen peroxide, as in Scheme 10.37. Alternatively, peracetic acid can be produced by acid-catalysed oxidation of acetic acid with hydrogen peroxide, as in Scheme 10.38. Characteristic of a peracid is the perhydroxide anion (H–O–O$^-$), or in some instances the peroxo dianion ($^-$O–O$^-$). Originally, the bleacher had a choice of using either commercial peracetic acid (as a 38% solution) or preparing the peracetic acid *in situ* using acetic anhydride as in Scheme 10.37. The 38% peracetic acid solution has a pungent odour, attacks human skin and is highly inflammable; it requires special transport and storage facilities. Preparation of the peracid *in situ* is both hazardous and unpleasant, as it requires the handling and storage of acetic anhydride. One part of peroxide is reacted with six parts of anhydride for 4 hours at ambient temperature to give 80% yield [244,250,251], during which the explosive diacetyl peroxide may also be formed as a by-product, as in Scheme 10.39. Thus, although peracetic acid is environmentally friendly, hydrolysing to acetic acid and oxygen, its manufacture and use do pose quite severe hazards. Hence it is hardly surprising that it has been used only rarely.

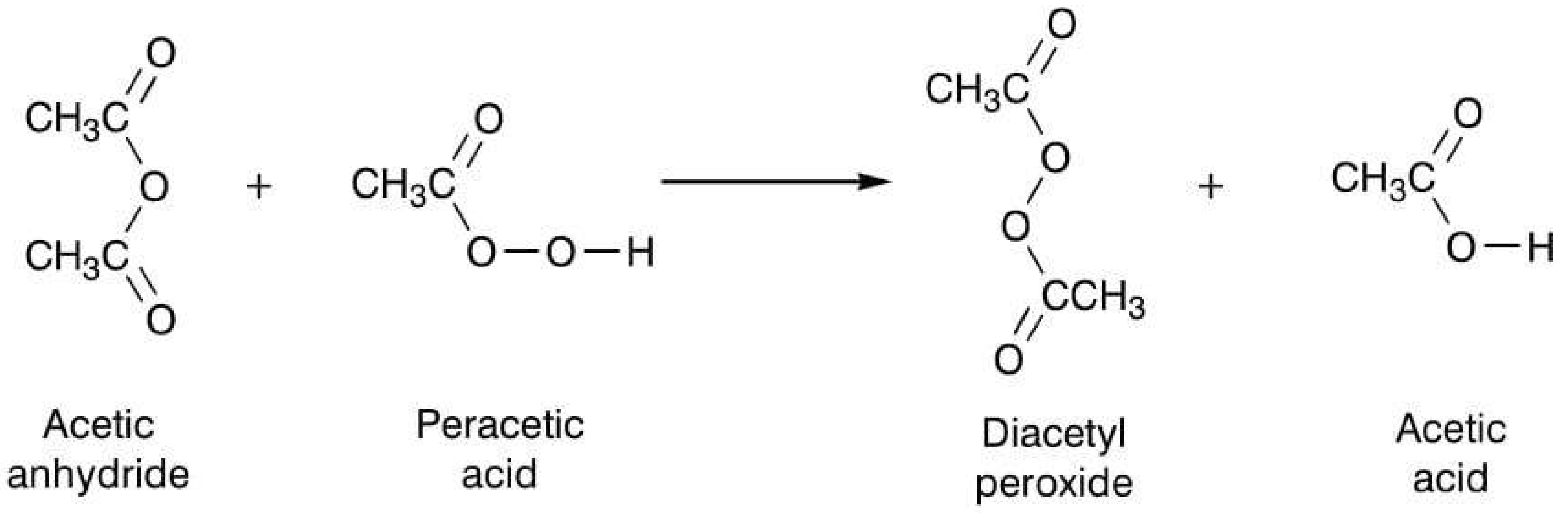
More recently, manufacturers have introduced safer versions containing only 12–15% active material [225]. Typical formulations of these so-called equilibrium mixtures are given in Table 10.23, together with their flash points [251–253]. Although these lower-strength



Scheme 10.37



Scheme 10.38

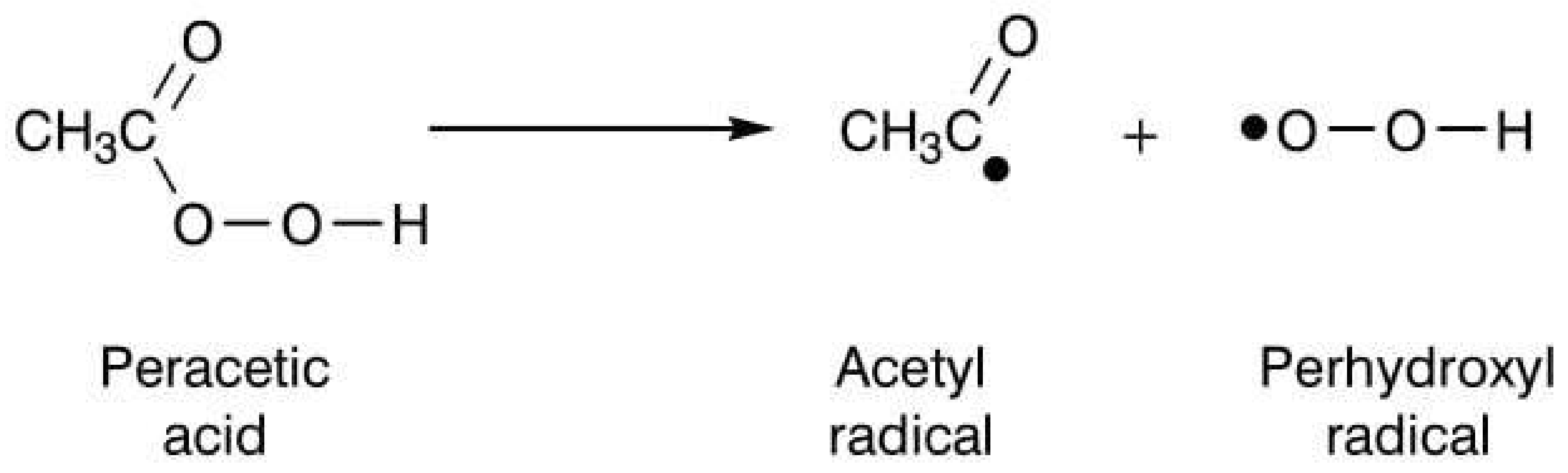


Scheme 10.39

Table 10.23 Typical formulations of lower-strength peracetic acid equilibrium mixtures

Peracetic acid	35–38%	15%	5%
Hydrogen peroxide	7%	23%	27%
Acetic acid	39%	16%	6%
Flash point (°C)	62	96	97

The remainder of these formulations consists of water, catalyst (e.g. sulphuric acid) and stabiliser



Scheme 10.40

mixtures are less hazardous than the 38–40% strength, they still pose problems in use. Oral ingestion, inhalation or contact with skin or mucous membranes leads to strong and sustained cauterising or burning and eczema that is difficult to heal [254]. They are quite stable when correctly stored but should not be stored in enclosed vessels or pipework, nor in contact with catalysing metals: ventilated containers of stainless steel or aluminium of at least 99.5% purity are suitable [254]. These hazard constraints are likely to continue to restrict the use of peracetic acid in comparison with relatively hazard-free peroxide.

Bleaching is thought to take place through the perhydroxyl free radical (Scheme 10.40) [223]. Various attempts have been made over the last decade to elucidate the mechanism and demonstrate the potential of peracetic acid in bleaching. Temperature and pH are critical parameters with regard to the rate and degree of bleaching on the one hand and the extent of fibre damage on the other. It is difficult, however, to be dogmatic about these effects since the published results (and conclusions!) show variability because of the different conditions and substrates selected by the researchers.

Examination of the influence of pH is complicated by the fact that the bleaching reaction lowers the pH due to the liberation of acetic acid [254]. Hence the results are affected by whether this effect is counteracted by the use of a buffer. It has been pointed out that this pH shift increases with the content of bleachable material present [254]. In theory, optimal bleaching should take place at pH 8.2, which corresponds to the pK value of peracetic acid [253]. The results in Table 10.24 have been obtained on knitted cotton bleached for 30 minutes at 60 °C with 2.5 g/l peracetic acid, the original degree of polymerisation of the cotton cellulose being about 2600. An investigation on linen [254] revealed no bleaching under acidic conditions. Whiteness reached a maximum at pH 7–8 but there was no increase beyond pH 8 as the peracetic acid decomposed to give acetic acid solution. Likewise, pH 8 has been recommended for the bleaching of cotton/acrylic blends with 2–10 g/l peracetic acid at 75 °C in the presence of a phosphate buffer [252]. Conversely, pH 3–6 has been indicated for the bleaching of nylon carpets with 1–5 g/l peracetic acid for 15–45 minutes at 60–70 °C [252]. Somewhat conflicting results [255] have been obtained on a starch-sized cotton fabric using 1% peracetic acid for 30 minutes at 75 °C and a long liquor ratio (Figure 10.35).

Table 10.24 Effect of the pH of peracetic acid bleaching on the brightness and degree of polymerisation of cotton cellulose [251,253]

pH	Brightness value	Degree of polymerisation
3	37	2650
5	43	2720
7	62	2630
9	65	2430

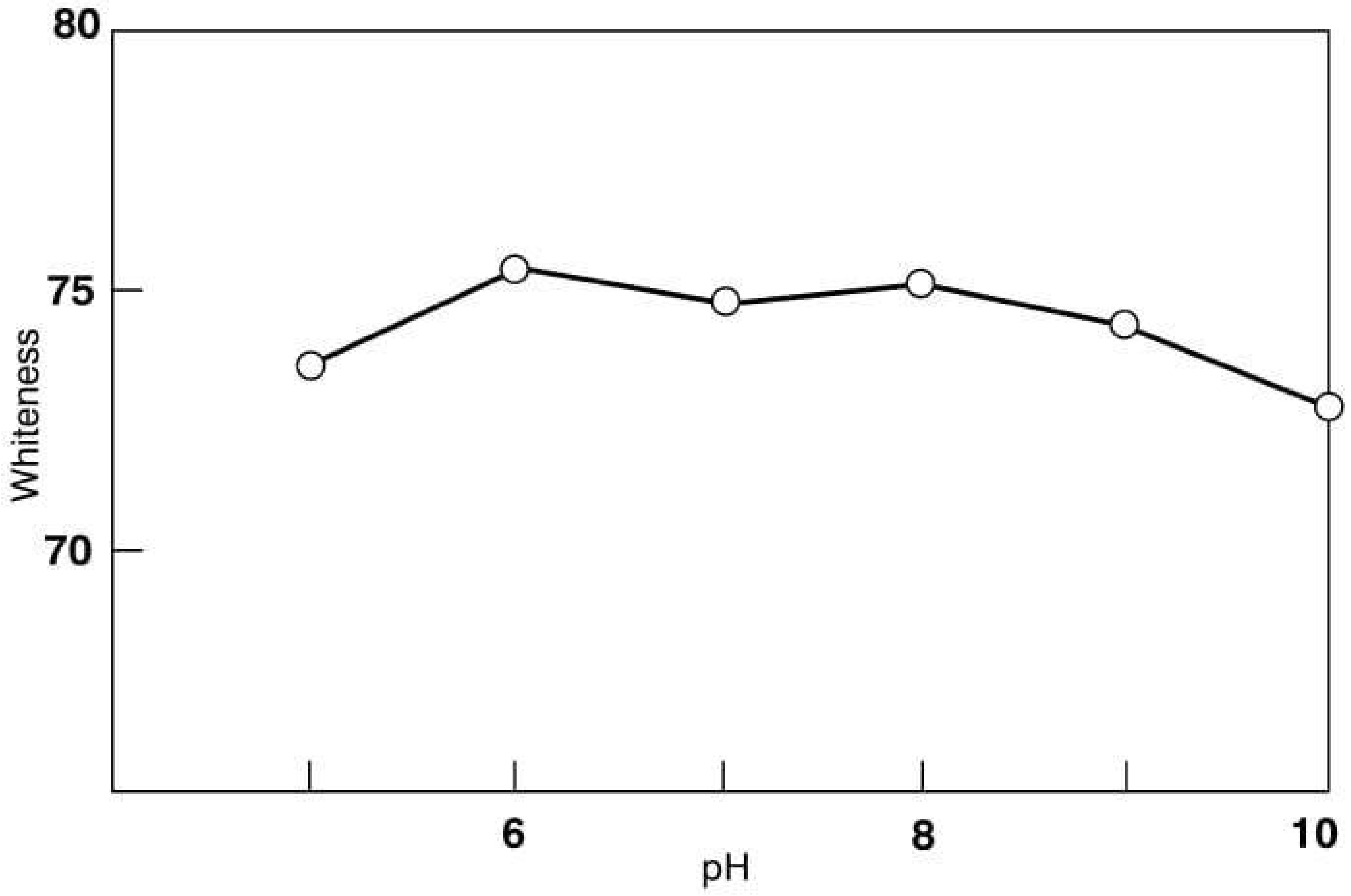


Figure 10.35 Effect of pH on the whiteness of starch-sized cotton fabric in a one-stage pretreatment with peracetic acid at a long liquor ratio [255]

As indicated in Table 10.25, markedly different effects can be obtained at alkaline pH values depending on whether sodium hydroxide or sodium carbonate is used to obtain the required pH [256]. These results were obtained on desized and scoured cotton bleached with 1% peracetic acid for 1 hour at 50 °C and 50:1 liquor ratio. It is evident that fibre damage was much higher in the region of the pK value of peracetic acid when sodium carbonate was used compared with sodium hydroxide. Sodium carbonate resulted in more rapid decomposition of peracetic acid above pH 6, although this was not accompanied by increased formation of the species active in bleaching, both alkalis giving virtually the same degree of whiteness for a given pH. The optimum conditions in most cases are found at pH 6–7.

Table 10.25 Effect of alkali used with peracetic acid at various pH values on the degree of polymerisation of cotton cellulose [256]

pH	Alkali:	Degree of polymerisation Na_2CO_3	Degree of polymerisation NaOH
4		2750	2780
5		2800	2550
6		2850	2550
7		2680	2720
8		1850	2760
9		1350	2800

Table 10.26 Effect of temperature of peracetic acid bleaching on the brightness and degree of polymerisation of cotton cellulose [251,253]

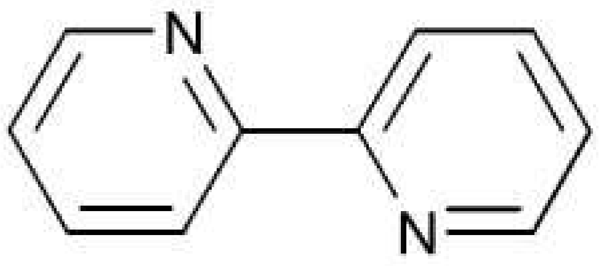
Temperature (°C)	Brightness value	Degree of polymerisation
20	38	2650
40	44	2600
60	60	2550
80	66	2500

The effects of temperature are shown in Table 10.26 for the bleaching of knitted cotton for 30 minutes at pH 6–7 with 2.5 g/l peracetic acid, the original degree of polymerisation being about 2600 [251,253]. Thus both whiteness and fibre damage increase progressively with bleaching temperature. In practice it is desirable to avoid excessive treatment temperatures, the preferred range being 50–80 °C [251,253]. At higher temperatures a pungent vapour is evolved.

Under optimum conditions of pH and temperature, a treatment time of 20–60 minutes is generally adequate. The degree of whiteness increases with increasing concentration of peracetic acid. The optimum concentration is dependent on the type of process and substrate, but relatively high concentrations of peracetic acid have little effect on the degree of polymerisation. For example, increasing the oxidant concentration from 1.75 to 8.75 g/l improved whiteness by about 25%, whilst the degree of polymerisation was lowered by only about 9% [253]. This is in marked contrast to bleaching with sodium hypochlorite. Tests with 100 mg/l iron showed that this transition metal has no significant influence on whiteness or fibre damage [253] under otherwise optimum conditions. The addition of a surfactant can improve wettability and penetration. Indeed, this may exert more influence on whiteness than raising the treatment temperature [256].

In the context of peracid bleaching it is worthwhile recalling the reaction outlined in Scheme 10.30, in which peracetic acid is produced *in situ* by the action of the activator tetra-acetylethylenediamine (10.86) on hydrogen peroxide [244].

Peracetic acid bleaching is not widely practiced, so it is not possible to give typical formulations and conditions. However, various process recommendations have been given [251–256]. It has been demonstrated that peracetic acid bleaching combined with ultrasonic treatment gave higher whiteness values and less fibre damage than conventional bleaching with peroxide [257]. Low temperature bleaching with peracetic acid at 30 °C, catalysed by incorporation of 2,2′-bipyridyl (10.89) in an alkyl sulphate surfactant, has been proposed [258].



10.89
2,2′-Bipyridyl

Combined bleaching processes

Combinations of more than one bleaching process can be beneficial. The sequence of a hypochlorite bleach followed by a peroxide bleach is common: the second stage can considerably reduce the AOX value imparted by the preceding hypochlorite treatment. It has also been suggested that the sodium hypochlorite in this two-stage sequence can effectively be replaced by peracetic acid, lowering the AOX values even further. A review of combined bleaching processes for weftknit cotton fabrics is available [225].

Monitoring bleaching processes

Accurate monitoring of bleaching processes is essential for efficiency, economy and protection of the environment. The importance of checking raw materials, including the substrate, should be obvious. There is also a need to monitor the actual process liquors and to evaluate the results obtained on the substrate. A useful account of such procedures is available [143].

Bleaching from the viewpoint of fibre type

Most cotton is bleached with peroxide, by far the greater proportion by continuous methods. Synthetic fibres seldom require bleaching, but where it is necessary either peroxide or chlorite bleaches are recommended. Most regenerated cellulosic fabrics are only bleached for fluorescent whites and pastel shades. Any of the three oxidative bleaches may be used [143]. Peroxide bleaching requires 5–15 g/l hydrogen peroxide (35%) at 80–100 °C, depending on the type of machinery selected, together with sequestrant, caustic soda and stabiliser for the peroxide. Chlorite bleaching on the winch requires 0.5–1.5 g/l sodium chlorite (80%) at pH 4, treatment conditions being 45–90 minutes at 90–95 °C. Peracetic acid (3 g/l) treatment for 60 minutes at 65 °C and pH 7 in the presence of sodium hexametaphosphate is also suitable.

Wool bleaching

Wool poses special problems, although only approximately 1.5% of the world production of wool is bleached directly. However, an unknown amount of so-called 'top-up' bleaching also takes place, usually by adding hydrogen peroxide to the last bowl of the scouring process. Reviews of wool bleaching, which includes oxidation, reduction and sequential oxidation–reduction processes, are available [11,259,260]. A particular problem with wool lies not so much in its initial natural colour as in its tendency to show yellowing under the influence of light, dry heat or wet alkaline treatments. It is particularly important to realise that bleaching often exacerbates this problem. The complex chemical mechanisms involved in the yellowing of wool have been reviewed in detail [259] and will not be discussed further here.

Oxidative bleaching of wool is invariably carried out with hydrogen peroxide. The active species involved is likely to be the same as on cellulosic substrates but specific reactions with wool amino acid residues must be considered. The primary reaction is oxidation of cystine disulphide bonds leading to the formation of cysteic acid residues (Scheme 10.41). The rupture of disulphide crosslinks, with attendant increase in urea-bisulphite and alkali solubility values, adversely affects fibre properties. As the severity of bleaching conditions increases, the urea-bisulphite solubility remains little changed but the relationships between alkali solubility and cysteic acid (Figure 10.36) and between cystine and cysteic acid (Figure 10.37) are almost linear [259,261,262]. Tyrosine, tryptophan and methionine residues are oxidised by hydrogen peroxide [259]. In order to retain commercially acceptable fibre properties, the alkali solubility of bleached wool should not exceed 30% [259,263]. The degree of attack on the fibre depends on the nature of the wool itself. Chlorinated wool is more sensitive than untreated wool but Hercosett-treated wool is less sensitive (see Figure 10.38) [259,264].

As with cellulosic fibres, the bleaching of wool with peroxide requires careful optimisation of several parameters: peroxide concentration, pH, temperature, treatment time, choice and concentration of stabiliser and possibly choice and concentration of activator. A typical formulation for batchwise bleaching of wool is given in Table 10.27. Sodium pyrophosphate (10.16) or tripolyphosphate (10.17) are generally the stabilisers of choice but silicates can also be used. Bleaching for two hours at 50–60 °C and pH 8.5–9 is common, although in some cases careful optimisation can reduce the time to one hour [11]. Alkaline conditions are appropriate for cellulosic bleaching but may cause quite severe damage with wool and thus careful control is necessary. Alternatively, acidic conditions (pH 5 at 80 °C) can be chosen, using a suitable peroxide activator to produce a peracid.

Only 15–25% of the hydrogen peroxide present is consumed in a typical bleaching process. In order to minimise wastage, some bleachers reuse liquors several times, replenishing the bath with fresh peroxide after determining the deficit by titration. The number of batches that can be bleached in the same replenished liquor is limited by discoloration of the bath by impurities desorbed from the wool [259]. There is a further economic benefit in that the peroxide replenishment decreases with each successive batch (Figure 10.39), possibly because of the build-up in the bath of soluble proteins, which have a stabilising effect.

$$—CH_2—S—S—CH_2— \xrightarrow[HO^-]{H_2O_2} —CH_2—SO_3H \quad + \quad HO_3S—CH_2—$$

Cystine

Cysteic acid

Scheme 10.41

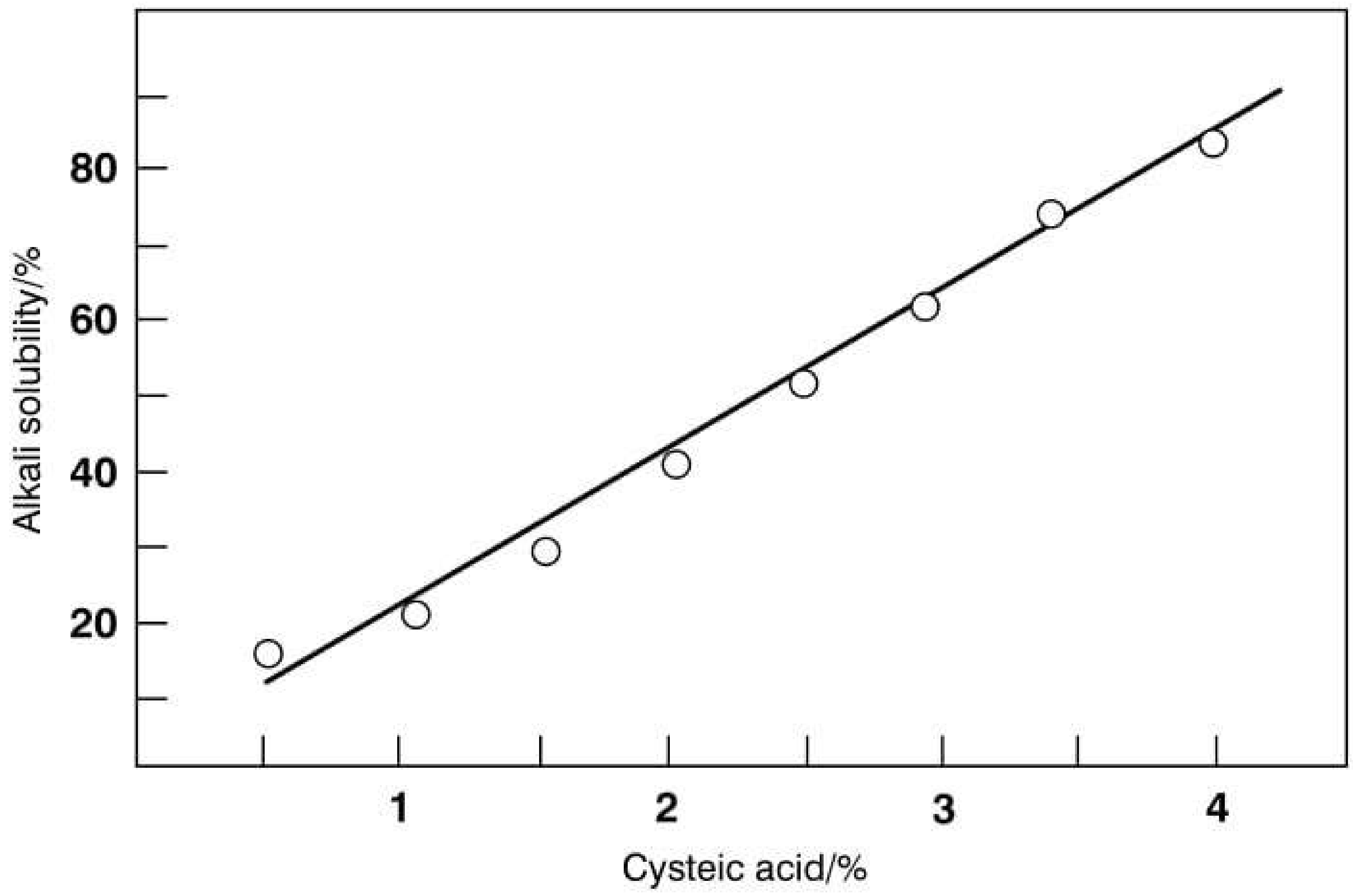


Figure 10.36 Relationship between alkali solubility and cysteic acid content of peroxide-bleached wool [259,261]

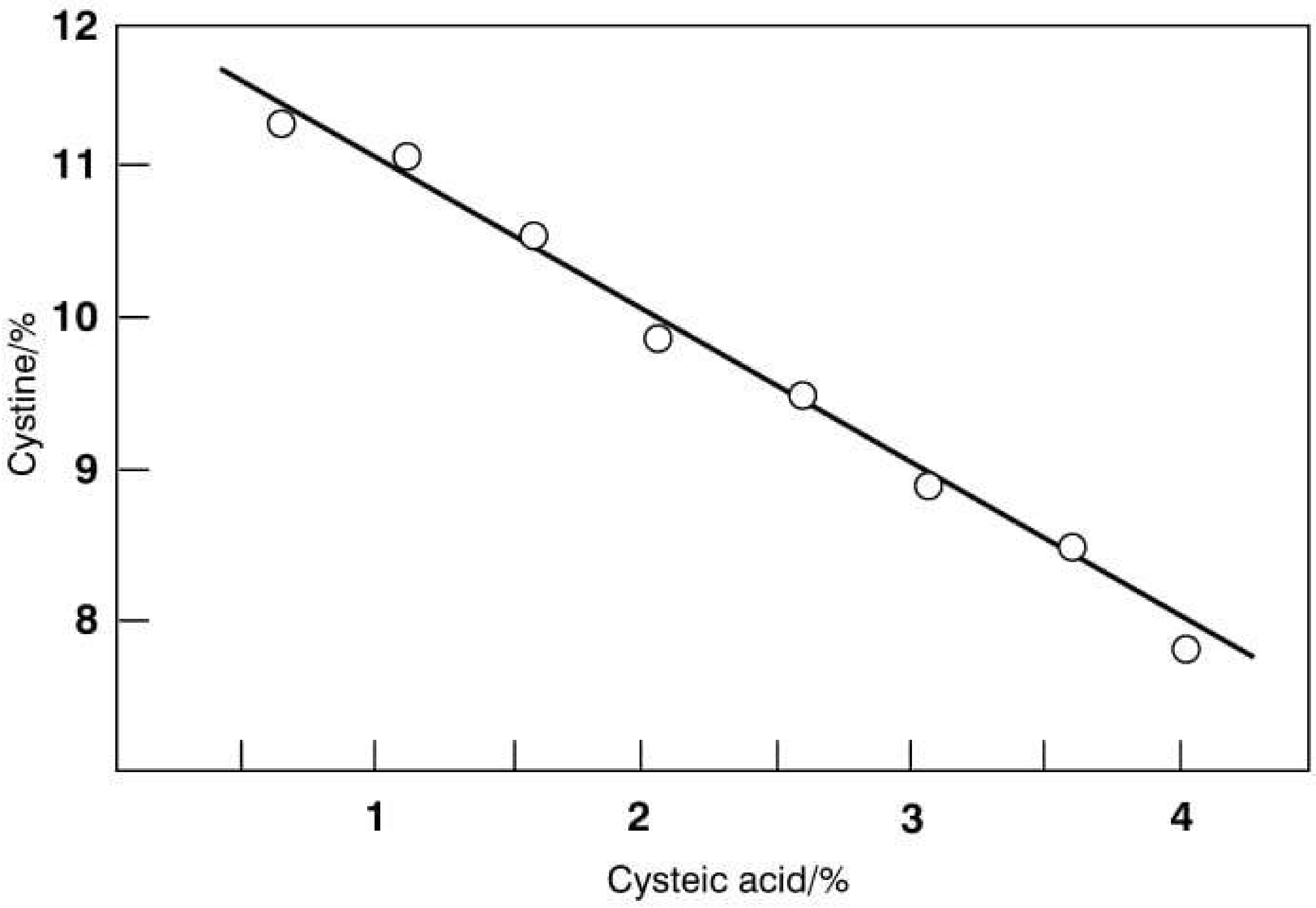


Figure 10.37 Relationship between cystine and cysteic acid content of peroxide-bleached wool [259,261]

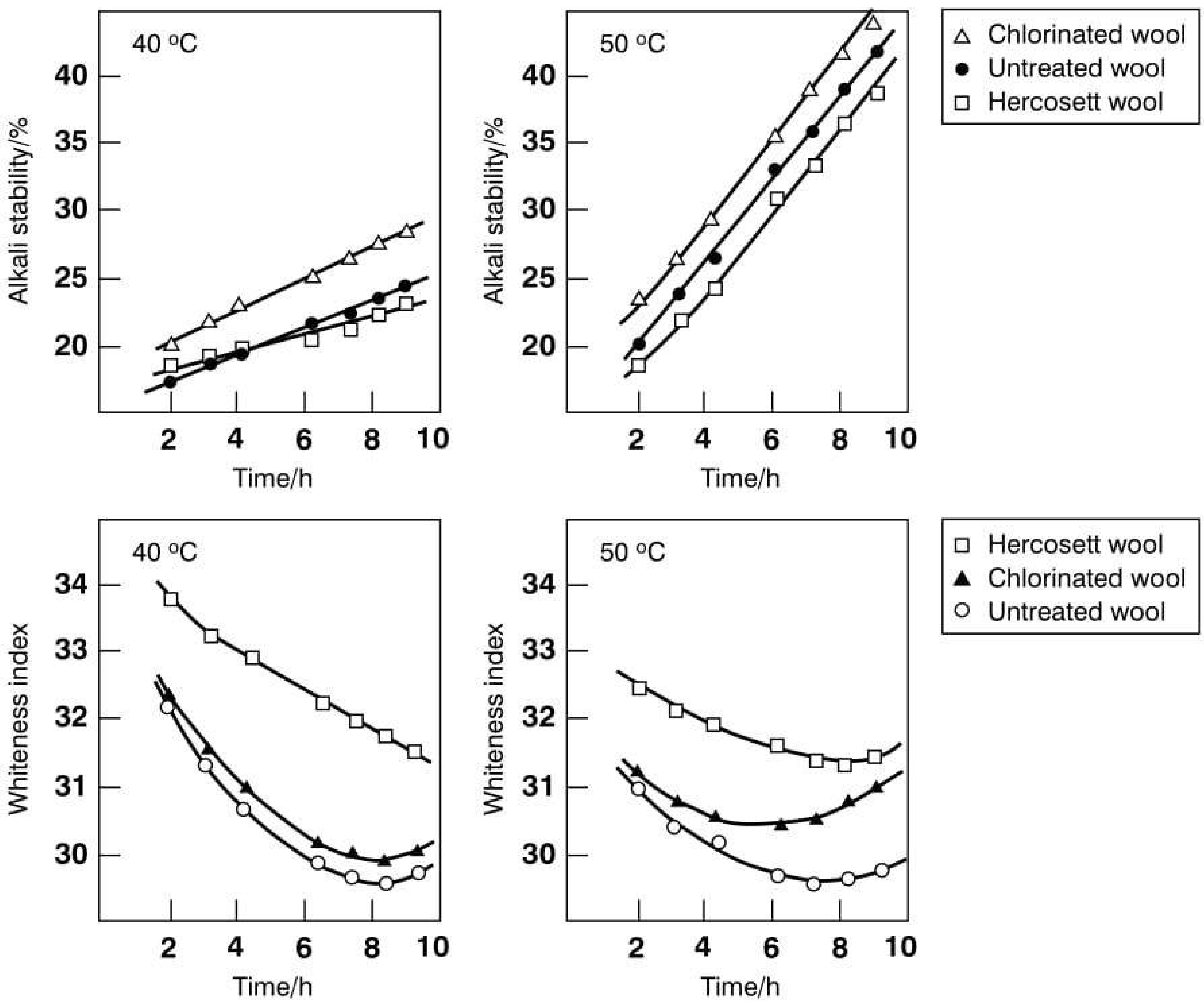


Figure 10.38 Effect of treatment time on the alkali solubility and Jaquemart whiteness index of wool bleached with 2-vol. hydrogen peroxide at 40 °C and 50 °C [259,264]

Table 10.27 Recommended conditions for the peroxide bleaching of wool [259]

Hydrogen peroxide (35%)	10-30 ml/l
Phosphate stabiliser	2-4 g/l
Wetting agent	1 g/l

Treatment for 1–16 hours at 40–60 °C

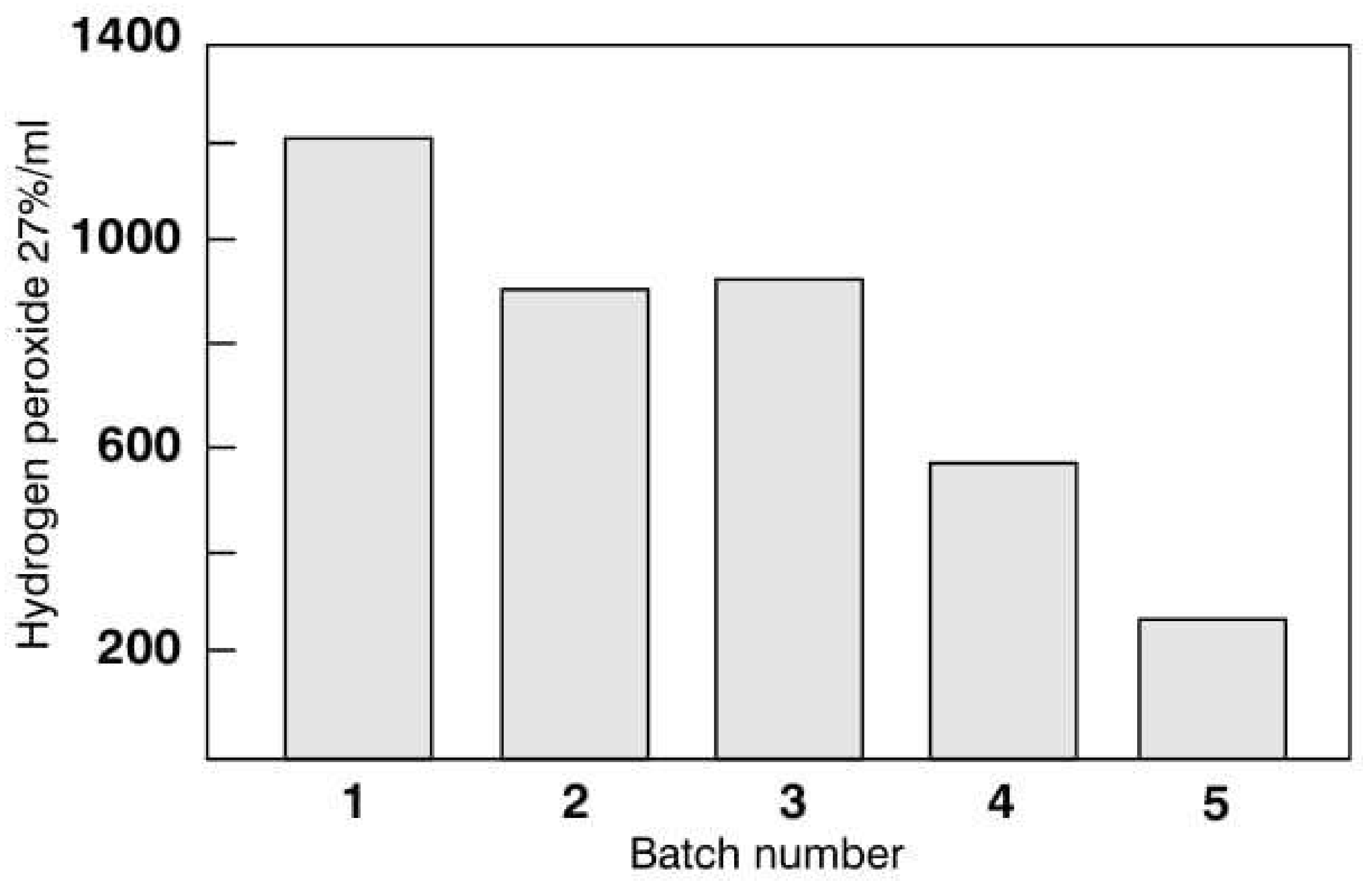


Figure 10.39 Bleach bath regeneration in the peroxide bleaching of wool [259]

A typical liquor formulation for pad application in a continuous or semi-continuous system is given in Table 10.28. Batching for 24–48 hours is followed by backwashing, although the use of radio-frequency heating to give a batch temperature of 50–60 °C can reduce the treatment time to 2–4 hours.

Table 10.28 Recommended conditions for the pad bleaching of wool [259]

Additives	g/kg
Hydrogen peroxide (35%)	40
Thickener	8
Isopropanol	16
Wetting agent	10
Formic acid	2
Antifoam	3
Fluorescent brightener (optional)	5

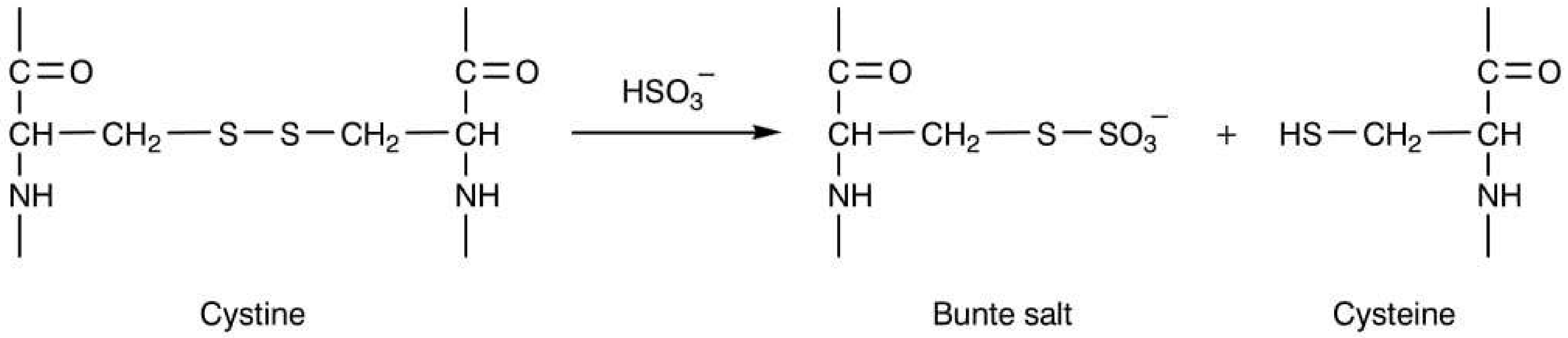
Although various processes may have been subjected to optimisation in recent years as a result of economic pressures, a survey in the 1980s revealed disparities between different sectors of the industry as summarised in Table 10.29 for batchwise wool bleaching methods.

Table 10.29 Worldwide practice of batchwise wool bleaching [259]

Processing time:	<3 hours	>3 hours	Totals
Loose stock	17.8	34.3	52.1
Slubbing	5.1	10.5	15.6
Yarn	11.6	10.2	21.8
Piecegoods	4.7	5.8	10.5
			100.0

As with the peroxide bleaching of cellulosics, the presence of transition metals in the bleaching of wool with peroxide has a catalytic effect that can damage the fibre. This catalytic effect has been exploited in a process for the bleaching of heavily pigmented wools. The fibre is first mordanted with a ferrous salt in the presence of hypophosphorous acid (H_3PO_2), then rinsed to remove the iron from the wool keratin but not from the melanin pigment granules. Hydrogen peroxide is then added to destroy the pigment granules by a free-radical mechanism [11,259,265].

Reductive bleaching of wool is mostly carried out with stabilised sodium dithionite. Derivatives such as sodium formaldehyde-sulphoxylate (CI Reducing Agent 2) or zinc formaldehyde-sulphoxylate (CI Reducing Agent 6) as well as thiourea dioxide (CI Reducing Agent 11) are also used. The chemistry of these reducing agents is discussed in Chapter 12. Apparently little is understood about the reactions between these reducing agents and the pigments responsible for the natural colour of wool. Sulphitolysis of the wool is known to take place, the reducing agent reacting with the disulphide bonds of cystine to give a Bunte salt (Scheme 10.42) [266]. Rupture of the disulphide bonds results in an increase in alkali solubility of the fibre, to which the formation of sulphonic groups also contributes.

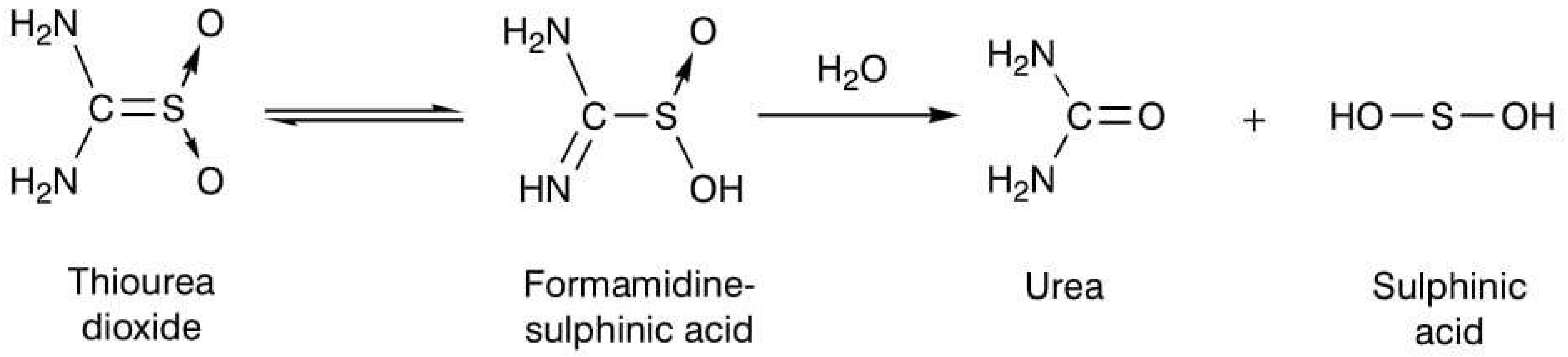


Scheme 10.42

Typical conditions for bleaching with stabilised dithionite are given in Table 10.30 [11,259]. A warm rinse is then given, with an addition of 1 ml/l hydrogen peroxide (35%) in the final rinse to eliminate sulphurous odours. The sulphoxylates are used at pH 3.0 for up to 30 minutes at 90 °C, but these tend to produce a harsh handle as well as an unpleasant residual odour. Thiourea dioxide (1–3 g/l) can be used at 80 °C and pH 7 for one hour [11]. A sequestering agent is added to prevent metal-catalysed decomposition of the thiourea dioxide. The active bleaching species is sulphinic acid (Scheme 10.43) [11]. Thiourea dioxide has less effect on the physical properties of the fibre than other reductive bleaching agents [267]. Fluorescent brighteners can be applied together with a reductive bleach but they may increase the subsequent tendency to photo-yellowing.

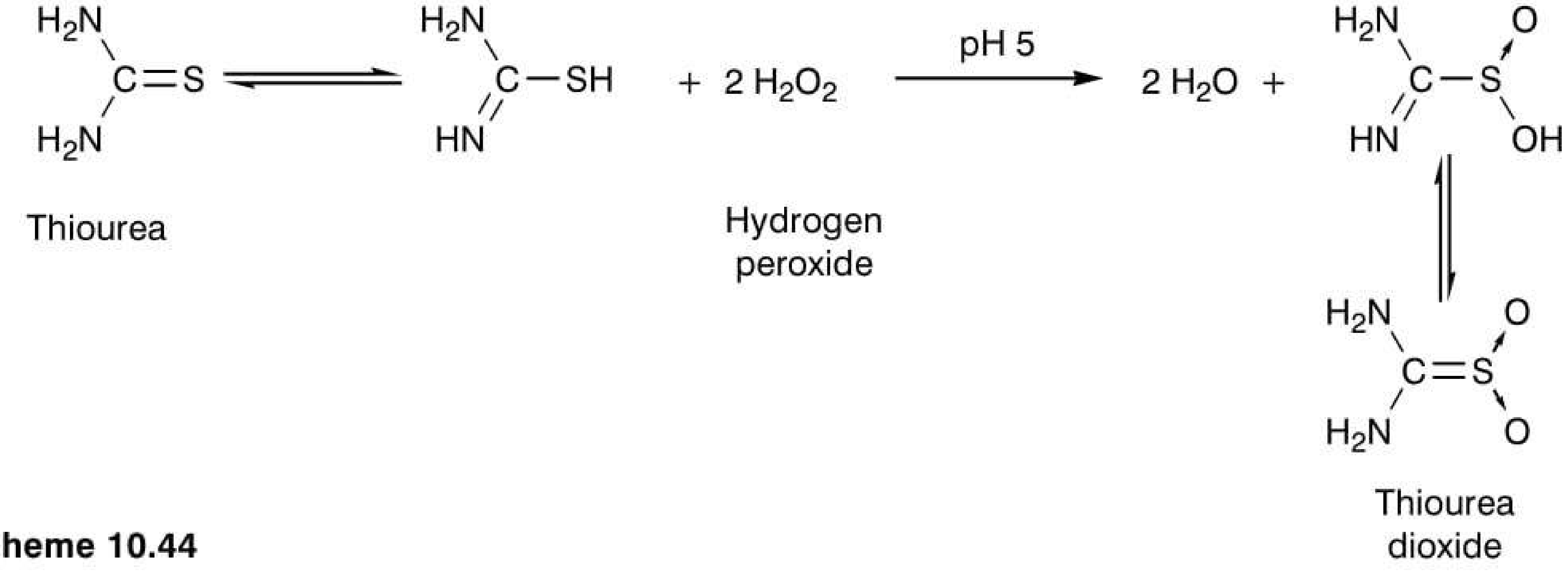
Table 10.30 Recommended conditions for the reductive bleaching of wool [11,259]

Stabilised sodium dithionite	2–5 g/l
Wetting agent	1%
pH	5.5–6.0
Temperature	45–65 °C
Time	up to 1 hour

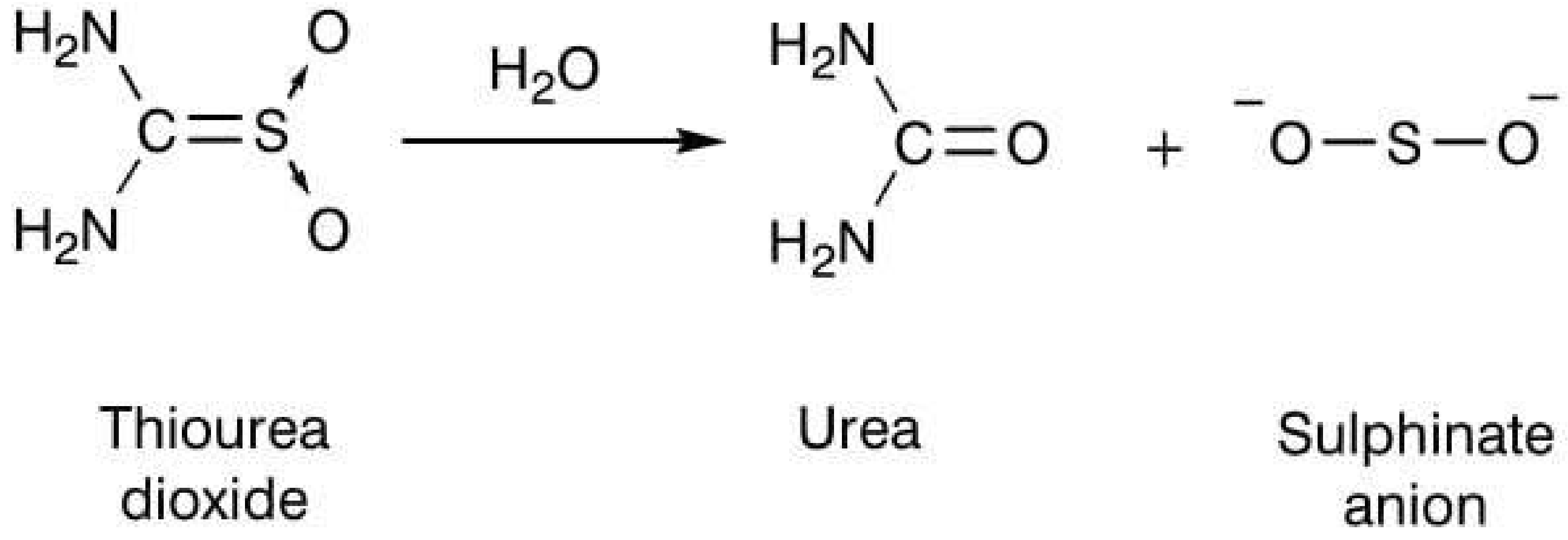


Scheme 10.43

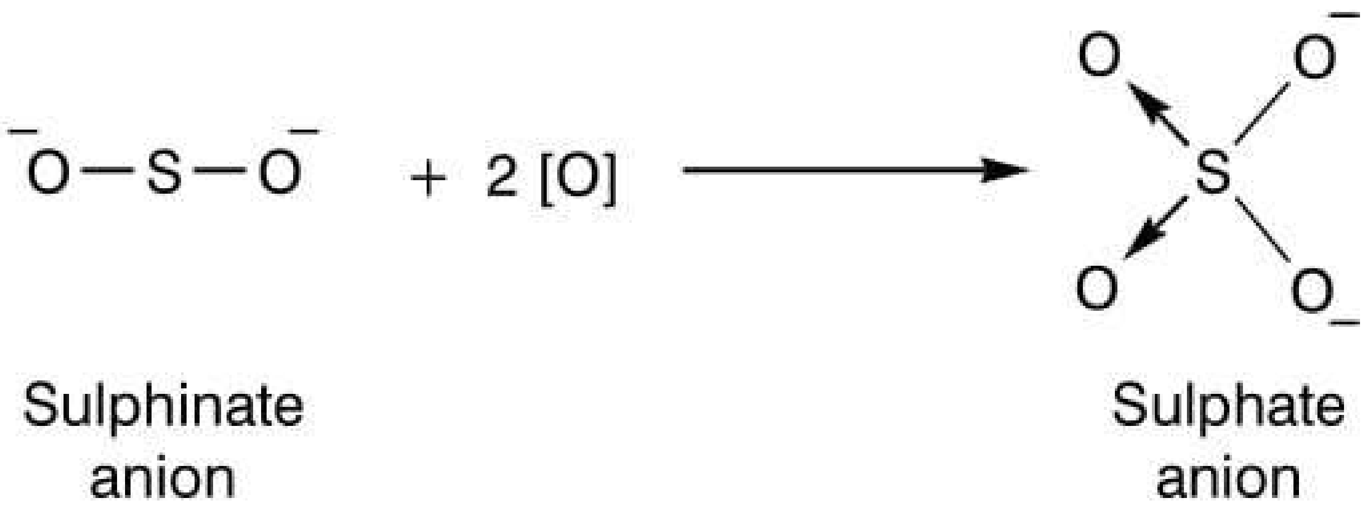
Reductive bleaches are generally less costly than oxidative bleaches but tend to give a greenish white compared with the reddish white tones from peroxide. Combining the two in an oxidation/reduction sequence gives a more neutral white, this being known as 'a full bleach'. The sequence is generally carried out in separate baths. However, an interesting attempt has been made to integrate the two processes [268–271]. This approach is of significant interest chemically. A combination of hydrogen peroxide and thiourea is used but the sequence of reactions is complex. Initially the wool is given a conventional oxidative bleach with 8 g/l hydrogen peroxide (30%) and 2 g/l sodium pyrophosphate (10.16), beginning at pH 9.0 and ambient temperature, then raising at 1 °C/minute to 60 °C and maintaining at this temperature for one hour. Titration shows that only about 10% of the peroxide is consumed and the redox potential is around +200 to +400 (i.e. oxidative). The objective in the second stage is to make use of the residual peroxide. The pH is lowered to 8.2–8.7 and then to 5.0–5.5 with acetic acid, whilst still at 60 °C. Thiourea (1.68 g/l) is then added and ten minutes is allowed for thiourea to react with peroxide to give the reducing agent thiourea dioxide, as in Scheme 10.44. Adequate time at this pH for the reaction to take place is essential. Ammonia is then added to give pH 6.8–7.2. The redox potential becomes -600 to -700 (i.e. reductive) and reductive bleaching proceeds at 60 °C for 25 minutes. The thiourea dioxide formed in Scheme 10.44 is hydrolysed to urea and the active reducing species, the sulphinate anion, during this phase, as in Scheme 10.45. The sulphinate anions in turn react with wool and with the coloured pigments present on the wool, being thereby oxidised to sulphate anions (Scheme 10.46). Any residual reducing activity can be quenched by adding a small amount of peroxide.



Scheme 10.44

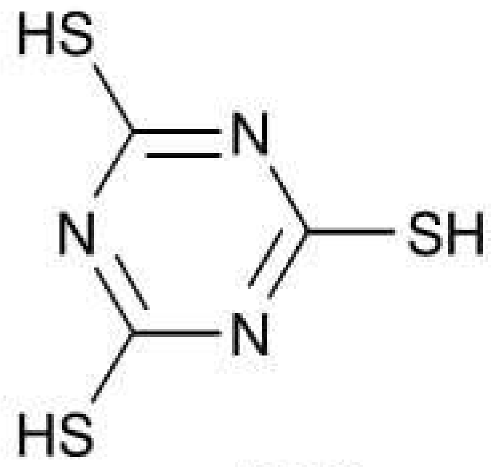


Scheme 10.45



Scheme 10.46

The control of conditions, particularly of pH and the molar quantities of reactants, is critical; otherwise, variant reaction routes are possible. Unfortunately, thiourea is a suspected carcinogen and this appears to be one reason why this two-stage redox process has not been readily adopted, even though thiourea is easy.to handle and the bath can be monitored colorimetrically to ensure complete conversion. In an attempt to overcome this problem, it has been found [272] that a cyclic analogue of thiourea, namely thiocyanuric acid or *s*-triazine-2,4,6-trithiol (10.90), can replace thiourea in this application. Thiocyanuric acid is commercially available, being used as a heavy metal precipitant in waste water treatment and as a vulcanising agent. It is best used in the bleaching process as a 15% solution of the trisodium salt. The process is claimed to produce exceptional whiteness with minimum fibre damage [272].



10.90

Thiocyanuric acid

Semi-continuous and continuous reductive processes are best carried out with activated hydroxymethanesulphinates, since dithionites (even when stabilised) are unsuitable due to being oxidised too quickly by air [273].

The environmental aspects of wool bleaching have recently been reviewed [273]. There is a tendency to replace phosphates by phosphate-free activators. Reductive bleaching agents are not environmentally friendly as they are oxygen-depleting, but pollution by dithionite is kept to acceptable levels if the residual concentration is less than 0.3 g/l. Thiourea dioxide offers the advantage of contributing only half the sulphur load from dithionite, but it also introduces detrimental nitrogen. The carcinogenic potential of thiourea has already been mentioned.

Bleaching in particular is an area where many formulated commercial products are offered. These have the advantage of providing the bleacher with a single (optimised) product to simplify the preparation of bleach liquors, compared with having to store and prepare several separate components. Little information is available on the detailed constitution of such mixture products, although hints are sometimes given by the suppliers. Some bleachers, however, may prefer the greater freedom to adjust liquors according to requirements by the judicious use of separate components. Special considerations are needed where bleaching is carried out in association with other processes or as a means of 'brightening' goods that have been already dyed.

10.5.4 Mercerising

Mercerising is an alkaline treatment often given to cotton yarns or fabrics, the objective being to increase fibre lustre, strength and dyeability. These effects are brought about by alkaline swelling of the fibres with or without tension. Accounts of practical aspects of mercerising treatments are available [143,235,274]. Processing options include: cold or hot, wet or dry, chain or chainless and batchwise or continuous. Consideration must be given to the position of mercerising in the overall sequence of preparation, since it may be carried out on grey, partially prepared or fully prepared goods. The maximum degree of swelling attainable decreases the later the stage at which mercerising is carried out. Accordingly, mercerising of grey-state goods gives the maximum potential for swelling but fibre penetration and uniformity of treatment are most difficult to achieve. Grey mercerising also has the severe disadvantage of giving maximum fouling of the caustic soda liquor.

Mercerising is usually positioned either between desizing and boiling-off or between boiling-off and bleaching [274,275]. Care should be taken to avoid carry-over of iron impurities into the bleaching stage. It is also important to ensure thorough and uniform rinsing after mercerising, as any localised residual alkali will lead to uneven bleaching [275]. Whilst these are generally the two most favourable positions for mercerising, their disadvantage lies in interrupting the flow of the continuous preparation sequence, since mercerising is the slowest pretreatment stage. This is where hot mercerising (60 °C) can become an advantage, because the quicker rate of swelling allows this step to be more easily incorporated within the processing range as a whole [275].

Mercerising after bleaching gives the least fouling of the liquors but increases the possibility of fibre yellowing. Moreover, fibre swelling and absorptivity are less evident, sometimes leading to problems in subsequent processing, particularly in continuous processes where rapid uptake and maximum absorption are required [275].

In chain mercerising, the weft threads of the fabric are kept under tension on a clip stenter. In a chainless merceriser the fabric dimensions are controlled by a series of rollers. The fabric is usually woven slightly wider to allow for some weft shrinkage. Yarn is mercerised in hanks between two movable rollers which create the required tension whilst knitted constructions may be mercerised in either slit or tubular forms. Chain and chainless mercerising have been compared [276].

It is important to be aware of the machine configuration as this influences the target conditions, including the concentration of caustic soda applied and its subsequent washing-off. The three stages that are important from the viewpoint of auxiliaries are: mercerising zone, stabilising zone and washing zone. In the mercerising zone the goods are impregnated with caustic soda liquor and are subjected to the relevant means of controlling tension. In the stabilising zone the concentration of alkali is reduced to a level at which the fabric again becomes dimensionally stable, losing the plasticity imparted by the concentrated alkali in the mercerising stage. The counterflow washing principle is applied to reduce the alkali concentration. Only when dimensional stability has been restored are the goods ready for the washing-off section in which residual alkali is removed and the fabric neutralised.

Traditionally, mercerising has been carried out cold (10–20 °C). This imparts the maximum degree of swelling but this is attained at the slowest rate. Hot mercerising has been introduced more recently and this is carried out at 60–70 °C. The characteristics of the two processes are compared in Table 10.31 [274,277]. Table 10.32 presents a comparison of these processes from the viewpoint of results obtained in relation to the stage at which mercerising is carried out, as well as analogous trends for modal fibres [275,277]. The characteristic feature of hot mercerisation is that the essential chemical and physical changes do not take place at the higher initial temperature but in the subsequently cooled fabric as it passes through a traditional tensioning process [143]. Hot mercerising, however, has not yet achieved significant commercial success [143]. In cold mercerising, the treatment time needs to be longer and is usually 40–45 seconds, compared with 25–35 seconds when mercerising at 60 °C [276]. The optimum effect is achieved when the fabric takes on a glassy, transparent appearance just before the stabilising section. A combination of hot and cold impregnation is possible [276].

Table 10.31 Comparison of hot mercerising with conventional cold mercerising of cotton [274,277]

Conventional mercerisation (10–20 °C)	Hot mercerisation (70 °C)
strong fibre swelling	less fibre swelling
slower swelling	rapid swelling
slower relaxation	rapid relaxation
incomplete relaxation	good relaxation
higher residual shrinkage	lower residual shrinkage
surface swelling	complete swelling
unevenness	evenness
tighter fibre packing	looser fibre packing
firmer handle	softer handle
slow NaOH diffusion	rapid NaOH diffusion
less lustre	optimised lustre
less strongly swollen fibres in surface zone of yarn	moderately swollen fibres throughout yarn cross-section
background less lustrous	background equivalent lustre

Table 10.32 Comparison of cold and hot mercerising processes for bleached and unbleached cotton and for modal fibres [275,277]

Property	Substrate	Cold mercerised	Hot mercerised
Degree of polymerisation	grey cotton	=	=
	bleached cotton	=	=
	modal fibre	…	…
Breaking strength	grey cotton	=	=
	bleached cotton	=	=
	modal fibre	<	>
Dyeability	grey cotton	≤	≥
	bleached cotton	>	<
	modal fibre	>	<
Lustre	grey cotton	<	>
	bleached cotton	<	>
	modal fibre	>/<	>/<
Dimensional stability	grey cotton	<	>
	bleached cotton	<	>
	modal fibre	<	>
Handle (flexibility)	grey cotton	≥	≤
	bleached cotton	…	…
	modal fibre	>	<
Crease recovery angle	grey cotton	<	>
	bleached cotton	…	…
	modal fibre	<	>

= Similar to
< Less than
> Greater than the other method

There is a so-called dry mercerisation process [275] in which the fabric is padded with caustic soda liquor at 20–25 °C and then dried in a stenter at about 130 °C. An immersion time in the pad trough of 7–10 seconds is sufficient but the goods need a total saturation time in the alkaline liquor of 30–40 seconds, i.e. from the nip to entry into the drying zone.

The type of cotton and its condition determine to a large extent the degree and uniformity of mercerisation. Fibres with a relatively rounded cross-section, exceptional fineness and consistency tend to give the highest degree of mercerisation [274]. These properties also play a part in determining the mercerising conditions.

Ideally, the maximum possible degree of mercerisation would be obtained if the goods were repeatedly mercerised (for example, twice at around 70 °C and then for a third time at 10–15 °C) but such a procedure is economically impractical [274]. In practice it is essential to aim for an optimum rather than the maximum degree of mercerisation, a compromise between what is desirable or ultimately possible and what is economically feasible on available machinery.

In the context of the above basic requirements of the process, the chemicals used are sodium hydroxide as the primary agent and a surfactant-based auxiliary to aid rapid and even penetration as an important secondary requirement.

The viscosity of solutions of sodium hydroxide increases with concentration and decreases with temperature as shown in Figure 10.40. It is the higher viscosity of cold concentrated solutions which makes fibre penetration so difficult in cold mercerising. Nevertheless, despite the slower rate of penetration at low temperatures, the ultimate degree of swelling is greater (Figure 10.41). Thus in this investigation, maximum swelling at 25 °C was obtained with 4–6 mol/l sodium hydroxide solution. These curves illustrate that the change in swelling behaviour with temperature becomes more critical at low concentrations of alkali. Traditionally, solutions of sodium hydroxide in the 6.25–6.5 mol/l range have generally been used in cold mercerising. In fact cellulose swells even in pure water but to a lesser extent than in alkali, the swelling in water being reversible whereas alkali-induced swelling is irreversible. Aqueous swelling affects only the readily accessible amorphous regions of cotton, whilst alkali also greatly affects the crystalline regions.

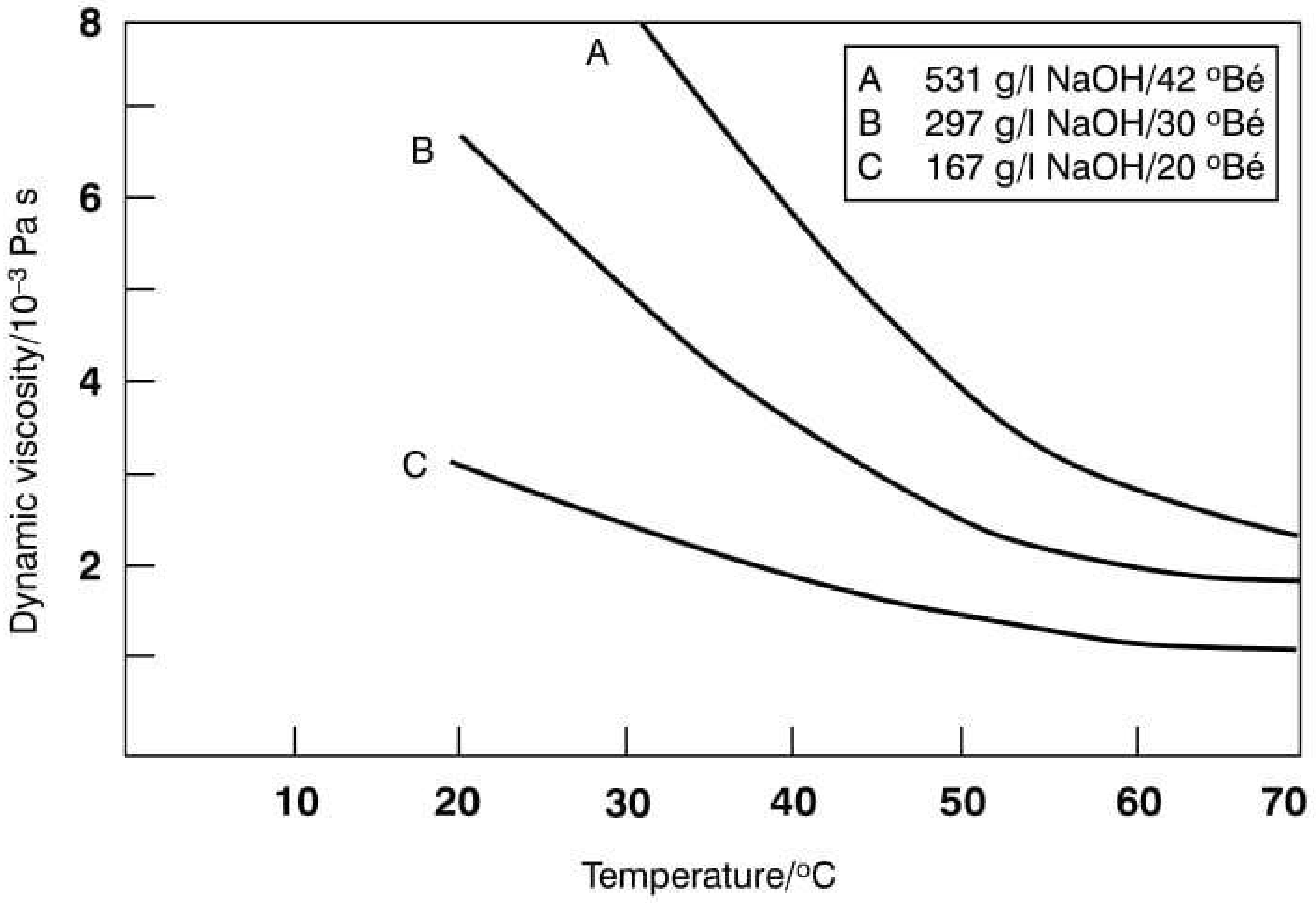


Figure 10.40 Change in viscosity of NaOH solutions with temperature [274]

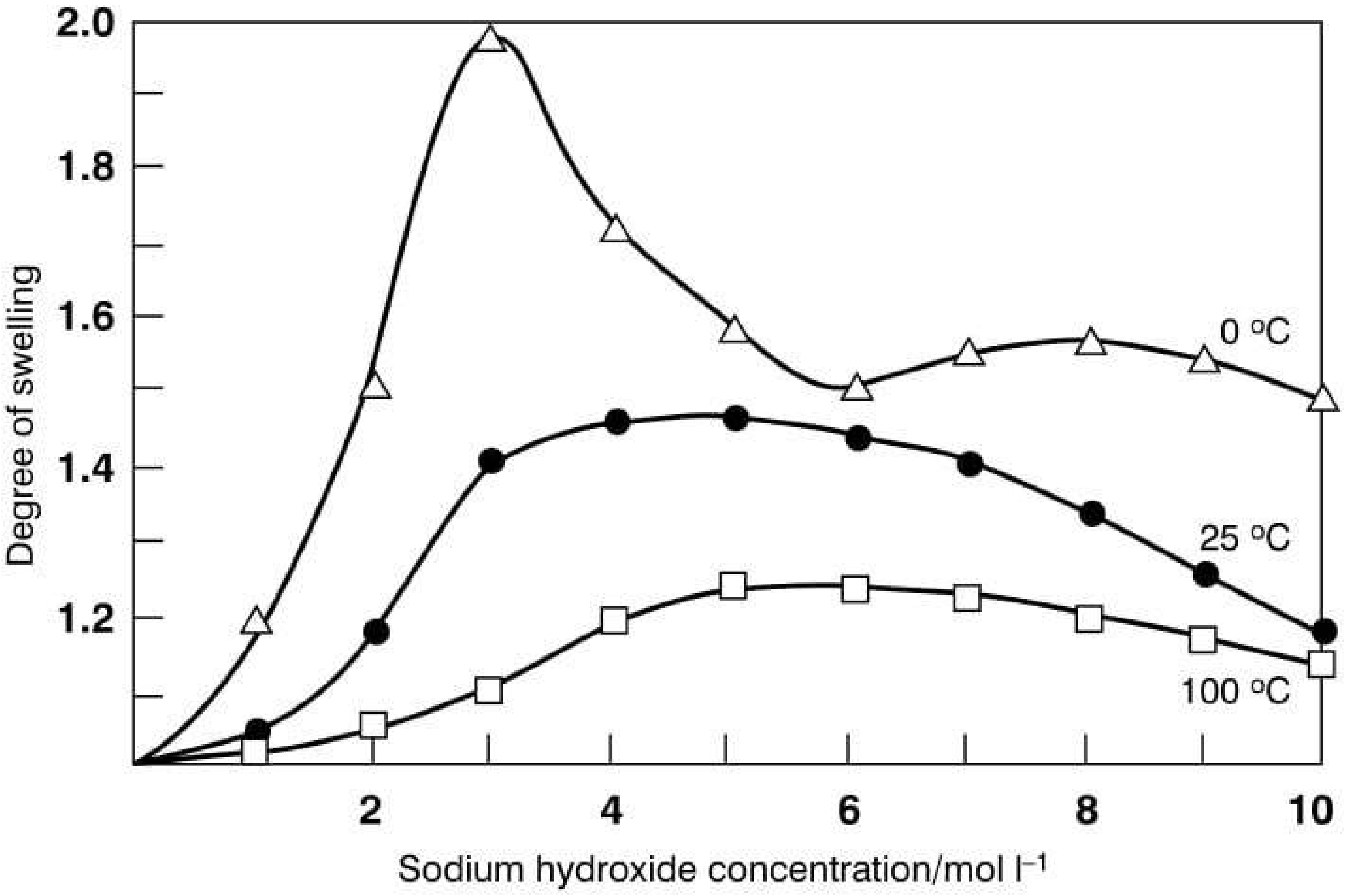
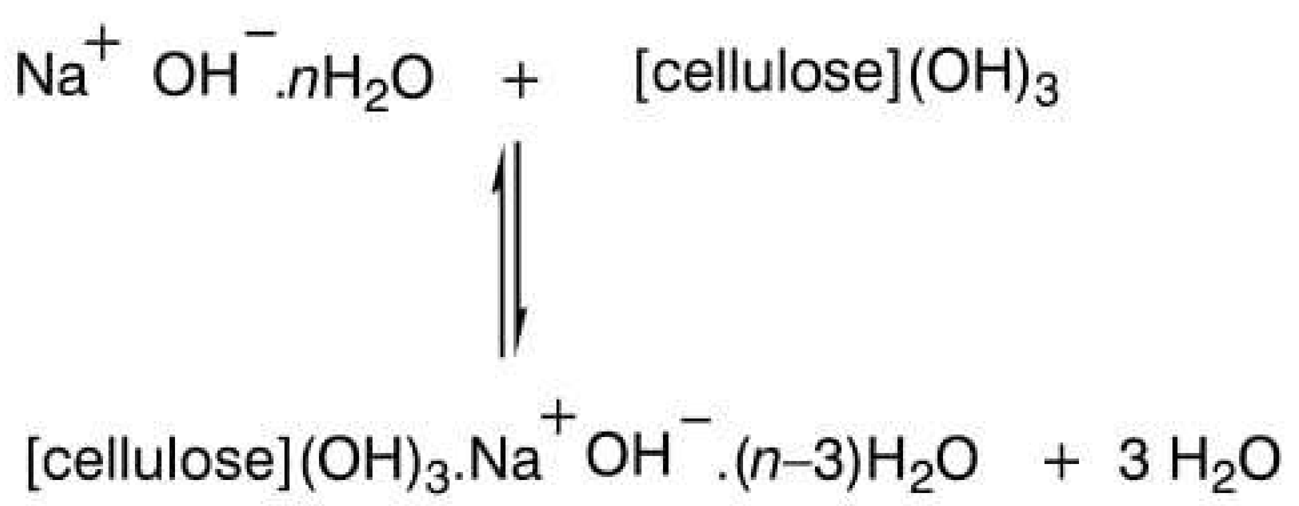


Figure 10.41 Effect of temperature on degree of swelling of cotton fibres by sodium hydroxide (molar sodium hydroxide solution contains 40 g/l NaOH) [278]

The mechanism is thought to be one of ionic hydration [143,279,280], arising from replacement of some of the water of hydration by cellulosic hydroxy groups as shown in Scheme 10.47. When a hydrated ion pair is absorbed by the cellulose, three molecules of water are released and are replaced by three hydroxy groups. These are unlikely to be located in the same anhydroglucose unit. The liberated water molecules now occupy a greater volume than when associated with the ion pair, thus causing swelling of the fibre [143]. It is important to realise that swelling involves only partial molecular disruption of cellulose; complete disruption would produce dissolution or at least dispersion. Hydrogen bonds in the crystal structure are ruptured but the van der Waals forces remain intact, thus enabling the cellulosic matrix to behave as mobile sheets held in close contact by the van der Waals forces. This parallel arrangement of the cellulose chains is enhanced by the tension applied during mercerisation and the surface of individual fibres becomes smoother, giving an increase in lustre [276].



$$\mathrm{Na^{+}\,OH^{-}.}n\mathrm{H_2O} + \mathrm{[cellulose](OH)_3} \rightleftharpoons \mathrm{[cellulose](OH)_3.Na^{+}OH^{-}.}(n{-}3)\mathrm{H_2O} + 3\,\mathrm{H_2O}$$

Scheme 10.47

The more highly crystalline the fibre, the more it will resist the mercerising treatment. Initial swelling always takes place in the amorphous regions, followed by penetration of the crystalline material by alkali. As indicated earlier in Figure 10.41, optimum conditions for swelling are obtained with about 4–4.5 mol/l NaOH at 25 °C, this being the most favourable concentration for penetration of the crystalline regions and thus for enhancing dye affinity. A further optimum is reached at a concentration of 6.5–7.5 mol/l NaOH, since it is at this concentration and 0 °C that the fibre cross-section changes from kidney-shaped to circular, giving enhanced lustre. This is why 6.25–6.5 mol/l NaOH has been the standard concentration in traditional cold mercerising. Greif considers that a concentration of at least 6.75 mol/l and preferably 8.75 mol/l NaOH is necessary for the highest degree of mercerisation [274]. In the so-called continuous addition mercerising process, a liquor concentration of about 13 mol/l sodium hydroxide is used at 70 °C, applied to squeeze-wet goods [274]. This facilitates quicker penetration and gives a higher degree of mercerisation. The active concentration, however, falls to the usual level of about 6.75–8.75 mol/l after a dwell time of about 15–25 seconds, since the fabric already contains about 60% moisture. Nevertheless, it is claimed that a better effect is obtained by this technique of 'dilution from above'.

Strictly speaking, regenerated cellulosic fibres cannot be 'mercerised' although they can be given a 'causticisation' treatment. There is a critical concentration of caustic soda that causes dissolution of regenerated cellulose: about 65 g/l. The much higher concentrations used in conventional mercerising do not cause dissolution of cotton cellulose, of course. Regenerated cellulosic fibres can be given a causticisation process using 15–50 g/l sodium hydroxide. There is some advantage in using higher temperatures as swelling is thereby reduced. Viscose staple fabrics for dresswear are often causticised to enhance dye receptivity, increase the brilliance of colour and obtain a softer handle [279].

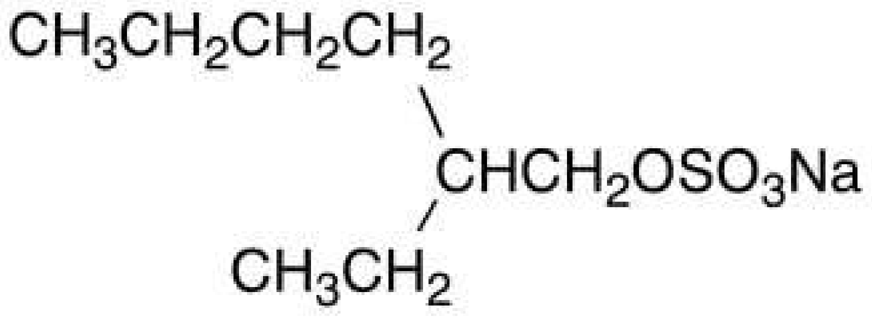
Addition of a wetting agent to the mercerising liquor gives better penetration and more even treatment. However, the choice of wetting agent depends on the fabric to be mercerised and the position of mercerising in the preparation sequence as a whole. The need for this additive is greatest with grey yarn or piece goods. Goods that have been given an alkaline boil-off or bleach already have much better wettability, so the need for a wetting agent is not so great. Indeed, such goods may still be saturated from a previous process and if fed directly into the mercerising liquor, there is no need for a wetting agent [280].

The properties of a wetting agent for mercerising can be summarised as follows [235,280]:

- good solubility and stability in 10M (400 g/l) sodium hydroxide solution; the stability should be maintained under the conditions of alkali recovery by centrifugal separation or vacuum evaporation
- high wetting ability and high efficiency at low concentrations in the strongly alkaline solutions used; this is particularly critical in continuous processing and on grey goods
- low affinity for the fibre; together with high efficiency at low concentrations this aids subsequent rinsing and recovery
- low foaming.

Suitable products include [235,280]:

- alkylarylsulphonates
- sulphated aliphatic alcohols, the most efficient being those of low molecular mass (i.e. 4–8 carbon atoms), such as sodium 2-ethylhexylsulphate (10.91); branched chains are more efficient than linear ones [235]
- some short-chain alkylphosphonate esters, e.g. sodium methyloctylphosphonate.



$$(CH_3CH_2CH_2CH_2)(CH_3CH_2)CHCH_2OSO_3Na$$

10.91

A product such as 10.91 may require blending with about 10% each of butanol and unsulphated 2-ethylhexanol to give an effective formulation in terms of solubility, stability and wetting power. It is useful for a wetting agent to exert some degree of detergency across the whole range of caustic soda concentrations, including the lower concentrations for efficiency during washing-off [281].

Yarn shrinkage provides a good measure of the efficiency of a wetting agent under mercerising conditions [280]. Figure 10.42 illustrates results for an effective product, yarn shrinkage being complete in about 30 seconds.

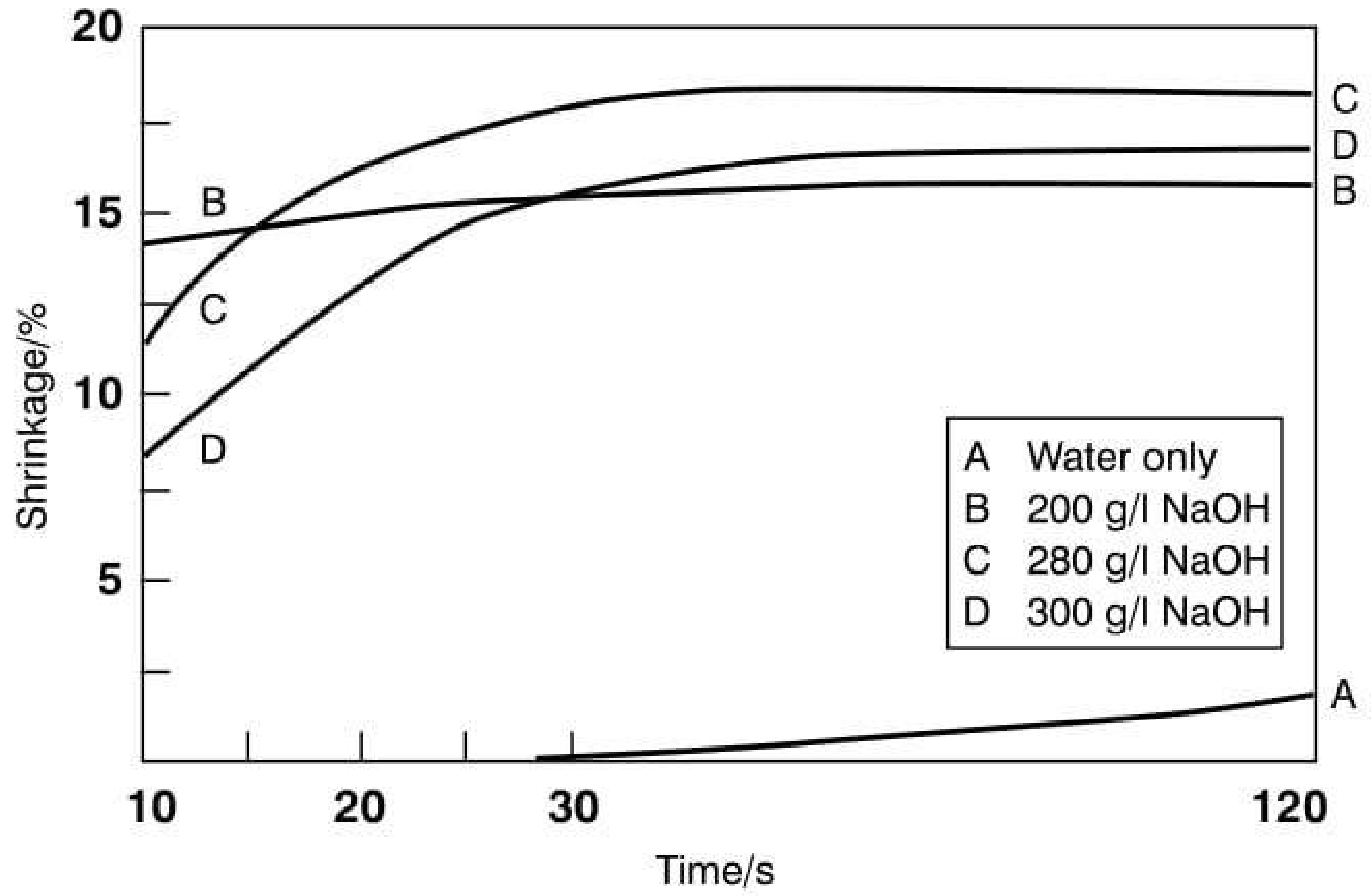


Figure 10.42 Mercerising shrinkage rate using 5 g/l of a commercial wetting agent [280]

In the so-called stabilising zone, the concentration of the alkali is reduced, by a counterflow washing system for example, until the fabric regains dimensional stability. In the succeeding washing-off zone, most of the residual alkali is removed and the fabric is neutralised, typically with acetic acid [274,276]. The stabilising zone generally gives a spent liquor containing 40–80 g/l sodium hydroxide [274,282,283]. Desorption is more rapid the better the preparation of the cotton and the remarkable claim has been made that it is possible to remove more than 75% of the alkali in only 2 seconds [284]! Even after thorough rinsing, however, there is always a small amount of residual bound alkali in the fibre [285].

The spent liquors may contain lint and residual size that can be removed by filtration. Weakly alkaline liquors represent a cost problem, however. Although limited amounts of less dilute liquor may be recycled and used in boiling-off or scouring, the major proportion becomes a rather troublesome component of the effluent load. Neutralisation simply increases the salt content of the effluent. Recovery of the alkali by vacuum evaporation is the usual procedure [282,283].

Anhydrous liquid ammonia can also be used to enhance the absorption properties of cotton [143].

10.5.5 Wool processing

Milling, a process peculiar to wool, is carried out to develop its felting propensity. Traditional wool goods such as felt hats and blankets are milled under slightly acidic conditions, sulphuric acid being the main agent. Acid milling is particularly useful for dyed goods, which may not have adequate fastness to neutral or alkaline treatments. Alkaline milling conditions are still used for woven piece goods traditionally known as milling cloths, maximum milling taking place using soap at pH 10. The higher-melting soaps, such as those based on tallow and palm oils, have been preferred to give the required gelatinous solution and lubricating properties. Greasy woollens are often milled in sodium carbonate solution, which saponifies the natural grease to a soap. Even with such woven pieces, however, the trend is towards milling in almost neutral conditions, for which milling aids based on nonionic and anionic surfactants are useful. Some wool yarns are milled simply by tumble drying of the wet yarns, whilst knitted garments are milled in rotary-type machines using a nonionic surfactant with sodium bicarbonate or polyphosphate. Solvent-based systems in which a small amount of water is emulsified in the solvent by an appropriate surfactant have also been used [146], this often forming part of a sequence in which scouring, milling and shrink-resist finishing are all carried out in the same machine.

Another process peculiar to wool is carbonising. This exploits differences between wool keratin and cellulose in their response to strong acid, wool being substantially more stable whereas cellulose is degraded. Hence strongly acidic conditions are required to remove cellulosic impurities from wool. Dilute sulphuric acid (4–8%) is most commonly used [286]. Other mineral acids (e.g. hydrochloric acid) or inorganic compounds that are strongly acidic in solution (e.g. aluminium chloride) may also be used. However, whilst aluminium chloride has been used to carbonise wool blends containing other fibre types such as polyester or cellulose acetate that are sensitive to sulphuric acid, it is not used commercially to any great extent [286]. Arylsulphonic acids and thionyl chloride ($SOCl_2$) are also suitable. Thionyl chloride is hydrolysed to hydrochloric acid and sulphur dioxide, so it has been used in carbonising either as a vapour or as a solution in perchloroethylene [286].

All carbonising processes involve the following steps [286]:

(1) Immersion (or spraying) to impregnate the wool with the appropriate acid solution
(2) Drying to concentrate the acid
(3) Baking to dehydrate and carbonise the cellulosic impurities
(4) Crushing and dedusting to remove the charred cellulosic debris
(5) Neutralisation of the residual acid.

As already mentioned, sulphuric acid is by far the most common carbonising agent. In traditional processes, it is applied at 4–5% concentration with a dwell time of 3–5 minutes. So-called rapid processes apply 7–8% sulphuric acid with very short dwell times, typically 5 seconds. When used alone, there is a danger that localised droplets of highly concentrated sulphuric acid can be formed, with consequent damage to the wool. The critical conditions for this to occur are met when the acid concentration reaches 40–45% [286–288].

Auxiliaries are generally used to prevent this localised damage and to ensure efficient wetting and penetration. Many products have been suggested [286], surfactants being the most important. These must be stable to the hot acidic treatment, of course. Anionic surfactants such as alkylbenzenesulphonates have been used, as well as nonionic types such as nonylphenol polyoxyethylenes of 6 to 9 ethylene oxide units per molecule. Typically, the concentration of surfactant present is only 0.025–0.04%, depending on the composition of the surfactant [286]. Mixtures containing a polyethoxylated nonionic and an alkylarylsulphonate anionic, however, can significantly increase the risk of wool damage compared with the use of either component separately [286,289].

Since wool is attacked most rapidly by sulphuric acid of intermediate concentration, it is important that drying is carried out either at a relatively low temperature so that reaction of the acid with wool is slow, or very quickly so that the time of exposure of the wool to the critical acid concentrations is brief [146]. Ideally, all the sulphuric acid in the wool is absorbed chemically as bound acid that causes little hydrolytic damage. It is the free acid that can concentrate locally and cause serious degradation. The acid picked up by the vegetable impurities, on the other hand, is free acid that has the desirable effect of beginning the process of attacking the cellulose [286].

Large amounts of residual acid may cause damage to the wool, so that careful neutralisation after baking is an essential and important stage of the process. Carbonised fabrics allowed to accumulate without neutralisation at moderate humidity may suffer considerable damage, so it is essential that neutralisation should take place as soon as possible after carbonising. Neutralisation with ammonia or a mixture of ammonia and ammonium acetate is achieved more rapidly than with sodium carbonate or sodium acetate; the ammonia is best used cold [146,286,290].

The pH of carbonising effluent can be adjusted, of course, to meet discharge requirements. However, this can lead to undesirably high levels of sulphate. The slime in sewage pipes produced under anaerobic conditions in turn produces hydrogen sulphide from the sulphates present. This hydrogen sulphide gas is oxidised on the sewer walls, promoting the growth of sulphuric acid-producing anaerobic bacteria with consequent damage to concrete pipes [286]. It is possible to minimise sulphate levels by coagulation with a combination of aluminium salts and lime at pH 10 [286,291].

Mechanism of shrink-resist finishing

Shrink-resist processes for wool came into prominence with the growth in importance of machine-washable wool. These processes have a decisive bearing on the selection of dyes as regards fastness demands. Numerous approaches have been suggested, normally involving oxidative modification of the epithelial scales, the application of a polymer to the fibre surface, or a combination of both. In the case of polymer deposition, two approaches are possible. The polymer may be applied either as a surface film masking the epithelial scales or to link together neighbouring fibres in a process sometimes known as 'spot-welding'. These differences are clearly illustrated in Figure 10.43. Special equipment is needed for interfacial condensation polymerisation, however, and a further restriction is that it can only be applied

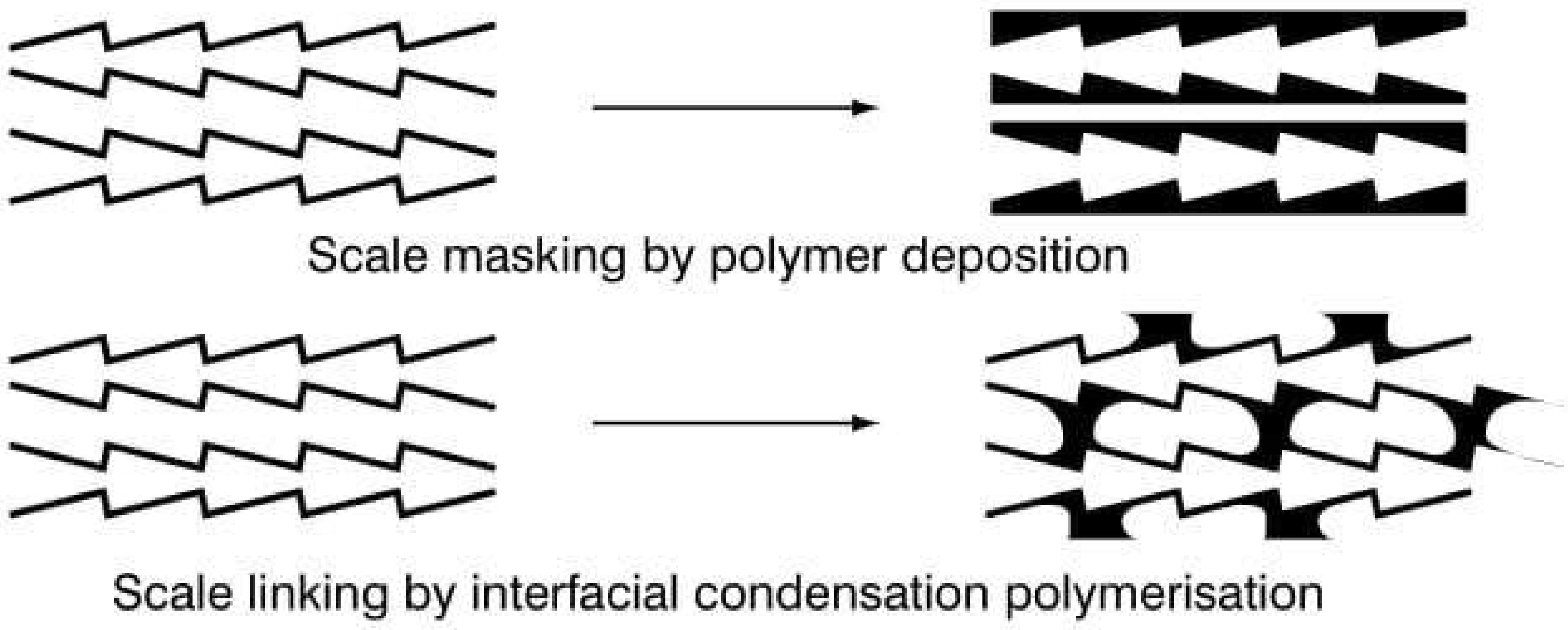
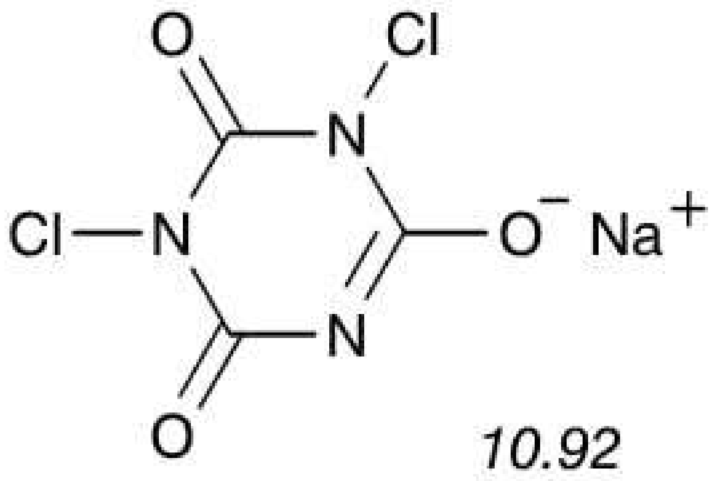


Figure 10.43 Mechanisms of shrink-proofing by polymer application [292]

to fabric, whereas polymer deposition can be used at any stage of wool processing. For these reasons, polymer deposition remains by far the most popular method commercially. The degradative modification or removal of the wool scales is sometimes referred to as 'subtractive' shrink-resist finishing, whilst polymer deposition techniques are described as 'additive' [293].

Subtractive shrink-resist treatments

The chemical basis of subtractive treatments is the oxidative breakdown of disulphide bonds in the cystine-rich epithelial scales of wool to form cysteic acid residues (Scheme 10.41). There is also some hydrolysis of amide groups in the main peptide chain. Acidified sodium hypochlorite was originally the preferred oxidising agent. However, difficulties in achieving consistent and uniform treatment without excessive fibre damage led to its replacement by sodium dichloroisocyanurate (10.92), also applied under acidic conditions. The use of this 'chlorine generator' provides a more gradual and controlled release of chlorine than can be achieved with hypochlorite. Additives include sodium dioctylsulphosuccinate as wetting agent, as well as the acidifying medium such as acetic acid with a buffer such as sodium formate/formic acid.



10.92

Liposomes (section 10.3.4) have been suggested as auxiliary agents in wool chlorination since they give improvements in the consistency and homogeneity of the oxidative treatment, minimising degradation of the wool and facilitating subsequent treatments [61,62].

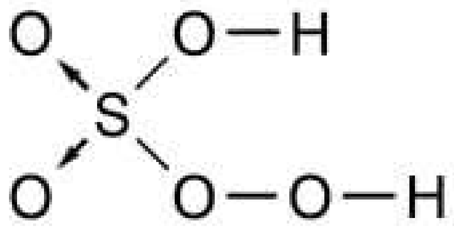
Although chlorination with sodium dichloroisocyanurate is still by far the most commonly used method of shrink-resist finishing, there is considerable concern over the environmental influence of its AOX contribution. For this reason, its usefulness could decline in future and there has been considerable investigation of alternatives to this attractively cost-effective treatment.

One possibility is to use an atmosphere of nitrogen containing 3% fluorine gas, for which a commercial-scale plant is available [294]. This dry fluorination process provides an effective subtractive treatment capable of replacing chlorination. Since it requires a halogen gas, it might be thought to be just as likely as chlorination to infringe AOX regulations. However, organofluorides cannot be detected by the current AOX test method. In any case, owing to the strength and stability of the carbon-fluorine bond, it is unlikely that carcinogenic species are formed. Furthermore, as this is essentially a surface modification, the formation of fluoride ions is limited. It is considered that current effluent legislation covering fluoride ions should not restrict commercial adoption of this process [294]. The design of the machine eliminates the risk of loss of gaseous fluorine.

Corona discharge, bombardment of the wool fibre surface with electrons of sufficient energy to break covalent bonds, has also been applied to the improvement of shrink resistance [294–296]. Collisions between electrons and molecules of oxygen and nitrogen in the atmosphere results in the formation of ozone and oxides of nitrogen. Subsequent reaction between free-valence species on the substrate surface and the corona atmosphere leads to the formation of a polar surface. This can facilitate adhesion of polymer if the subtractive stage is followed by an additive phase [294]. The plasma glow discharge treatment of wool in non-polarised gases like air, oxygen or nitrogen, usually combined with a polymer treatment, also shows promise as a zero-AOX treatment for the shrinkproofing of wool [297–299]. The plasma treatment does not damage the fibres, yet considerably reduces the felting potential of the wool, particularly by enhancing the effectiveness of polymer treatment.

Enzymes have been proposed as a means of subtractive shrink-resist treatment. Their use has been discussed already in section 10.4.2. There are difficulties, however, in the commercially successful application of enzymes to wool at present.

Alternatives to sodium dichloroisocyanurate as oxidising agent include potassium permanganate and peracids such as peracetic acid, peroximonosulphuric acid (Caro's acid) and peroximonophthalic acid, of which by far the most important in terms of current interest is peroximonosulphuric acid (10.93), usually known as permonosulphuric acid The pure acid can be obtained in crystalline form, but its salts are unstable. In a detailed study of the effect of oxidising agents on wool, their relative reactivities generally corresponded with the degree of shrink resistance but this was not related to redox potential [300], the order of reactivity being: aqueous chlorine > dichloroisocyanurate = permonosulphate > permanganate and salt > peracetic acid > permanganate > persulphate = hydrogen peroxide. Permanganate does not produce adequate effects unless it is applied from saturated salt solution [301], a situation hardly likely to make it a preferred commercial choice.



10.93

Permonosulphuric acid looks quite promising and appears to have the greatest potential of all other oxidants as an alternative to chlorination. The high reactivity of permonosulphuric acid with wool makes it particularly suitable for continuous treatments, where only a short time is available for reaction. The reactivity can be controlled by pH adjustment (Figure 10.44), the most suitable range being pH 3–5. Lowering the pH increases the rate of oxidation but also increases the likelihood of uneven treatment. Compared with chlorination this product shows the following advantages, although it is less effective in minimising felting of wool fibres [301]:

- No AOX problems
- No yellowing of the wool
- Superior uniformity of treatment
- Almost odourless
- Less likely to attack dyes by oxidative fading.

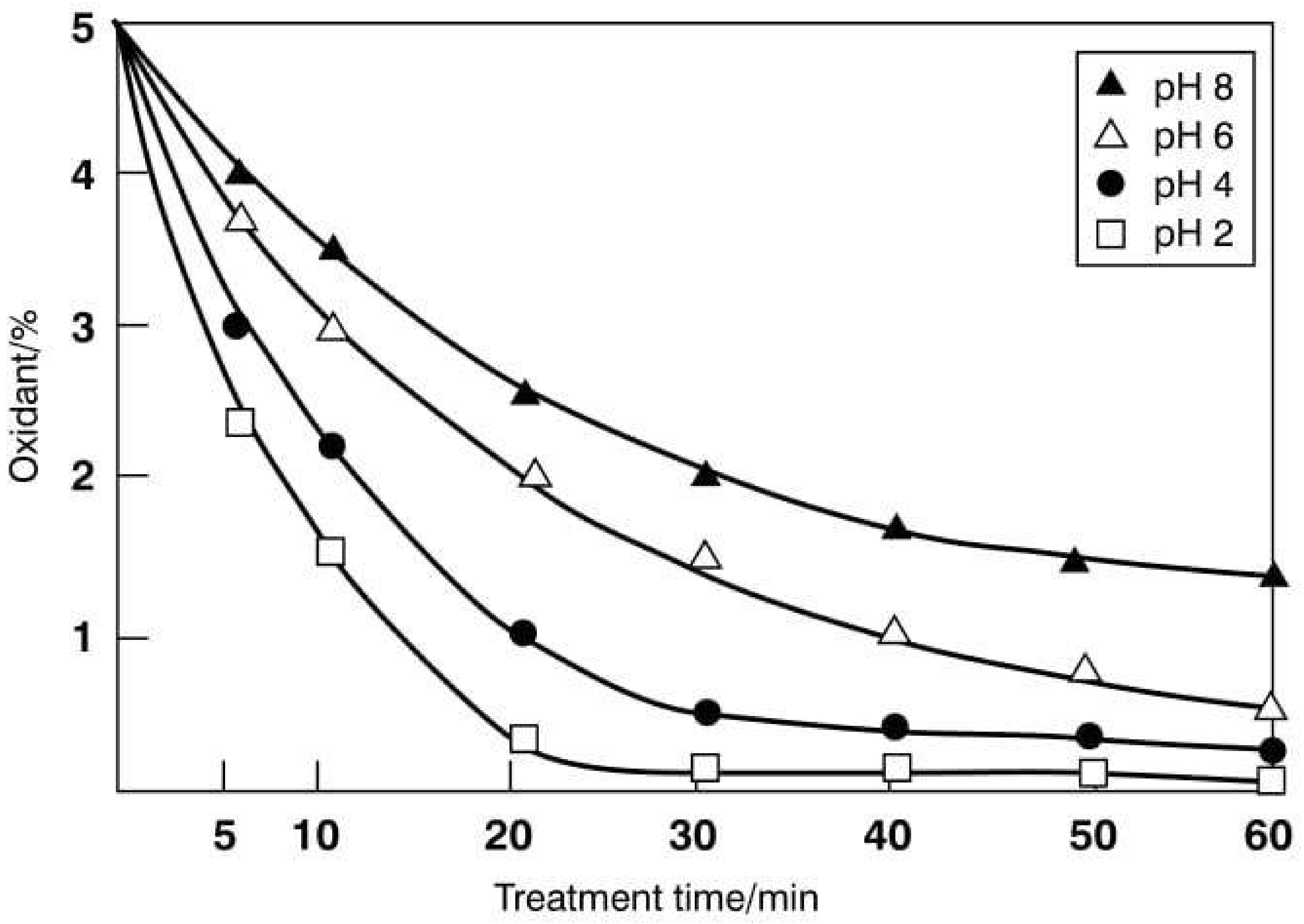


Figure 10.44 Influence of pH value of treatment bath containing a commercial permonosulphate formulation on the rate of reaction with dyed wool at 25 °C and 20:1 liquor ratio [301]

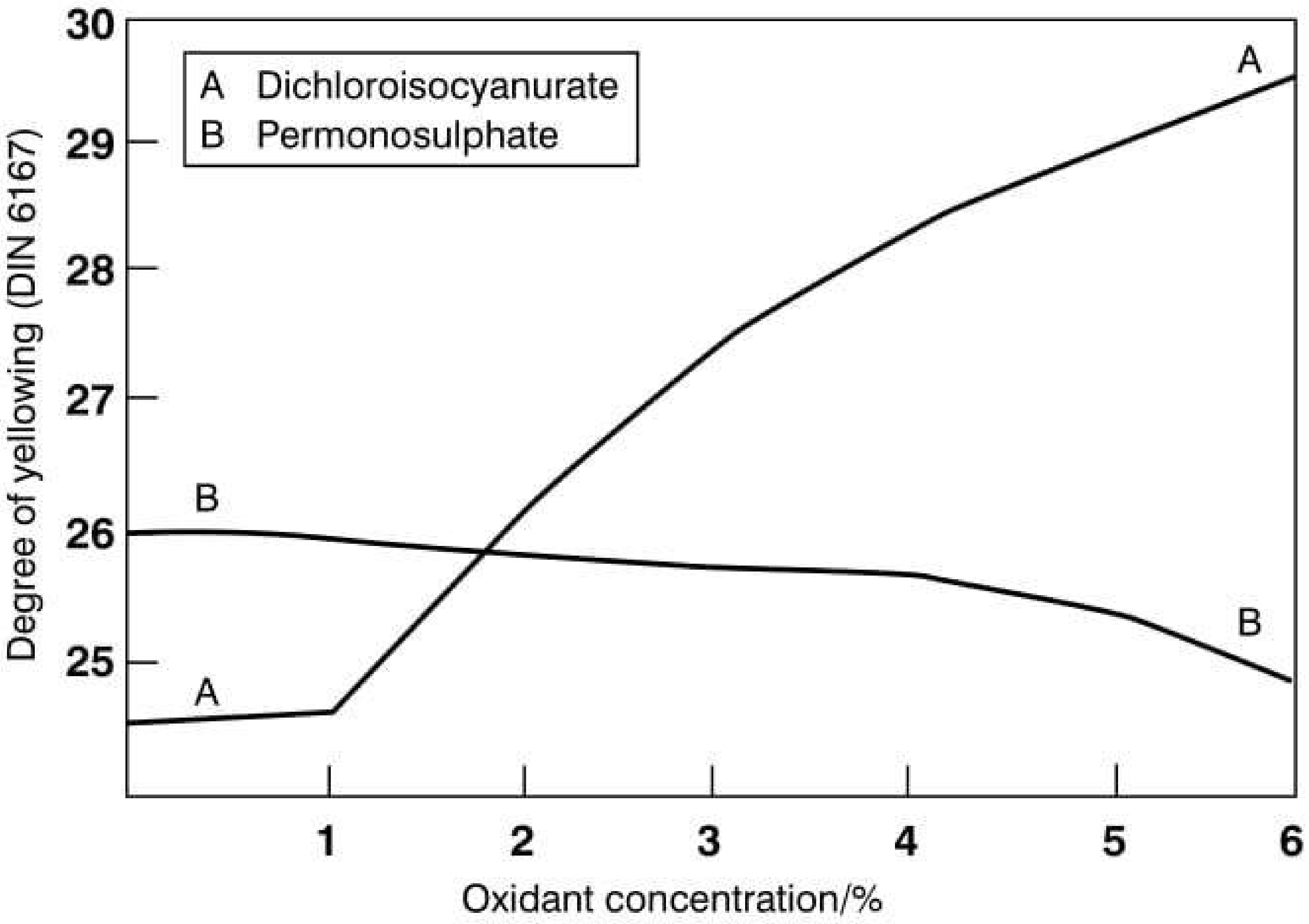


Figure 10.45 Variation of degree of yellowing of wool with concentration of commercial dichloroisocyanurate and permonosulphate formulations [301]

The difference with regard to yellowing of the wool is quite marked (Figure 10.45). Permonosulphuric acid is suitable for use at any processing stage and on all the usual dyeing equipment. The goods are first treated in an acidic liquor at ambient temperature until virtually all the active oxygen has been consumed. A reductive treatment with sodium sulphite is then given in the same liquor at a slightly alkaline pH, followed by rinsing. There is some conflict regarding the parameters involved but careful investigation [301] has led to the following recommendations:

(1) After wetting out, the wool is treated in the same bath with 4–6% of a commercial permonosulphuric acid formulation for 30–60 minutes at 25 °C and pH 4–5

(2) To the same bath are then added 0.5% sodium carbonate and 5% sodium sulphite (pH 8). The temperature is raised to 35–50 °C and maintained for 20 minutes.

Chlorination treatments, of course, are invariably followed by a reductive aftertreatment. In the case of permonosulphuric acid, this is even more important as the sulphite treatment significantly enhances the shrink resistance (Figure 10.46).

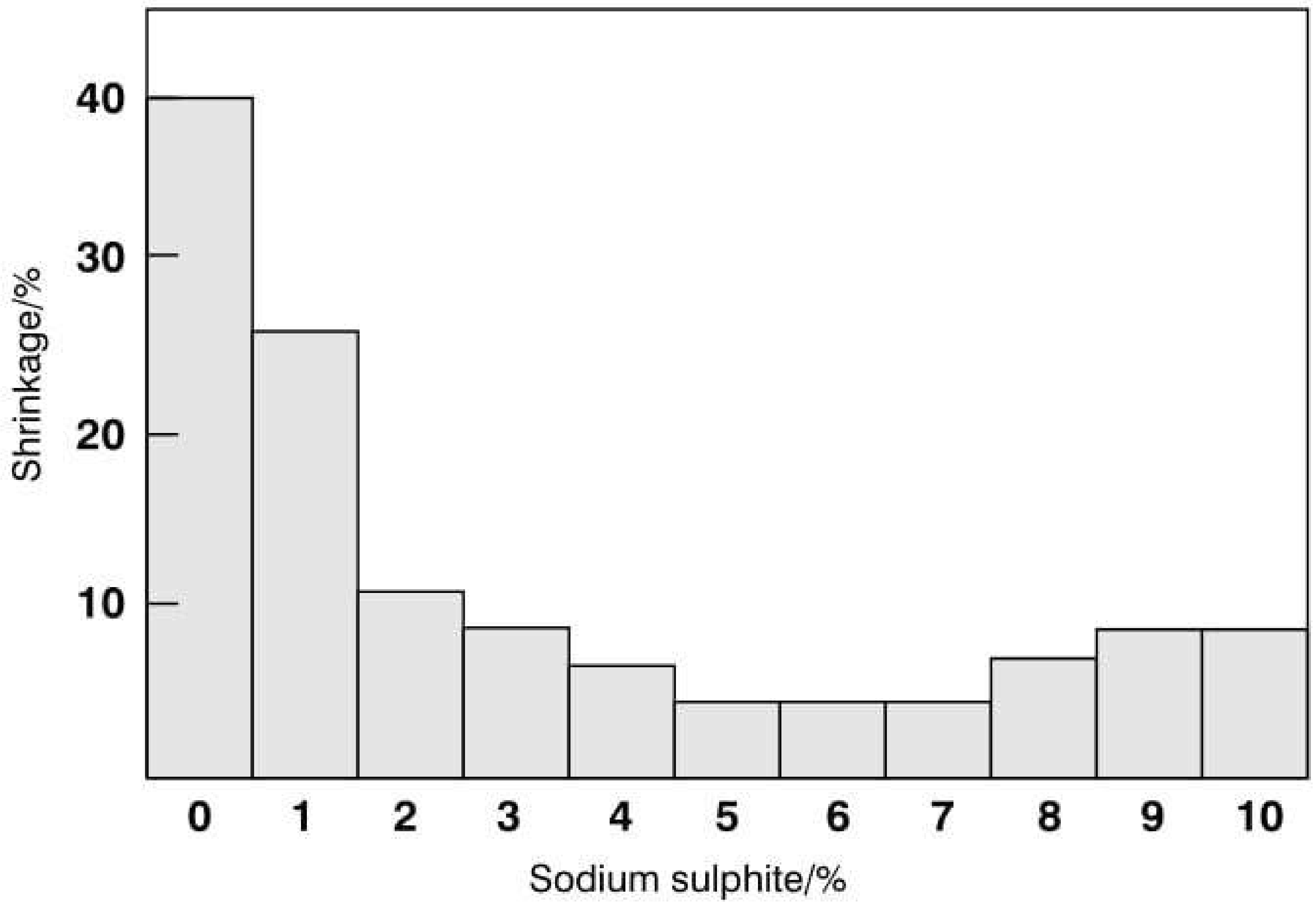
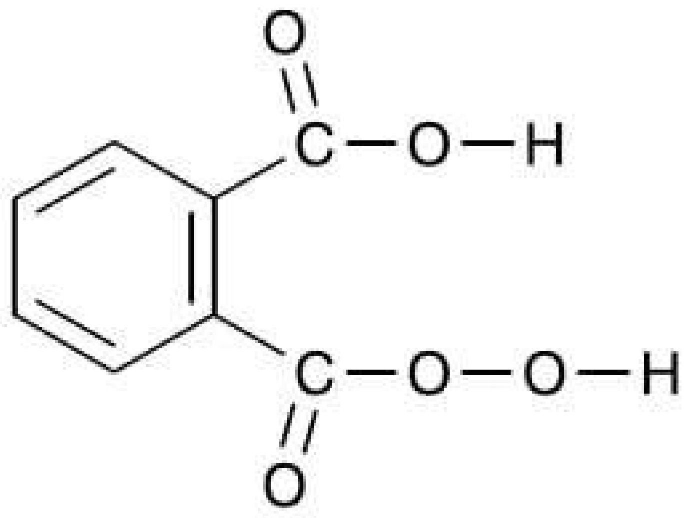


Figure 10.46 Influence of sulphite concentration on the felting shrinkage (IWS TM31) of dyed wool treated with 5% of a commercial permonosulphate formulation [301]; untreated wool shrinkage 60%

Permonosulphuric acid treatment confers only a modest shrink-resist effect which usually needs to be improved by a subsequent additive treatment. It has been suggested [300] that the most likely mechanism for inhibiting felting by permonosulphuric acid treatment is the removal of degraded protein from below the exocuticle, producing a modified surface with a reduced differential friction. The direct formation from cystine residues of low concentrations of Bunte salts has been confirmed, as indicated in Scheme 10.42.

The use of peroximonophthalic acid (10.94) has been reported as a shrink-resist agent [302,303]. When comparing dichloroisocyanuric acid, permonosulphuric acid and permonophthalic acid, it was observed [303] that dichloroisocyanuric acid reacts so rapidly that it is difficult to control the evenness of chlorination. This treatment tends to cause stiffening and yellowing of the wool. Consequently, it is used at lower concentrations than would be needed for full shrink-resist properties, the balance being achieved by subsequent application of a polymer. Permonosulphuric acid does not cause these problems but can only be used successfully on woven cloth, unless a polymer is applied subsequently. Permonophthalic acid does not exhibit the disadvantages of dichloroisocyanuric acid. Furthermore, it can be applied to wool in all its forms to give an adequate degree of shrink resistance without the need for subsequent polymer treatment.



10.94

Since the handle of the wool is not impaired, permonophthalic acid can be applied at a level that gives full protection from shrinkage, this being the reason why the cost of polymer treatment can be avoided. Currently however, there is a major disadvantage: although available for experimental work as its magnesium salt, this is expensive and not yet available in commercial quantities. However, a process has been proposed [303] whereby it can be readily and inexpensively prepared in about 80% yield at 25–30 °C by stirring together phthalic anhydride and hydrogen peroxide in water for about an hour, maintaining the pH at about 5. This process is analogous to that for the preparation of peracetic acid (Scheme 10.37), although phthalic anhydride is less hazardous and easier to handle than acetic anhydride. Nevertheless, the stability of the resulting permonophthalic acid is poor, its oxidising power decreasing through decomposition by about 5% per hour. As with permonosulphuric acid, a subsequent reduction stage using sodium sulphite is needed to eliminate residual oxidant.

Additive shrink-resist treatments

As mentioned previously, additive treatments involve the application of a polymer to the fibre. This is usually prepared before application and contains reactive groups. However, it is also possible to form the polymer *in situ* within the fibres. The traditional approach is to apply the polymer after a subtractive oxidation treatment but environmental concern over AOX problems is increasing demand for additive treatments that can stand alone. There is no denying that the oxidative step can facilitate subsequent treatment with a polymer, since the scission of cystine disulphide bonds to yield cysteic acid residues provides useful reactive sites for crosslinking or anchoring the polymer.

The desirable properties of shrink-resist polymers are [301]:

(1) The treatment must impart maximum shrink resistance.
(2) High substantivity for wool. This is clearly linked with the foregoing requirement. These two factors are particularly important when application takes place after an AOX-free oxidative stage, since such treatments generally impart lower initial shrink resistance than chlorine-based subtractive treatments. Indeed, these two requirements may need to be fulfilled so effectively that the oxidative stage before polymer treatment can be omitted.
(3) Uniform application properties on wool in all forms.
(4) The treatment should not lead to harshness or stiffness of the fabric, thus obviating the need for a softener. Indeed, if the polymer itself provides a degree of softness, this is an added bonus.
(5) Suitable for application by batchwise or continuous methods.
(6) Should have no adverse effects on frictional characteristics of wool fibres or yarns.
(7) Should have no deleterious effects on the colour or fastness of dyes.
(8) Should not contribute to AOX values.

No shrink-resist polymer developed so far meets all the above requirements [301]. There is clearly some similarity with easy-care finishing of cotton. Although effective crosslinking agents are readily available for application to cotton, the morphological complexity of the wool fibre is such that an equally effective polymer has yet to be identified for wool treatment [304].

Still the most widely used shrink-resist polymer treatment is that associated with the Hercosett process. This treatment always follows on from an oxidative treatment with dichloroisocyanuric acid. Despite its popularity, it is doubly suspect environmentally because both the oxidative first stage and the polymer itself contribute to AOX values. The polymer has aqueous solubility and is a cationic polyamide-epichlorohydrin resin, the epichlorohydrin contributing to AOX values. Since the polymer is cationic it has substantivity for the anionic sites in wool, including those produced by the oxidative treatment. The polymer contains azetidinyl cationic groups, which are reactive with a variety of nucleophiles leading to insolubilisation of the polymer [11]. Covalent bonding is also possible through cysteine thiol groups.

Despite the popularity of the chlorination-Hercosett route, it is clear that AOX problems will often enforce the adoption of alternatives, many of which have already been developed. Non-AOX polymers include polyethers, polyurethanes, polysiloxanes, polyquaternary compounds and multifunctional epoxides.

Polyethers of various types are of particular importance and include the following types:

- polyethers solubilised by reactive Bunte salts
- polyethers solubilised by carbamoyl sulphonate groups
- thiol-terminated polyethers
- aziridine-terminated polyethers.

The first two types are of long-standing commercial availability. They are applied using magnesium chloride as catalyst and are crosslinked by addition of ammonia. An important factor is that magnesium chloride induces a cloud point at about 50 °C, leading to the physical form essential for functioning of the polymer [11].

Polyurethanes have also been used for many years. They can be applied from a solvent such as perchloroethylene, but such solvents are increasingly under environmental scrutiny. An aqueous polyurethane formulation is normally applied by padding, followed by baking at 150 °C using sodium carbonate as catalyst.

Polysiloxanes as shrink-resist finishes have been developed from their traditional uses as softeners and water repellents; as such their chemistry is discussed in section 10.10.3. This was a natural trend as many shrink-resist finishes tend to impart a harsh handle to wool.

Polyquaternary compounds are useful in that as well as conferring shrink resistance they may also improve acid dye fastness to wet treatments.

A useful and detailed comparison between specific examples of a polyether, a cationic polysiloxane and a polyquaternary compound is available [301]. This review includes details of practical application via various processing routes available for loose stock, tops, yarn, knitted garments and woven or knitted piece goods. As mentioned earlier no single polymer fulfils all requirements and combinations of different types are sometimes used. Some indication of this is given in Table 10.33.

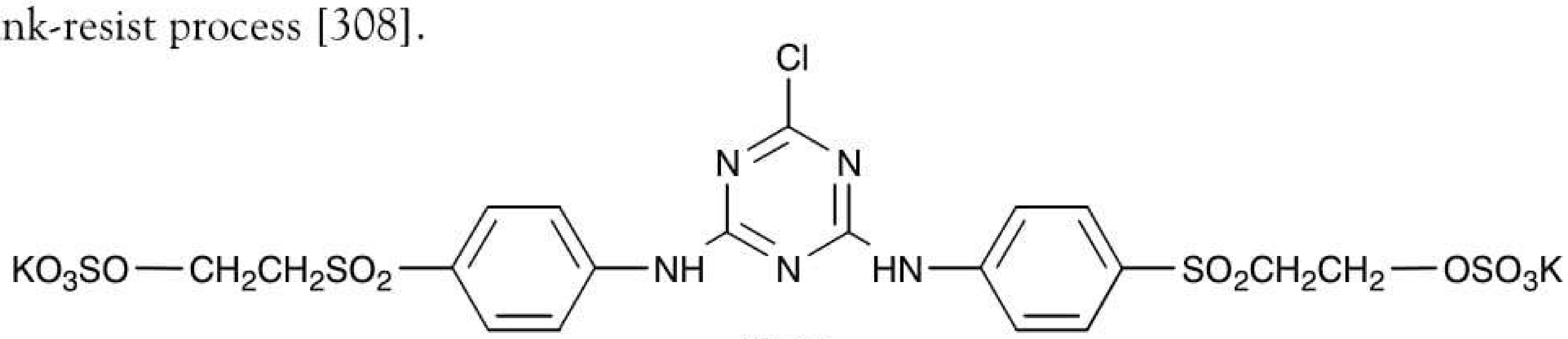
Whilst many methods have been proposed for preventing shrinkage of wool fibres, no satisfactory method operates without some damage to the hydrophobic nature of the fibre surface [305,306]. Nevertheless, it has been claimed that treatment of wool with a multifunctional epoxide, glycerol poly(glycidyl ether), in a saturated solution of sodium chloride gives excellent shrink resistance without impairing the wool surface [305,306]. Apparently this polymer is able to crosslink the cuticular cells and decrease the prominence of their edges. There must be doubts, however, about the commercial feasibility of using the

Table 10.33 Comparison of typical shrink-resist polymers of the non-AOX types for application to wool [301]

Polymer type	Advantages	Restrictions
Polyether with reactive groups	Outstanding shrink-resist effect on pre-oxidised wool Durable soft handle Suitable for piece goods, garments and loose stock. Cost advantage over polysiloxane type	Restricted range of applications Not applicable before dyeing Special dissolving requirements
Polysiloxane with amino groups Semi-microemulsion	Most effective shrink-resist silicone Durable handle after finishing. No crosslinking agent or catalyst required All processing stages suitable Long liquor application after pre-oxidation Padding possible without pre-oxidation	Costly but high-quality finish
Polyquaternary compound	Shrink-resist effect after pre-oxidation Exceptional improvement in fastness All processing stages suitable Improves shrink-resist effect of polyether and polysiloxane types	No improvement in handle Shrink-resist effect weaker than with other types Odour possible on chlorinated wool

saturated brine solution necessary to bring about effective treatment. Such a medium would be difficult to handle, costly and environmentally undesirable, even though it is AOX-free.

The dyeing of wool with bifunctional reactive dyes can enhance its resistance to felting. This observation has been exploited in a shrink-resist process using a specifically designed 'colourless reactive dye' as the effective agent [307,308]. The product developed is the trifunctional reactive compound, dipotassium 2-chloro-4,6-bis(4′-sulphatoethylsulphonylanilino)-*s*-triazine, also known as XLC (10.95). This reactant has substantivity for wool and imparts shrink resistance through crosslinking, being an example of a non-polymeric additive treatment. The crosslinking activity is centred mainly in the low-sulphur microfibrillar proteins through their high content of lysine and histidine residues. A particularly interesting approach is to apply this compound together with reactive dyes, in which case it reacts and crosslinks to an even greater extent than in the usually shorter shrink-resist process [308].



10.95

XLC

A variation of this technique utilises reactive surfactants based on Bunte salt acetate esters of dodecanol and dodecane-1,12-diol [309]. Results using mono-, bi- and trifunctional versions have been reported (10.96–10.98 respectively). These are water-soluble and highly surface-active compounds. They can be applied to wool by padding in combination with 20 g/l sodium sulphite and a locust bean gum thickener to give 100% pick-up, followed by batching at 20 °C for 24 hours. Rinsing completes the process. The results in terms of shrink-proofing are shown in Figure 10.47. It is evident that reactant efficiency increased with functionality: 15%, 10% and 3% of the mono-, bi- and trifunctional agents respectively were required to obtain zero shrinkage, from which it is predicted that only 1–2% of a tetrafunctional agent would be needed. The monofunctional

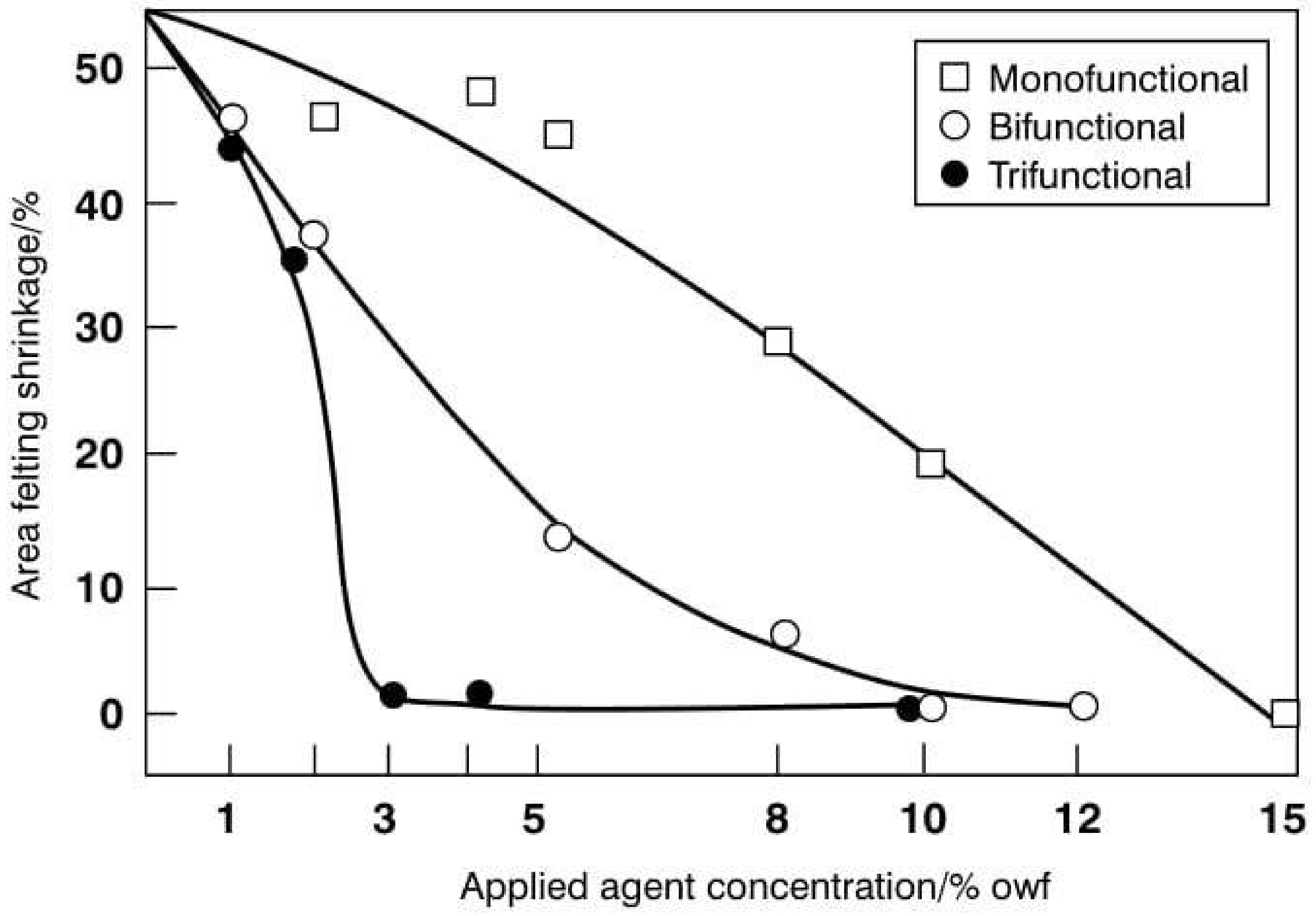
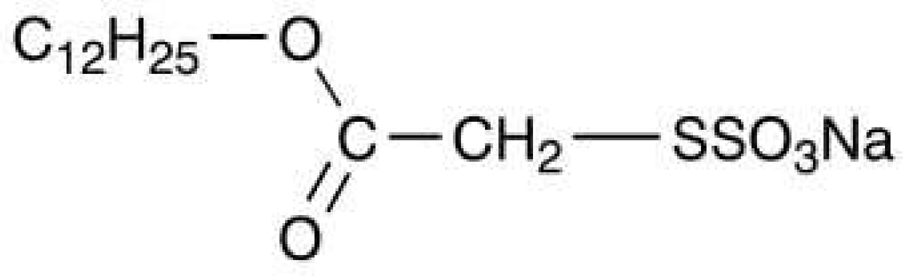
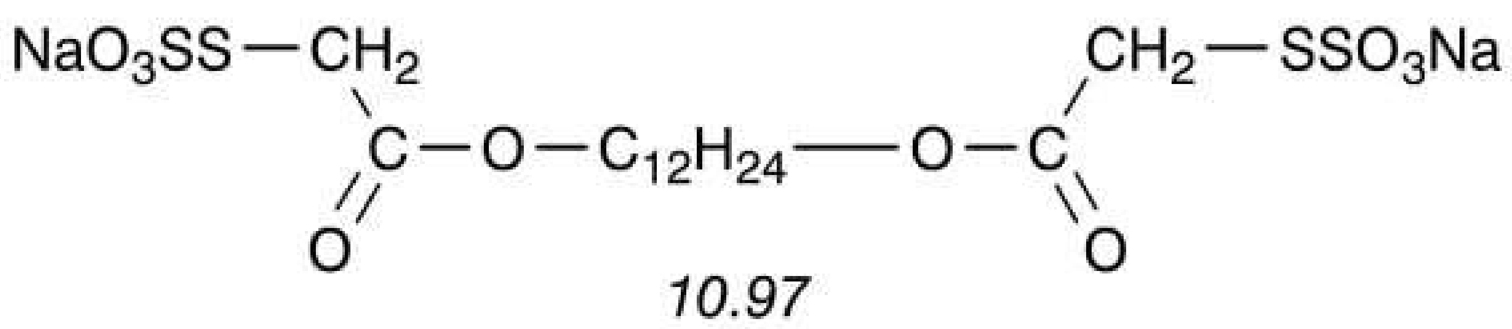


Figure 10.47 Effect on shrink resistance of functionality of agent applied by the pad–batch cold process [309]



10.96
Monofunctional



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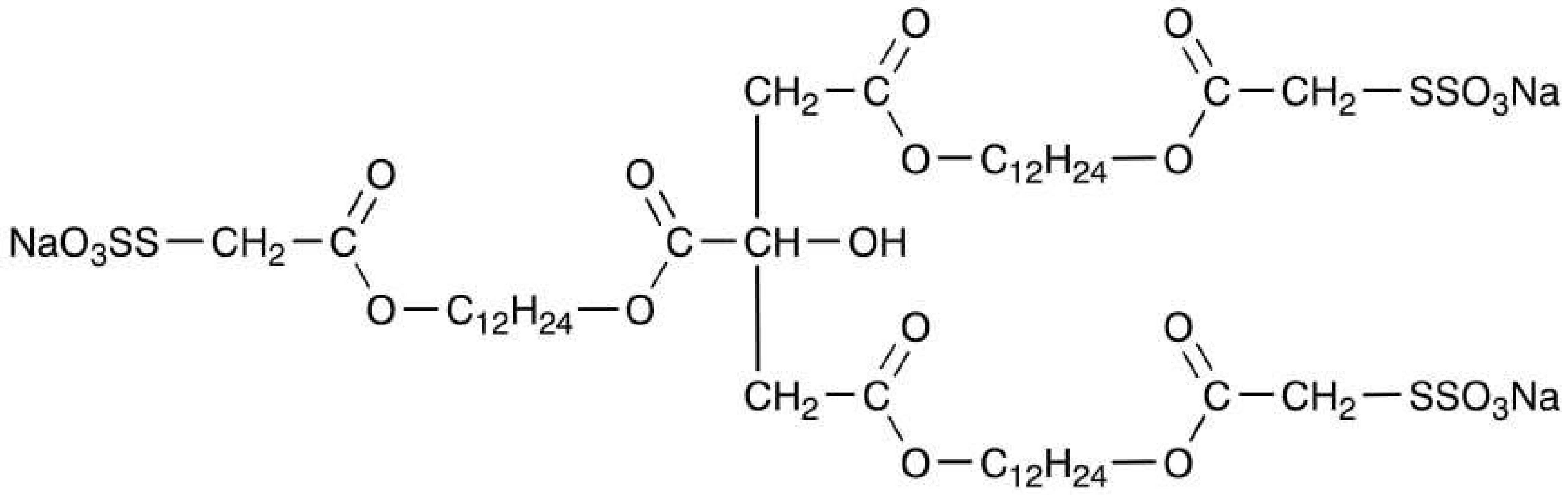
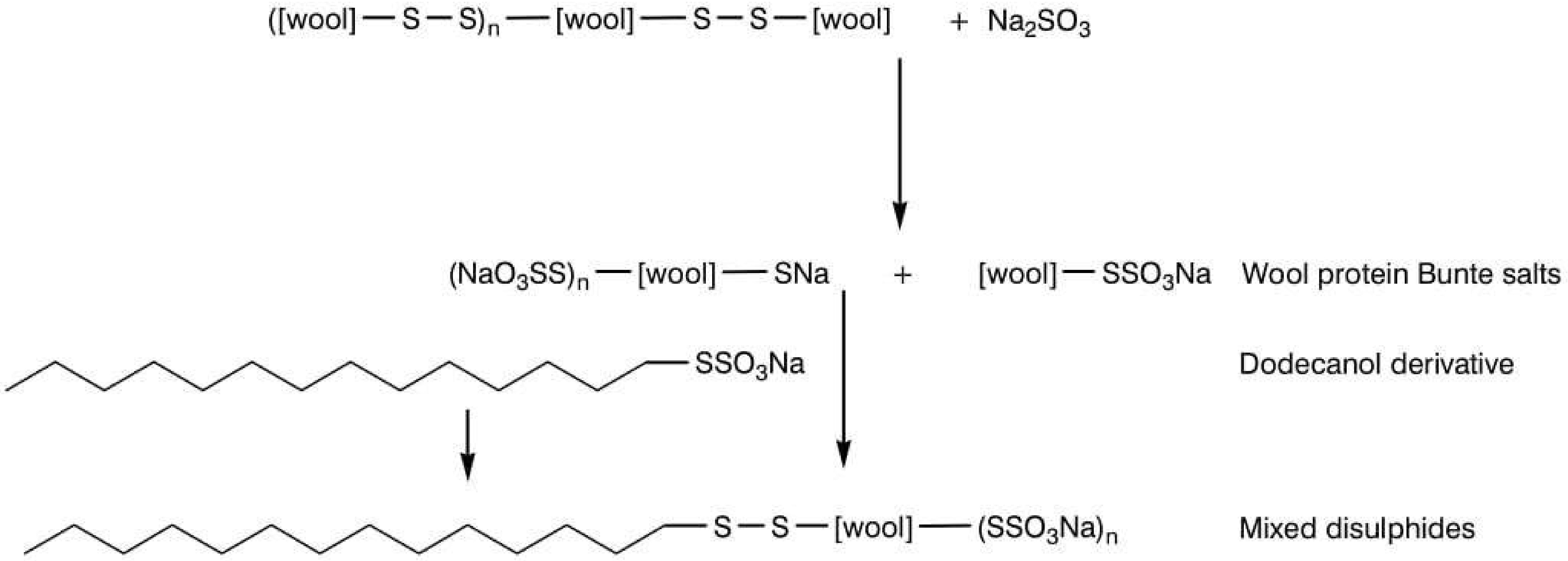
Bifunctional



10.98
Trifunctional



Scheme 10.48

agent in fact gave better results than expected, showing clear evidence in scanning electron microscopy of agent–fibre spot-welding. This is believed to occur via the formation of mixed disulphides from the dodecanol derivative and wool protein Bunte salts from the reaction of disulphide-rich proteins in the wool with sulphite (Scheme 10.48) [309].

Mention has already been made of the effectiveness of corona or plasma treatment in increasing the influence of subsequent or concurrent polymer treatment. As examples of polymers used in this way, mention can be made of reactive cationic polysiloxane [294] and polymerisation on the fibre of tetrafluoroethylene or hexafluoropropylene [299]. Water repellency was also improved by the fluorinated polymers. Tetrafluoroethylene gave superior shrink resistance; this polymer covered the scale edges of the wool, whereas this did not occur with poly(hexafluoropropylene).

Shrink resistance can be achieved by graft polymerisation of vinyl monomers onto wool [292]. Suitable monomers include methyl, ethyl and butyl methacrylate, particularly the methyl ester. Polymerisation is initiated by a redox system, potassium bromate and cobalt(II) acetate, with a co-solvent such as 2-butoxyethoxyethanol to improve both efficiency and selectivity. Grafting of 100% monomer is possible in three hours or less at 50 °C. Ultimately up to 950% can be achieved; such high levels, however, are impractical. There are some rather severe obstacles to the commercial development of this process: methyl methacrylate is flammable and is a respiratory irritant, whilst use of the co-solvent is also undesirable. It is suggested [292], based on a limiting volume model, that the mechanism is characterised by three stages: initial grafting and void-filling within the fibre, disruption of crystalline regions and polymer growth on or through the fibre surface with formation of interfacial bonds (i.e. spot-welding) at high levels of grafting.

Whilst elimination (by oxidation) or masking (by polymer deposition on the cuticular scales) are the accepted mechanisms by which shrink resistance is achieved, there is evidence that other factors need to be considered, particularly as it is possible to obtain a shrink-resist effect without degradation or masking of the scales. A review is available [310] of the mechanism of chlorine-based shrink-resist processes.

Whilst chlorine-based processes are well understood from a mechanistic viewpoint, there are differences between these and the permonosulphuric acid processes. Understanding of the mechanism of permonosulphuric acid treatment has improved in recent years but there are still aspects requiring elucidation [300]. An important difference between these two types of oxidative treatment is that chlorine-based processes lead to scale modification or destruction with zero differential friction as the target. Permonosulphuric acid processes, even when followed by a sulphite treatment, leave the differential friction essentially the same as untreated fibres, apart from some longitudinal striations at the base of the scales and some detachment and rounding of scale edges [300].

Chlorine water acting on wool produces Allwörden bubbles or sacs by raising of the epicuticle [11]. This occurs through the formation of osmotically active oxidation products. Cleavage of peptide bonds and especially oxidation of the disulphide bonds to produce sulphonic acid residues result in the formation of soluble peptides responsible for the increase in osmotic pressure within the semi-permeable membrane. Permonosulphuric acid treatment, with or without a sulphite aftertreatment, also forms Allwörden sacs, as do hydrogen peroxide, potassium permanganate and peracetic acid [300]. On immersion in water, wool treated with permonosulphuric acid shows major decreases in magnitude of friction and differential friction compared with untreated fibres, especially following a sulphite aftertreatment. This may be attributed to degraded protein at the fibre surface acting as a lubricant or to changes in swelling properties of the wool surface.

The sulphite aftertreatment is particularly important with permonosulphuric acid treatment. Evidence for the underlying mechanism is available from analysis of sulphur oxidation products formed in the various processes (Table 10.34). It is evident from these results that the concentration of $[RSSO_3]^-$ anionic groups necessary to change the hydration of the fibre surface is achieved by the reaction of bisulphite with cystine monoxide residues to give the required cysteine-*S*-sulphonate groups [311].

Table 10.34 Relative amounts of sulphur oxidation products formed during shrink-resist processing of wool [11,311]

Treatment	Oxidation product	Frequency (cm^{-1})	Quantity
Chlorine-Hercosett	Cysteic acid (RSO^-_3)	1042	***
Permonosulphate			**
Permonosulphate + bisulphite			*
Chlorine-Hercosett	Cystine monoxide (RSOSR)	1076	*
Permonosulphate			***
Permonosulphate + bisulphite			*
Chlorine-Hercosett	Cysteine-S-sulphonate ($RSSO^-_3$)	1024	**
Permonosulphate			*
Permonosulphate + bisulphite			***

In the case of polymer deposition, it has been pointed out [293] that the masking effect at the scale edges may be less important than mutual adhesion of fibres in the yarn, since the thickness of the polymer film (0.1 μm) is much less than the average height of scale edges (1 μm). This effect is more analogous to spot-welding.

The particular requirements of shrink-resist processes in relation to wool fabric printing have been described [312]. In addition to dimensional stability, there is a need for ease of diffusion and absorption of dyes in printing. Chlorination is particularly effective because the rapid reaction limits the oxidative attack to the fibre surface. Dye affinity and the hydrophilicity of the fibre are increased by the anionic sulphonic acid groups formed and the surface barrier to diffusion is lowered. However, this is an AOX-loading process. Permonosulphuric acid, although AOX-free, is an inadequate preparation for printing even with a polymer aftertreatment. Hydrogen peroxide, activated by the recyclable catalyst sodium tungstate, offers a suitable process [312] that is AOX-free. Oxidation remains concentrated at the fibre surface because of the high reactivity of peroxide, giving results analogous to those from chlorination. A subsequent polymer treatment may also be given. The process involves padding to 75% pick-up in a solution equivalent to 8% by weight of sodium tungstate and 3% by weight of hydrogen peroxide. The padded fabric is rinsed after a reaction time of two minutes and the tungstate can be recovered from the rinsing water.

10.5.6 Combined processes

The economics, at least on paper, of combining two or more processes to gain major savings in time and energy have long been sufficiently attractive to motivate research in this direction. For example, one-stage desize–scour, scour–bleach, desize–scour–bleach, scour–dye and even (paradoxically enough) bleach–dye operations have been, and are, operated. The major disadvantage of such combined processes stems from difficulties of operation, especially compounded where there is a high probability of incompatibility, as in enzyme desizing–bleaching or in bleaching–dyeing. In addition, any process that is combined with scouring and/or desizing may be subject to interference from the products desorbed or decomposed by those processes. Under these circumstances the choice of chemical additions becomes critical. For example, in combined desizing–bleaching the enzyme must be stable to oxidation and both processes must be operable under the same conditions of time, temperature and pH. Similarly, other products added, such as surfactants for wetting and detergency or metal ion sequestering agents, must fulfil their primary task and not interfere with other functions, while themselves being unaffected by the conditions.

Scour–dye operations in particular need careful planning backed by detailed knowledge, especially in regard to the effects of desorbed impurities on the stability and exhaustion of the dyes. In the combined scouring and dyeing of wool or nylon with acid dyes the detergent should ideally function as a levelling agent. The crucial factor in scour–dye processes involving disperse dyes is stability of the dye dispersion in the presence of the detergent and desorbed impurities. This becomes increasingly critical at higher temperatures (say 130 °C) and with difficult application conditions, such as tightly woven fabrics on beams. Hence such operations are more frequently used in jet dyeing, for example. Incompatible surfactants and greasy soil can have disastrous effects on dye dispersions, leading to agglomeration of dye particles and deposition of coloured oily stains on the substrate, with extensive breakdown of the dispersion in severe cases. Surfactants can have a highly selective effect on the rate and extent of exhaustion of disperse dyes and must therefore be selected accordingly.

In spite of these difficulties successful combined processes are indeed operated, although they require vigilant monitoring. The promised economies must not be squandered by lost processing time and costs of damage and reprocessing. It would be surprising if the manufacturers of dyes and chemicals were more enthusiastic than textile processors about such combinations, in view of their understandable caution about guaranteeing the behaviour of individual products in circumstances for which they are not intended. Now that environmental and economic factors limit research into new products, the fusing of normally sequential processes into a single one will remain a worthwhile technical and economic goal.

Possibilities for combining the three main preparatory processes for cotton (desizing, scouring and bleaching) remain economically attractive. One process for achieving this involves treatment of loomstate cotton with an aqueous solution containing 3 g/l sodium chlorite, 1 g/l hydrogen peroxide, 2 g/l nonionic wetting agent and 10 g/l disodium hydrogen phosphate for 90 minutes at 95 °C, pH 10 and 20:1 liquor ratio [313]. In another process the fabric is impregnated with 20 g/l sodium chlorite, 0.05 g/l potassium permanganate and 2 g/l nonionic wetting agent, followed by treatment for 30–60 minutes at 90 °C and pH 10 [314]. The concentrations of the oxidants, the pH and time of treatment were critical, however. In a modification of this process, impregnation with 20 or 30 g/l sodium chlorite, respectively 3 or 1 g/l potassium chromate and a nonionic wetting agent is followed by treatment for 90 minutes at 90 °C and pH 6 [315]. All these processes are subject to the usual criteria regarding machinery that is resistant to corrosion by sodium chlorite, whilst the discharge of effluent containing chromate has environmental implications in many countries.

An AOX-free alternative [316] is impregnation with 4 g/l hydrogen peroxide, 8 g/l urea and 2 g/l nonionic wetting agent, then treatment for 60 minutes at 95 °C, pH 8 and 20:1 liquor ratio [316]. This results in a bleached fabric with excellent wettability and without serious fibre degradation. The urea interacts with hydrogen peroxide to form an unstable complex, which then decomposes to form hydroxyl and perhydroxyl radicals, according to Scheme 10.28 [316]. Urea exhibits undesirable environmental characteristics in some respects, however.

In all the above processes, the optimised quantities of the chemicals indicated will be specific to the substrate quality evaluated. They would require further re-optimisation for each substrate to take account of the type and concentration of size, the presence of other impurities and the degree of natural yellowness. In particular, the amount of oxidant will need to be adjusted to give the optimum balance between oxidative desizing and the degree of bleaching required.

A commercially established system for the combined desizing, scouring and bleaching of cellulosic fibres and blends is the Raco-Yet (Kleinewefers) system [317,318]. The fabric is impregnated successively with 23–26 ml/kg sodium silicate (38°Bé), 32–40 g/kg sodium hydroxide (100%), 20–26 ml/kg Cottoclarin AS and 40–65 ml/kg hydrogen peroxide (50%) before steaming. Cottoclarin AS is designed specifically for this process, having excellent wetting properties, freedom from foaming, high dispersing, emulsifying, complexing and detergency powers. The process is applicable to a variety of size polymers and their mixtures, including starch, hydroxypropyl starch, poly(acrylic acid), poly(vinyl alcohol), carboxymethylcellulose and polyesters. Desizing, boiling-off and bleaching can be achieved in 1–3 minutes. Savings in processing costs and exceptional flexibility of operation are claimed, since recipe changes can be made in less than one minute. It is essential to carry out a thorough analysis of each substrate and to adjust the recipe and processing speed accordingly. Table 10.35 gives an indication of the flexibility of the process together with typical results [318].

Table 10.35 Examples of application of the Raco-Yet system to cellulosic fabrics and blends [318]

Fabric (130% pick-up)*	100% Cotton 320 g/m^2		100% Cotton shirting 190 g/m^2		Polyester/ cotton 65:35 170 g/m^2		Cotton/ polyester 88:12 290 g/m^2		Polyester/ viscose/ linen 70:20:10 185 g/m^2	
Size type	Starch		None		PVA		Starch		None	
Sodium silicate (38 Be) ml/kg	26		26		23		26		26	
Sodium hydroxide (100%) g/kg	40		40		32		40		40	
Cottoclarin AS ml/kg	26		26		20		26		26	
Hydrogen peroxide (50%) ml/kg	65		65		40		65		65	
Treatment time (min)	2		1.5		1.5		3		1.5	
Running speed (m/min)	60		80		80		40		80	
Evaluation	Grey	Treated	Grey	Treated	Grey	Treated	Grey	Treated	Grey	Treated
Absorptivity (mm)										
After 15 seconds	0	15	0	18	0	15	0	32	0	18
After 30 seconds	0	20	0	24	0	20	0	41	0	25
After 60 seconds	0	25	0	31	0	25	0	52	0	33
Whiteness:										
%REM	56.0	80.3			90.2	112.5	50.1	86.1	61.8	81.2
Berger	16.1	64.0			104.5	152.6	43.3	75.7	20.1	70.8
Degree of polymerisation	2760	2280	3080	2670						

* concentrations are per kg of fabric

It is possible to use an enzyme with hydrogen peroxide in a combined desize–bleach but great care is needed in selection of the enzyme and optimisation of the concentrations [319].

Mercerising (high concentrations of alkali; cold) is particularly difficult to combine with desizing, scouring and peroxide bleaching (lower concentrations of alkali; hot). Nevertheless, a combined one-stage desize, scour, bleach and slack mercerise process has been attempted [320]. This involves impregnation of the fabric in a 10–30% sodium hydroxide liquor containing 20 g/l hydrogen peroxide and 50 g/l trichloroethylene for

3 minutes, the results being dependent on impregnation temperature (20–100°c). The fabric is squeezed and (without predrying) is heated to 120 °C, the results being influenced by the duration of the heating step. It is claimed that, with a wet immersion treatment for 3 minutes at 40 °C and subsequent treatment for 30 seconds at 120 °C, the physical properties of the treated cotton are similar to those from a conventional two-stage approach. The use of trichloroethylene, of course, is highly sensitive both environmentally and as a health hazard (toxic to the liver).

An electrochemical system combining scouring, mercerising and bleaching has been proposed. It is a non-polluting method based on an electrochemical cell, the cathode of which produces the base to mercerise and bleach, whilst the anode produces an acid to neutralise the base remaining after mercerisation [321].

A mercerising-type effect and bleaching of viscose fabrics can be achieved simultaneously using liquid ammonia, the bleaching agent being a peroxidated urea derivative that causes less damage than conventional oxidants, together with improved dye absorbency [322].

Mercerising has been combined with vat dyeing in a continuous process [323]. Cotton fabric is padded with an aqueous suspension of a vat dye in a sodium chloride solution containing caustic soda for mercerising. After drying, the dyeing is developed by padding in an alkaline solution of reducing agent, steaming and soaping.

Further combined processes involving dyeing include:

(1) Dyeing cotton yarn with selected direct dyes and simultaneous bleaching with peroxide. It is claimed that the peroxide also increases the colour yield [324]
(2) Combined dyeing and easy-care finishing of cotton using bis-nicotinotriazine reactive dyes and DMDHEU in a pad–dry-HT steam process [325]
(3) Combined dyeing and finishing of polyester/cotton using a liquid ammonia medium [326]
(4) Dyeing polyester/cotton with reactive and disperse dyes and imparting a crease-resist finish [327].

10.6 DISPERSING AND SOLUBILISING AGENTS

10.6.1 Dispersing agents

Dispersing agents are substances that promote the more or less uniform and stable suspension of relatively small particles in a given matrix. We are concerned here with the most common type of dispersion encountered in textile coloration, the solid-in-water systems typified especially by disperse dye technology, as well as the insoluble forms of vat and sulphur dyes. Pigments are also extremely important examples of solid-in-liquid dispersions but form a specialised case fully dealt with in Chapter 2. Also excluded from this section are other systems that depend mainly on a large increase in viscosity for their suspending action; these are more appropriately dealt with in section 10.8. An in-depth account is available [328], covering in particular the essentials of colloid science as applicable to dispersions, the preparation of dispersions (solid-in-liquid and liquid-liquid) as well as foams (section 10.11). An extensive account of the uses of dispersions is also available [329]; this includes pigments and the incorporation of colorants in polymer melts but is otherwise concerned with non-textile applications.

Any formulation of solid particles in a liquid medium is more or less unstable as a result of

(a) gravitational settling effects and (b) attractive forces between particles tending to lead to particles adhering, thus increasing the susceptibility of the system to gravitational effects. Two aspects need to be considered: the initial preparation of the dispersion, and its subsequent stabilisation during storage and use; only rarely will one agent satisfy the needs of both. Individual dyes vary widely in their requirements and any given dye may require different treatments depending, for example, on its microcrystalline form and the application processes for which it is intended. Therefore specific types of dispersing agents, or mixtures of them, are frequently needed to obtain the optimum dispersing action. There are two main groups of such agents:

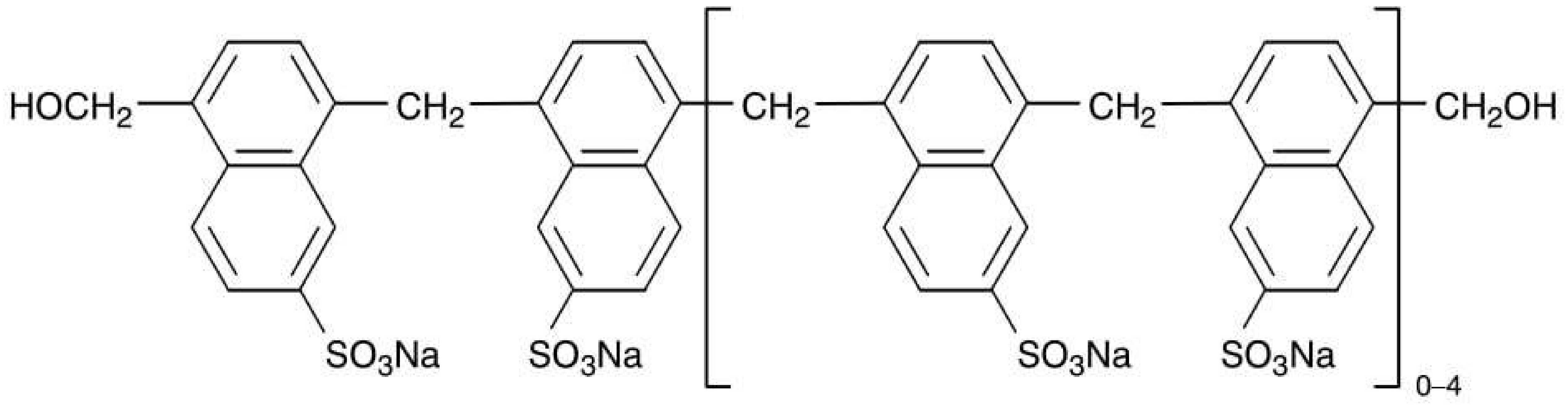
(1) Surfactants, mainly of the anionic and nonionic types
(2) Water-soluble polyelectrolytes, most usually of the anionic type.

The chemistry of surfactants has been described already. They usually play a subsidiary role in dispersions involved in textile coloration. The polyelectrolytes may be conveniently divided into two categories:

(1) Acrylic acid copolymers, sulphonated polyvinyl compounds, alginates and carboxymethylcellulose. Some of these may require addition of other chemicals (e.g. alkali) in order to ensure aqueous dissolution. These polymers are less important as dispersing agents for disperse, vat and sulphur dyes than in areas such as pigment applications and as thickeners in textile printing or migration inhibitors in continuous dyeing (section 10.8).
(2) The condensation products of formaldehyde with arylsulphonates or lignosulphonates, these being the major types of polyelectrolyte of interest in the manufacture and use of disperse dyes [330,331].

As with surface-active agents, the detailed chemistry of these products is a good deal more complicated than is indicated by the nominal structures frequently quoted. Most commercial products are mixtures of which the nominal structure represents a basic type only. Indeed, the detailed chemistry of the more complex products is still only partially understood. These provisos should be borne in mind when considering the structures given below.

The sulphonated aromatic condensation products form a large and varied group, since formaldehyde will condense with many aromatic compounds [330], including sulphonated arylamines, phenols and aliphatic ketones; the range of commercially important products is relatively limited, however. One of the oldest is the condensation product of naphthalene-2-sulphonic acid and formaldehyde (10.99), in which the degree of condensation is thought to



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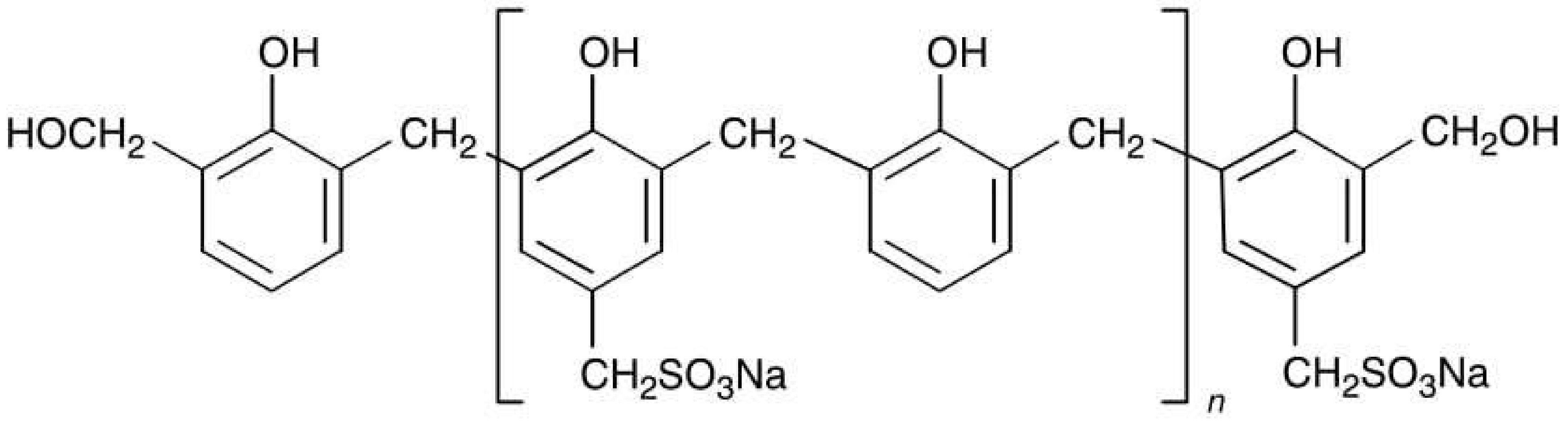

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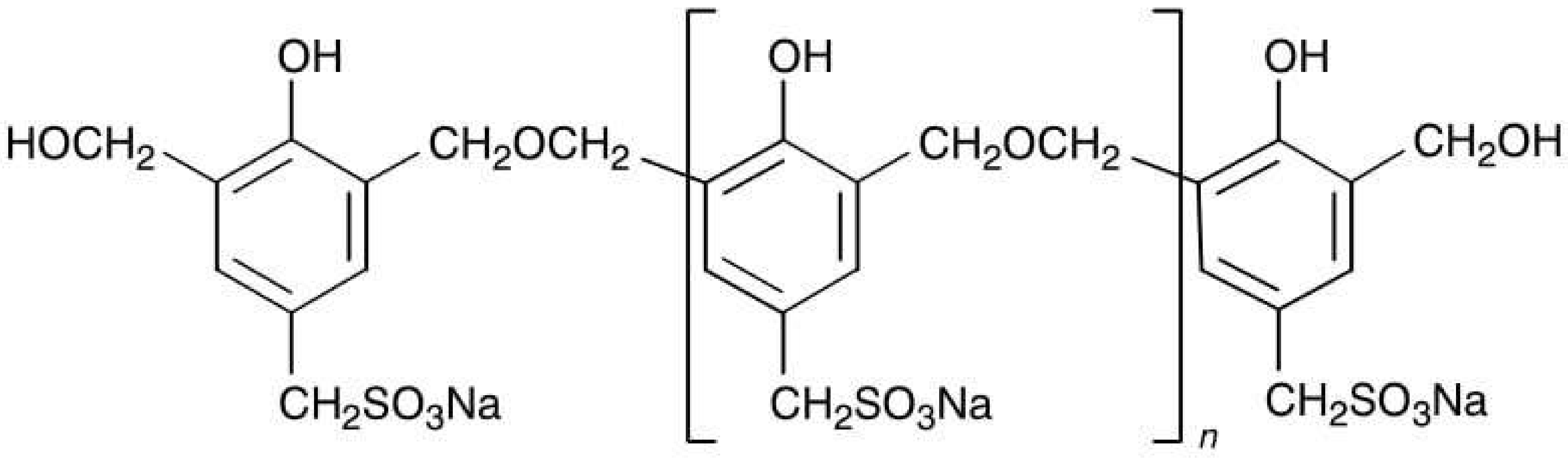

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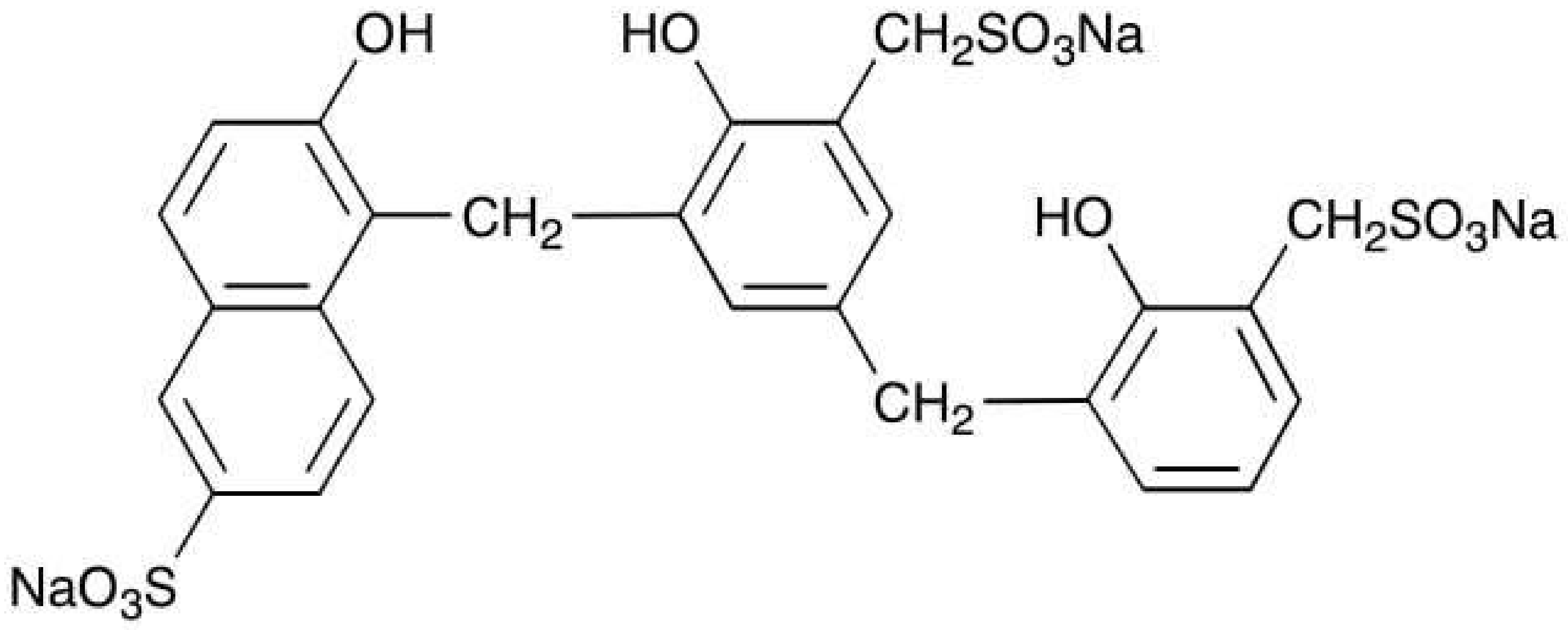

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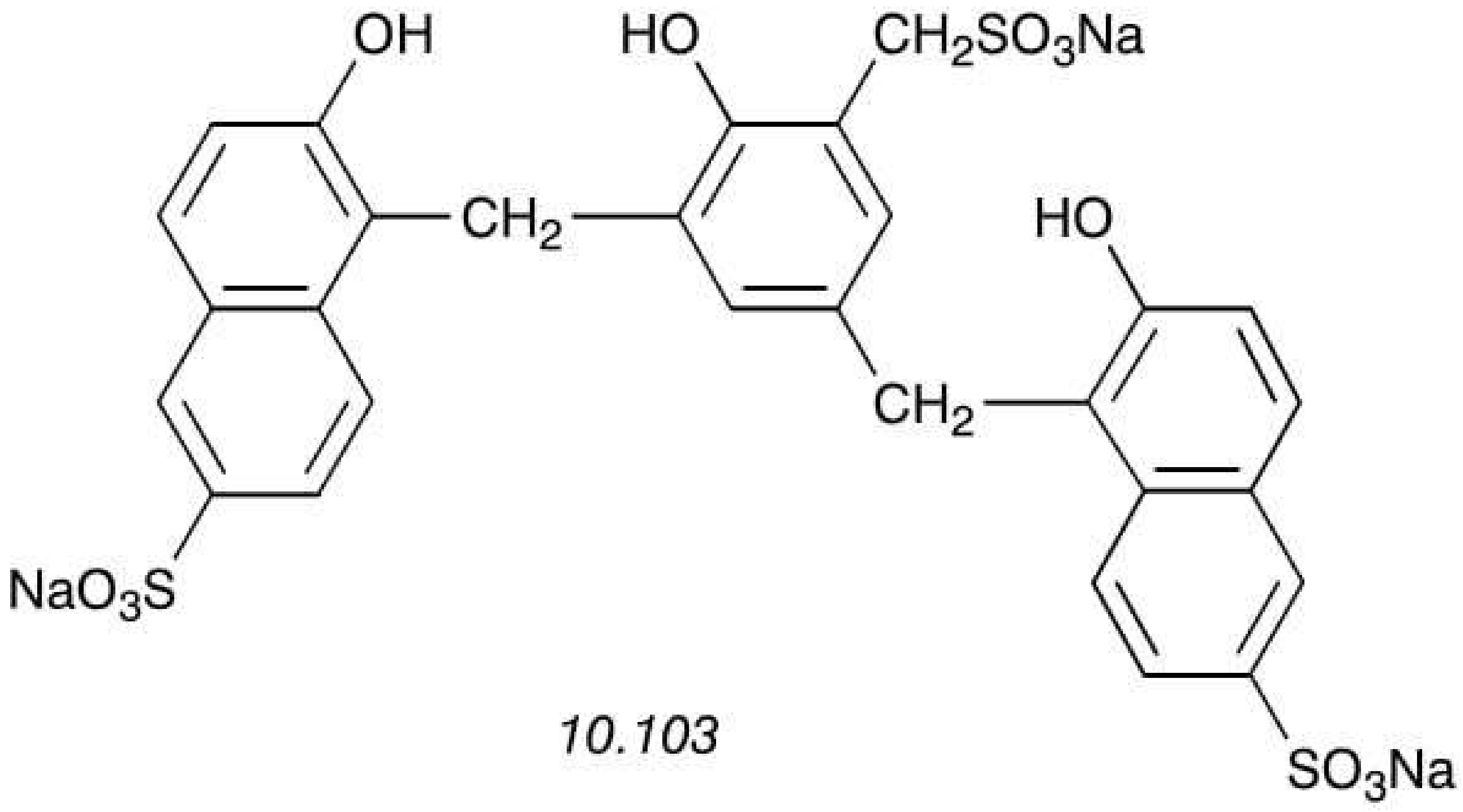


10.103

correspond to between two and ten naphthalene units, although the quantitative distribution of the condensates varies widely. Also of importance are the similarly structured condensation products of (a) phenols with formaldehyde and sodium sulphite (structures 10.100 and 10.101, depending on molar ratios) and (b) *p*-cresol and 2-naphthol-6-sulphonic acid with formaldehyde and sodium bisulphite (10.102 and 10.103). The types represented by structures 10.100–10.103 are also widely used as syntans (section 10.9.4).

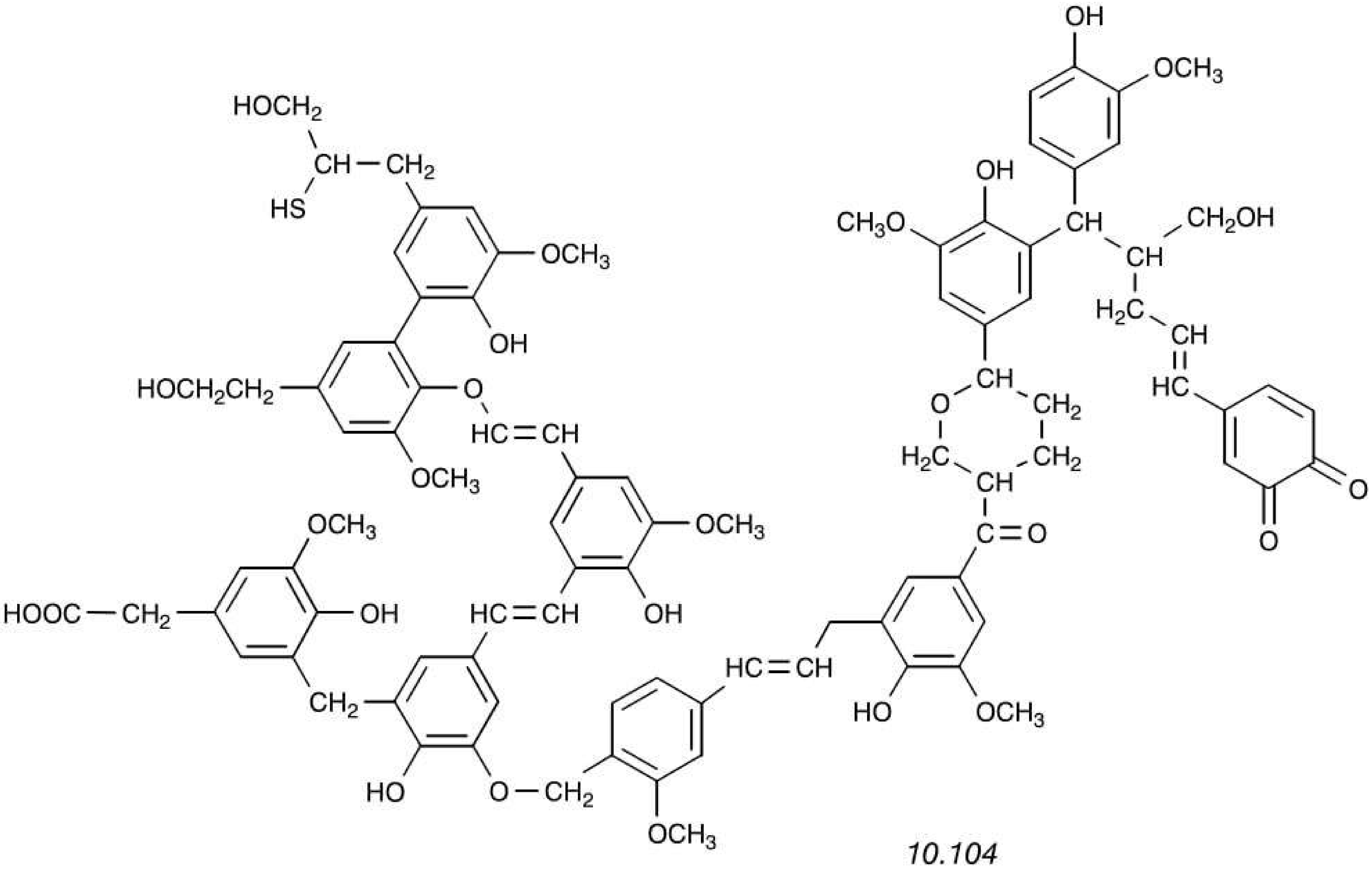
The lignosulphonates comprise a variable group of products derived from wood pulping.

Their highly complex structures are only partially understood, although enough is known to enable representative structures to be proposed showing the major functional groups. There are two distinct processes whereby lignins are extracted. The first is an acidic digestion process in which the wood is pulped with sulphite or bisulphite. The second is an alkaline process, the so-called kraft process, in which the wood is treated [331] with sodium sulphide in autoclaves at pH 13 and 160–175 °C. The product is precipitated by careful addition of acid, filtered off and washed free from inorganic ions, then sulphonated to increase its aqueous solubility. Structure 10.104 has been proposed as being representative of kraft lignin prior to sulphonation [331]. An alternative partial representation of a lignosulphonate structure [330] is that of structure 10.105, which shows sulphonation as having taken place mainly at the CH=CH link. The molecular configuration is such as to give spherical particles. The final nature of the product varies enormously depending, amongst other things, on:

(a) purity, especially the content of electrolytes such as sodium sulphate
(b) the number of hydroxy groups present
(c) the degree of sulphonation
(d) the relative molecular mass (2000–1 000 000) and its distribution.

This wide variability need not be a disadvantage provided it can be controlled to give reasonable consistency from batch to batch, since this enables products to be designed to give the optimum efficiency for the particular application concerned. The kraft lignins provide greater scope for modification, particularly of the degree of sulphonation and molecular size, and are also much more amenable to production in low-electrolyte forms [331]. Further information on the modification and behaviour of lignosulphonate dispersing agents is given in section 12.6.1.

The basic similarity between these major types of dispersing agents and the surface-active agents discussed earlier lies in their amphiphilic nature (the possession of a combination of



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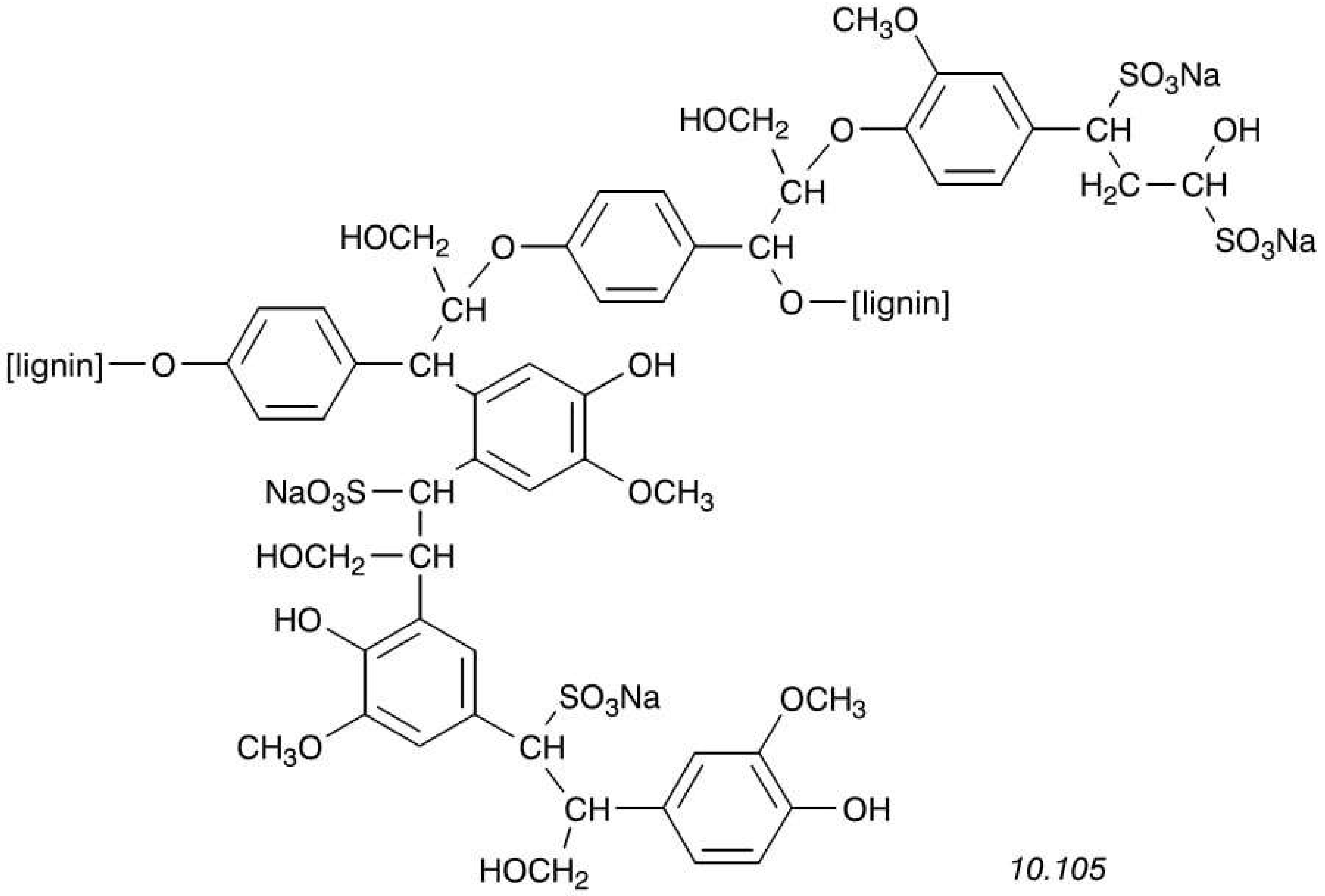


10.105

hydrophobic and hydrophilic moieties). The polyelectrolytes, however, are of much larger molecular size than conventional surface-active agents.

When converting a conglomerate mass of relatively coarse particles into an aqueous dispersion (as in the manufacture of disperse dyes) there are two broad phases to be considered. In the first phase the dual aim is that of mechanically grinding the particles down to the required size and of obtaining as narrow a range of particle size as possible during the actual preparation of the dispersion. Maintaining these particles in a stabilised suspension constitutes the second phase.

Particle size alone is not the main criterion; its distribution is equally important. This is because all dispersions are metastable. As well as tending to settle as a result of gravitational forces, there is also a thermodynamic tendency towards a reduction in the free energy of the system. This is manifest as a continuing increase in particle size leading ultimately to a severe deterioration in the dispersion quality (as already mentioned). Smaller particles tend to be attracted towards larger particles, with which they then form even larger particles. The opportunity for particle growth is therefore much less when all the particles are of similar size than when the range of sizes is large.

The actual comminution of the coarse particles is usually carried out mechanically – for example, by grinding an aqueous slurry of the colorant in a rotatory mill containing relatively large, hard and inert grinding media such as pebbles. The process is facilitated by efficient wetting of the particles and lowering of interfacial tension. It is therefore preferable to add dispersing agents that have some surface activity and good wetting properties. Microfissures are created as the particles are broken down. The surface-active properties of the dispersing agent enable it to penetrate these microfissures, hindering agglomeration and facilitating further comminution. The amphiphilic agent becomes adsorbed and oriented on the surfaces of the particles, providing a protective sheath of like repellent charges, the forces of which eventually exceed the forces of attraction between the particles and thus stabilise the dispersion. This protective sheath becomes of critical importance during the second phase by stabilising the suspension of particles, both in storage and in subsequent use. Hence different dispersing agents may well be required to provide optimum dispersing and stabilising power in the two phases.

The dual amphiphilic nature of the polyelectrolyte condensates and lignosulphonates described above, with their hydrophobic groups juxtaposed with many polarisable ionic groups, renders them highly efficient dispersing agents. It is necessary, however, to make a careful choice from the various grades of dispersing agents available with respect to their molecular size and charge distribution. Optimum dispersing ability depends on matching the steric, hydrophobic and ionic properties of the dispersing agents relative to the characteristics of the particles to be dispersed. The forces that may be operative in adsorption of surfactants onto disperse dye particles have been listed [330] as ion exchange, ion pairing, hydrogen bonding, van der Waals dispersion forces, polarisation of π–electrons on aromatic systems and hydrophobic interaction. It follows that anionic and nonionic surfactants, judiciously selected, may be used in conjunction with the polyelectrolytes to aid the dispersing mechanism [330].

10.6.2 Solubilisation

It is necessary to differentiate between *simple solutions* and the process of *solubilisation* in *colloidal solutions*. A non-colloidal solution is a homogeneous single-phase system of a solute dissolved in a solvent, examples being an aqueous solution of sodium chloride or a solution of methylnaphthalene in acetone. The term *solubilisation* refers to the homogeneous mixing of an otherwise insoluble agent, the *solubilisate*, into a liquid medium by addition of a solubilising agent, invariably a surfactant. This agent acts as an amphiphilic bridge between solubilisate and medium. For example, methylnaphthalene will not dissolve to any significant extent in water, but its solubilisation in water to give an apparently clear *colloidal solution* can be brought about by the use of a surface-active agent such as nonylphenol poly(oxyethylene) sulphate. Hence the distinction between solution and solubilisation in non-colloidal and colloidal situations generally.

Solubilisation can be viewed as one end of a reversible colloidal continuum that begins with wetting and proceeds through dispersion or emulsification to solubilisation, each of these stages being characterised by the size and nature of the particles. In this sense solubilisation is an extension of emulsification (or dispersion) in which the proportion of surfactant has been increased to the level where the discrete droplets (or particles) that characterised the emulsion (or dispersion) have become completely absorbed into the surfactant–medium phase. In some cases the surfactants used to produce an emulsion (or dispersion) may need modification (a change of hydrophile–lipophile balance) before complete solubilisation can be brought about. Similarly, if a solubilised system is diluted by addition of the liquid medium, a point will usually be reached at which the solubilised system changes to an emulsion (or dispersion). It is indeed possible to have all the stages of wetting, emulsification (or dispersion) and solubilisation present at the same time to different degrees.

It is beyond the scope of this section to discuss the complex physico-chemical parameters of solubilisation in detail. Useful relevant works of reference are available [332–335]. It follows, however, that since solubilisation is essentially an extension of emulsification (or dispersion), the factors discussed in section 9.8.3 in regard to emulsification are also pertinent to solubilisation. Theory in this area is a useful guide but much still depends on empiricism. As in emulsification, each system to be solubilised will present its own specific requirements with regard to the type and amount of surfactant(s) required. In some cases solubilisation is aided by adding a small amount of a water-miscible solvent such as an alcohol or glycol, although the environmental and the health and safety aspects of such additions nowadays requires careful consideration. Conversely, the presence of electrolytes can have a deleterious effect. Temperature too can be important; a system that is an emulsion (or dispersion) at one temperature may become solubilised at a different (usually higher) temperature.

There are two main approaches to solubilisation in textile wet processing. One is the deliberate preparation of a solubilised product for use as an auxiliary agent, as in the proprietary carriers formulated for dyeing polyester with disperse dyes. The other is as a concomitant of the process itself, as in the solubilisation of fats and oils during scouring processes and in the disperse dyeing process. In both situations more than one stage of the colloidal continuum of wetting-dispersion/emulsification-solubilisation may be present at any one time.

10.7 LEVELLING AND RETARDING AGENTS

Level dyeing problems can be divided into two broad categories [336]:

(1) Gross unlevelness throughout the material: this type of unlevelness is primarily related to the dyeing equipment or process; the substrate is often uniform in properties, both chemically and physically
(2) Localised unlevelness: this is primarily related to physical and/or chemical non-uniformity of the substrate; typical examples are barriness in nylon or polyester dyeing and skitteriness in wool dyeing.

There are also two fundamental mechanisms that can contribute to a level dyeing:

(1) Control of rate of exhaustion of dye so that it is taken up evenly
(2) Migration of dye after initially unlevel sorption on the fibre.

Either or both of these mechanisms may operate to a greater or lesser extent in a given dye–fibre system, although a general trend towards better fastness properties has dictated the use of dyes that show low, if any, propensity to migration, thus placing the emphasis for level dyeing on the control of exhaustion rate. Physical factors such as temperature and frequency of liquor/substrate contact (governed by rate of liquor circulation in a jet, beam or package machine) can be used to exert some degree of control over these mechanisms. Slower rates of heating usually favour more even uptake of dye and higher temperatures tend to increase migration or diffusion. In some cases level dyeing can be influenced by dyebath pH and/or the presence of electrolytes. This section, however, is more concerned with the control of levelness by means of chemical auxiliaries, generally known as levelling or retarding agents.

Since levelling agents are invariably surfactants, they may be anionic, cationic, nonionic or amphoteric in nature. Sometimes combinations of these are used. The chemical structure of commercial products is seldom revealed, however; hence only general principles can be covered here. The main mechanisms by which levelling agents operate [337–341] are as follows:

(a) nonionic agents usually form water-soluble complexes with the dye, some degree of solubilisation being involved
(b) ionic agents are primarily dye- or fibre-substantive; in the former case they tend to form complexes with the dye and there is competition between the levelling agent and the fibre for the dye, while in the latter case the competition is between levelling agent and the dye for the fibre.

In complex formation the principle, as far as levelling action is concerned, is usually the same irrespective of whether nonionic or ionic agents are used, although the mode of complexing is different. The attractive forces between agent and dye create a counterbalancing mechanism against dye–fibre attractive forces, restraining the uptake of dye by the fibre. As the temperature of the dyebath increases the complex gradually breaks down, progressively releasing the dye for more gradual sorption by the fibre. Clearly, for an effective levelling agent that functions by this mechanism the stability of the agent–dye complex, governed by forces of attraction between agent and dye, is crucial. If these forces are so weak that a relatively unstable complex is formed, restraining or levelling action may be inadequate. On the other hand, strong forces of attraction may result in a complex that is too stable to break down as the temperature rises, so that the dye is effectively entrapped by the agent in the solution phase and is not available for sorption by the fibre. The objective therefore is to formulate the levelling agent so that it forms a dye complex of optimum, rather than maximum, stability relative to the conditions of application. This is done by adjusting the hydrophilic–lipophilic balance of the surfactant. The problem lies in the fact that the dye–agent interaction is so specific that different members of a range of dyes may each require a different balance. Hence commercial levelling agents may contain more than one surfactant.

A difficulty that arises with ionic levelling agents is that they may form an insoluble precipitate with ionic dyes of opposite charge; this can be obviated in various ways. In the first instance attention should be paid to the concentration of the surfactant; where initial addition of surfactant to the dyebath causes precipitation of the agent–dye complex, further additions of surfactant often lead to its solubilisation. Alternatively, a further surfactant may be added to solubilise the complex; a nonionic agent will not itself react with either the dye or the original ionic surfactant to form a further insoluble complex, but its addition may further complicate the relationship between the hydrophobic–hydrophilic balance of the ionic agent and the dyes to be complexed. Due regard also needs to be paid to the cloud point of the nonionic agent under the conditions of use. This does not preclude the use of a relatively hydrophobic nonionic agent, since its cloud point may be effectively raised in the presence of the ionic agent (subject to possible interference from any electrolytes or solvents present in the dyeing system). Similarly, if there is any danger from the cloud point of a nonionic surfactant used as the primary levelling agent (as with disperse dyes, for example), a suitable anionic surfactant may be added to effectively raise the cloud point, again paying due attention to any effect the anionic agent may have on the complexing–liberating performance of the nonionic agent.

The third method of obviating precipitation of an ionic agent–ionic dye complex is to choose what effectively amounts to a 'modified' ionic agent. Ethoxylated anionic and ethoxylated cationic agents are particularly useful in this respect. The ethoxylation tends to reduce the ionic character of the agent, thus giving rise to weaker but more controllable forces of attraction for dye ions, and the oxyethylene chain can further function as a dispersing–solubilising moiety for the agent–dye complex. In a sense this is basically similar to using a mixture of ionic and nonionic agents as described above except that a single agent is used, thus facilitating the aim of obtaining the optimum complexing–liberating balance.

Dye–agent complexes of lower net charge are formed when the ionic agent is added to the ionic dye solution. As the concentration of agent is increased a point is reached at which all the dye is complexed and its ionic charge has been neutralised. Beyond this point, as more agent is added, the agent–dye complex takes on the charge of the complexing agent (i.e. the opposite to that of the dye itself). This brings about a change in the partition coefficient of the complex between water and organic solvents [336], modifying the electrical and solution properties of the dye and so altering its affinity for the fibre.

Fibre-substantive levelling agents are usually of the same ionic type as the dye, that is anionic agents are used with anionic dyes and cationic agents with cationic dyes, the aim being to create a system in which levelling agent and dye both compete for the sorption sites in the fibre. Just as the complexing type of levelling agent has to be carefully chosen so as to obtain the optimum complexing–liberating properties, so must the competing type of levelling agent be chosen such that its ionic power gives the optimum level of competition relative to the dye–fibre system concerned. If the ionic power is too weak, it will not function as an effective levelling agent; if it is too strong, it may exert blocking effects, preventing sorption of the dye. Ideally the balance should be such that the smaller surfactant ions are adsorbed by the fibre more quickly than are the larger dye ions, but the agent–fibre interaction needs to be weak enough to permit subsequent displacement of the surfactant ions by the dye ions.

As the forces of dye–fibre interaction vary from one dye to another, the ionic power of the levelling agent must be suitably adjusted through its hydrophilic–hydrophobic balance to give the optimum properties. This can be done either by careful choice of a single surfactant or by the use of mixtures, which has gained prominence in recent times. For example, the strongly anionic character of a long-chain alkyl sulphate or sulphonate can be modified (toned down) by mixing it with a more weakly anionic poly(oxyethylene) sulphate or with a nonionic agent.

Some levelling agents operate both by complexing and by competition. For example, in the application of acid dyes a weakly cationic agent may be used to complex with the dye and an anionic agent may also be used as a competing agent. This combination is more versatile because unlevelness may arise from different mechanisms. Unlevelness arising from process or equipment variables can often be controlled by dye–agent competition, whereas localised dye uptake variations generally respond better to dye–agent complex formation. Evidently, in this combined system the balance of properties is highly critical. In particular the oppositely charged surfactants must not mutually precipitate; hence the more weakly ionic ethoxylates are of particular interest, since the oxyethylene assists solubilisation of any complex so formed. A purely nonionic agent may also be used to prevent coprecipitation of the ionic types. Amphoteric agents, in a sense, fall within this combined system.

Theoretical considerations are clearly useful in formulating suitable levelling agents. Nevertheless, a good deal of empiricism is always involved in formulating well-balanced agents for specific dye–fibre systems. Table 10.36 shows the general types of levelling agents now being offered and their uses; more detail is given in Chapter 12 relative to each class of dye.

Many, but not all, levelling agents promote migration of dye in addition to retarding dyeing, such agents will obviously be a further aid to level dyeing. In some cases, however,

Table 10.36 Levelling agent types and their uses

	Recommended for use with	
Type of levelling agent	Substrate	Dye classes
Nonionic	Cotton Wool, nylon Polyester	Direct, vat, azoic Milling acid, metal-complex Disperse
Nonionic/anionic	Polyester Wool, nylon	Disperse Milling acid, metal-complex
Nonionic/cationic	Wool	Acid, metal-complex, reactive, chrome
Anionic	Wool, nylon Cotton Polyester	Acid Direct Disperse
Weakly anionic	Polyester	Disperse
Anionic/cationic	Wool, nylon	Acid, metal-complex
Cationic	Acrylic Wool, nylon	Basic Acid, metal-complex, reactive
Weakly cationic	Wool, nylon	Acid, metal-complex, chrome
Cationic/polymeric	Cotton	Vat, sulphur
Amphoteric	Wool	Acid, metal-complex, reactive, chrome

higher concentrations of levelling agent are needed to obtain significant migration and this may interfere unduly with dye sorption. Levelling agents are also widely used as stripping agents, either alone for non-destructive desorption or together with reducing agents such as sodium dithionite for destructive stripping. When used for this purpose, their hydrophilic–hydrophobic balance is not as critical as when they are used simply as levelling agents. Thus higher concentrations are often used in order to maximise rather than optimise desorption of the dye.

It should not be overlooked that electrolytes can play an important part in levelling and retardation. In recent times the use of bolaform electrolytes (section 10.1), cyclodextrins (section 10.3.1) and liposomes (section 10.3.4) as complexing agents has been proposed.

10.8 THICKENING AGENTS, MIGRATION INHIBITORS AND HYDROTROPIC AGENTS USED IN PRINTING AND CONTINUOUS DYEING

Most, if not all, textile printing and continuous dyeing processes entail the use of auxiliaries that considerably increase the viscosity of the application medium compared with conventional batchwise dyeing processes, the aim being to facilitate and stabilise the local application of colour prior to its actual fixation to the fibre. Such auxiliaries are generally known as thickening agents in printing and as migration inhibitors in padding operations.

They are characterised by undergoing marked macromolecular swelling in solution due to solvation (hydration in aqueous systems). While the principal role of thickening agents is to increase the viscosity of print pastes or pad liquors, certain other properties are also of importance, such as stability and rheology of the print paste, adhesion and brittleness of the dried thickener film, the effect on colour yield and penetration, ease of preparation and removal, and not least cost. A succinct account of these factors and of their interrelationships is available elsewhere [342]. The following discussion is restricted to rheology of print pastes, since an understanding of the basic principles of fluid flow is essential in appreciating the fundamental mechanism taking place during printing. The number of recent publications dealing with rheology, particularly in relation to specific types of thickening agents, is evidence of its importance, both as a concept and in current research [343–352].

The essential fact concerning thickening agents is that they are viscoelastic, exhibiting properties associated with both fluids and solids and showing what is known as pseudoplastic (non-Newtonian) flow behaviour [352]. This is best understood by comparison with simple liquids such as water or alcohol, which show Newtonian flow behaviour. The apparent viscosity of Newtonian liquids does not change when a shear stress is applied (curve A in Figure 10.48). All thickening agents, however, are highly viscous in a static state but apparently show reduced viscosity when a shearing force is applied. This is indeed their *modus operandi*: they must flow under shear to allow transfer through the screen, then resume high viscosity when the shear is removed so that colorants remain where they have been deposited.

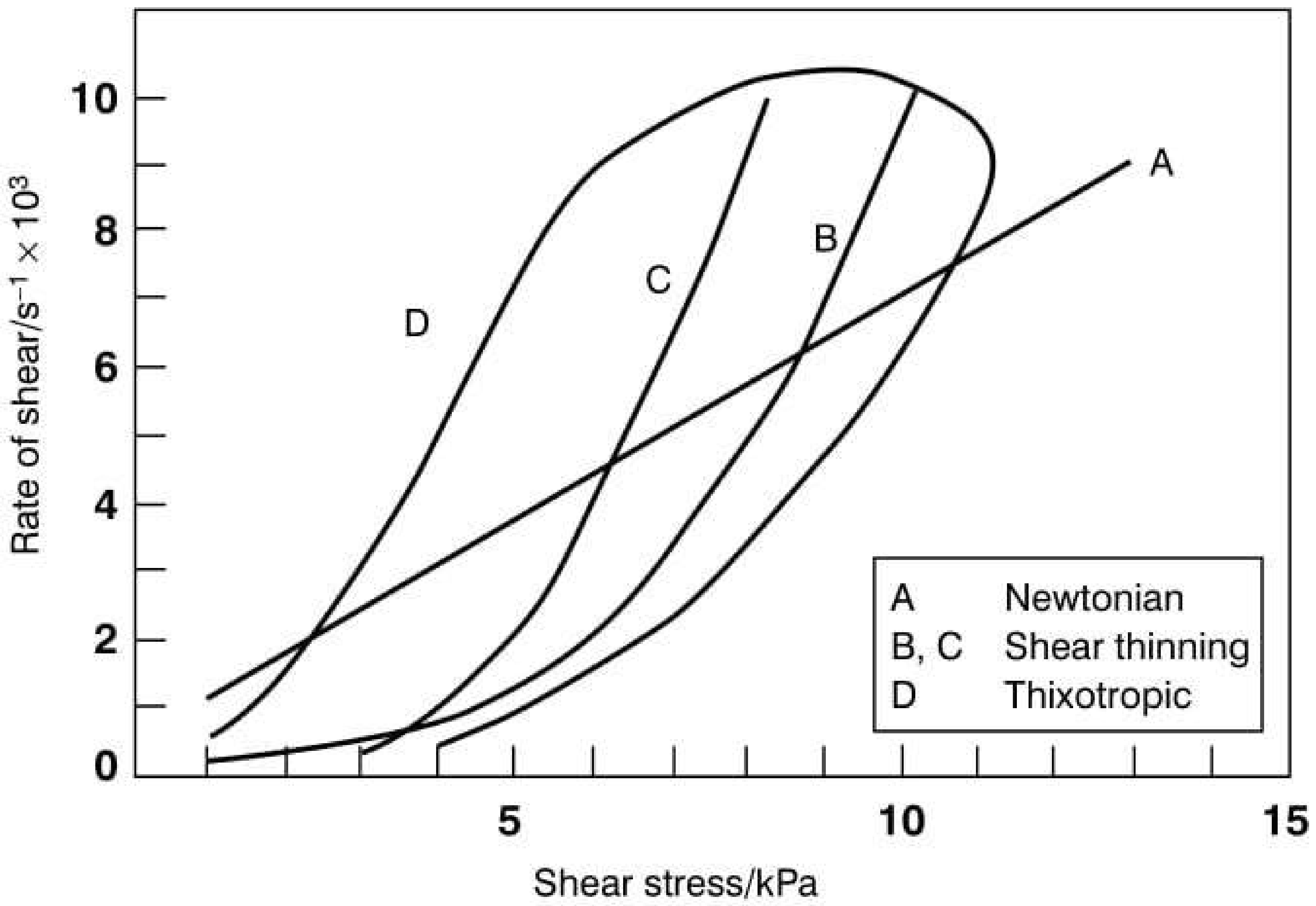


Figure 10.48 Typical flow curves demonstrating behaviour of viscous liquids [342]

Most thickening agents are of the shear thinning type represented by curve B, the apparent viscosity progressively decreasing as the shear rate is increased. It is important that this change is reversible, viscosity returning to its original level as soon as the shear is removed. In some cases, shear thinning may not begin until a certain critical shear has been applied (curve C). Thixotropic fluids (curve D) show time-dependent effects in that apparent viscosity depends on both the rate and duration of shear, the return to original viscosity being delayed. The opposite of shear thinning is shear thickening, often referred to as dilatant behaviour; such behaviour is clearly not suitable for textile printing. An alternative method of representing flow behaviour is shown in Figure 10.49.

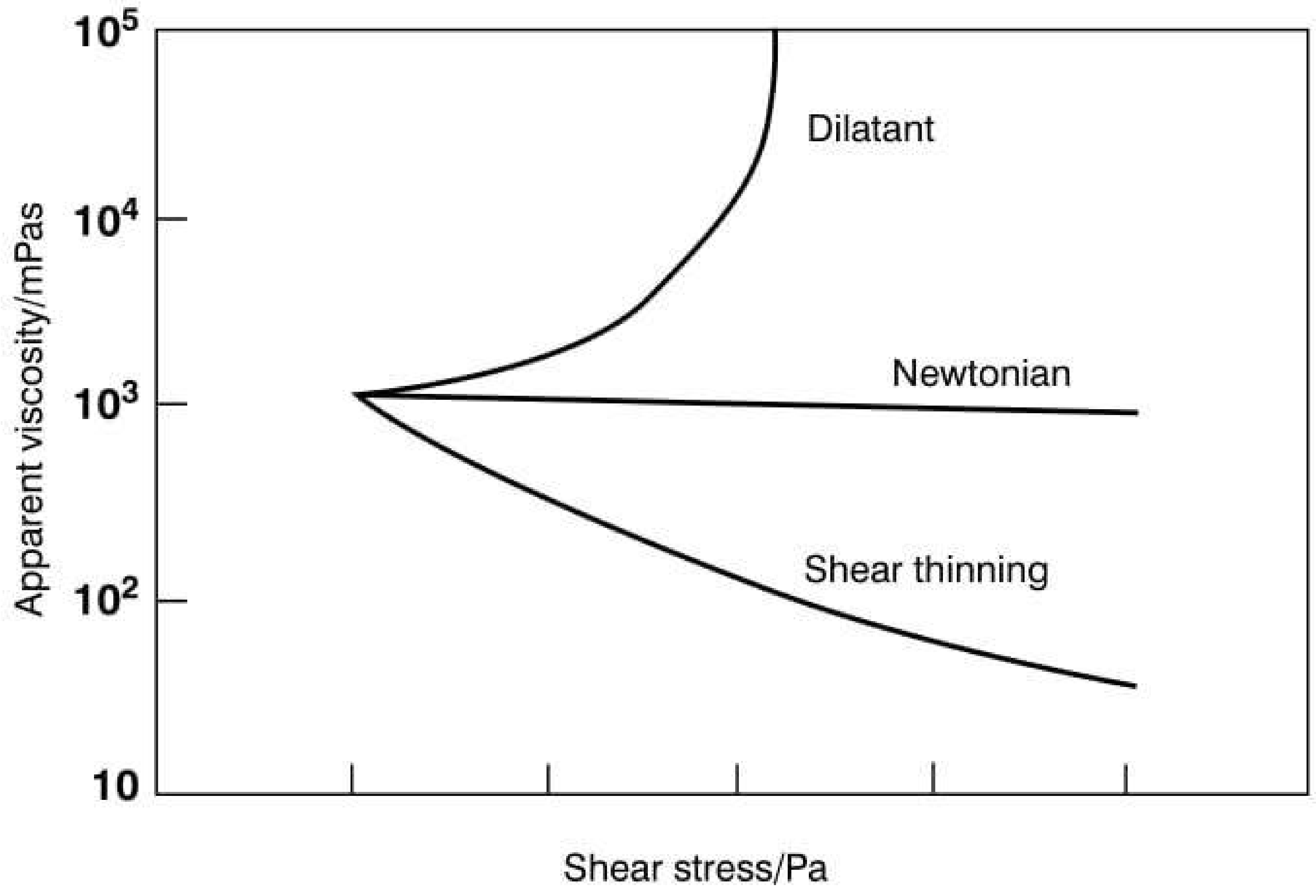


Figure 10.49 Relationships between apparent viscosity and shear stress [350]

Print pastes may be thickened by any of the following methods [342]:

(a) a relatively low concentration of a long-chain thickening agent
(b) a relatively high concentration of a shorter-chain thickener or one having a highly branched structure
(c) an emulsion
(d) a finely dispersed solid such as bentonite (derived from clay).

The first two methods, particularly the first, are most frequently used today; combinations of these methods are also possible.

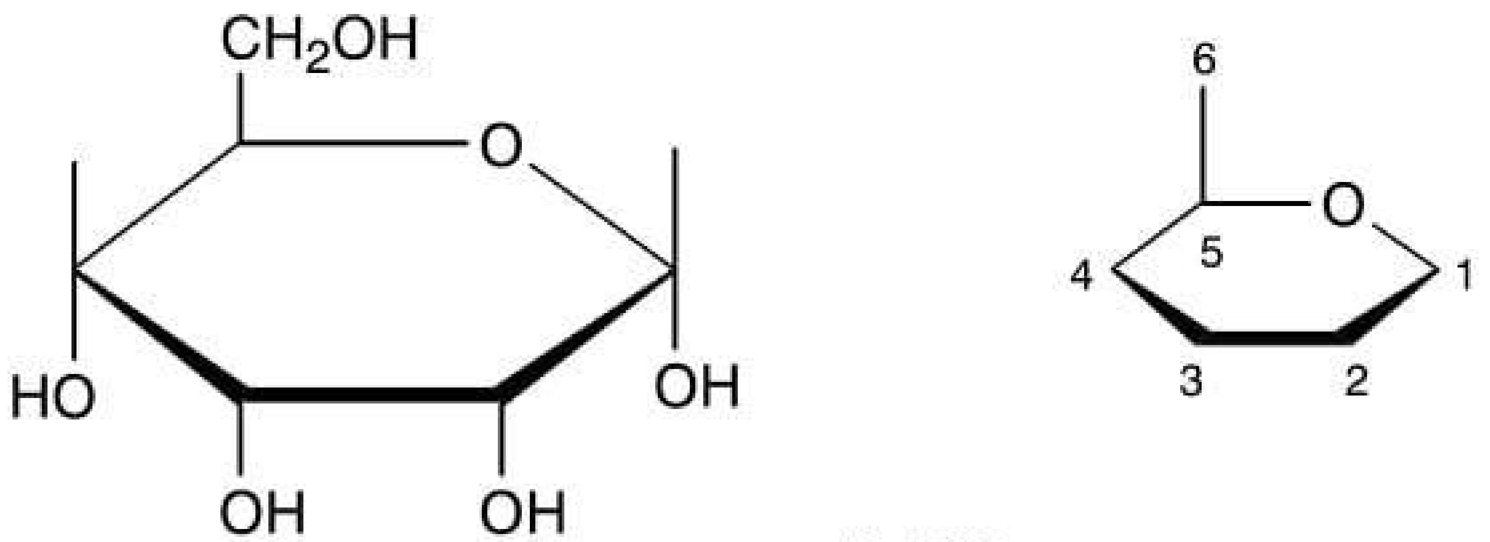
Thickening agents can be of natural or synthetic origin. Various natural gums and starches have been used traditionally in many printing styles. The materials from which they are extracted are valuable sources of foodstuffs, so availability and cost can depend on fluctuating demand from the food industry. The properties required of an ideal thickener can be summarised as follows [352]:

(1) Compatibility with colorants and other auxiliaries
(2) Adequate solubility and good swelling properties in cold water
(3) Good washing-off properties
(4) High degree of purity and conformity to standard
(5) Non-dusting
(6) Biodegradable
(7) Non-toxic
(8) Manufactured from replenishable raw materials.

10.8.1 Natural thickeners

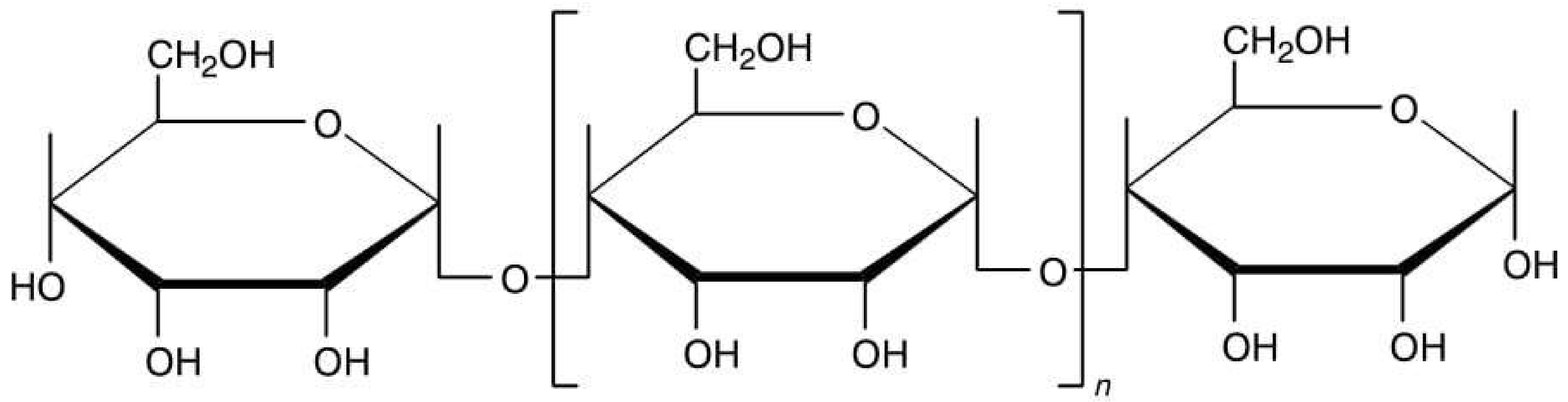
Natural thickeners are derived from plants by extraction from part of the plant itself or from a plant secretion; their biosynthesis is now a possibility. These products are generally polysaccharides and are thus closely related to cellulose. They consist of homo- or heteropolymers of simple hexoses, most commonly glucose, mannose or galactose [353]. Linear and branched segments are normally present, the degree of branching being important in relation to the technical properties of the product. Polysaccharides bear some structural similarities to anionic polyelectrolyte dispersing agents (section 10.6.1) and sizing agents (10.5.2). In particular, the nature of the side groups (mainly, though not always hydroxy or carboxyl groups) has a decisive effect on viscosity and other technical properties. Some, such as native starch, are used as extracted from their sources; others, such as starch ethers, are derived by introducing substituents or undergoing controlled hydrolysis to lower their viscosity. As with other polymeric auxiliaries already discussed, their detailed structure is still not completely understood and the formulae given are only indicative of their structures.

Although native starch is less important nowadays as a thickening agent for textile printing, some starch derivatives still make a significant contribution. Starch has two components, both of which are made up of linked α-glucoside units (10.106). In amylose, which accounts for some 20–30% of the polymer and has a relative molecular mass in the range 2–6 × 10^5 the α-glucoside units are linked in a linear 1,4 arrangement (10.107). Cellulose (10.108), by contrast, consists of β-glucoside chains. In amylopectin (M_r 4.5 × 10^4 to 4 × 10^5) the linear α-1,4-linked main chain is randomly branched at the 6-position every 15–30 glucose units to give an α-1,6-anchored side chain (10.109).



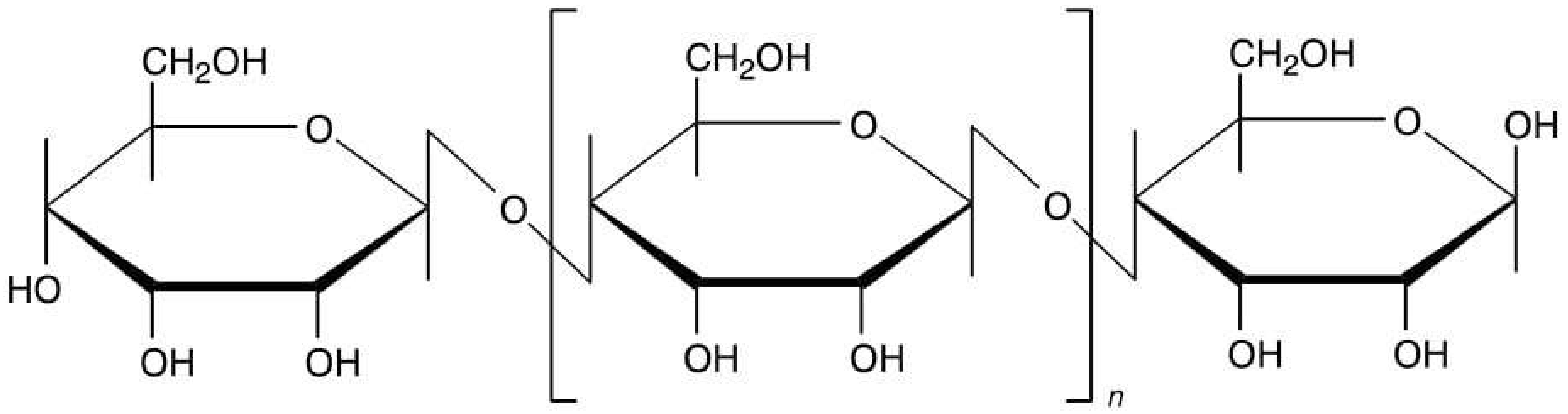
10.106

α-Glucoside unit



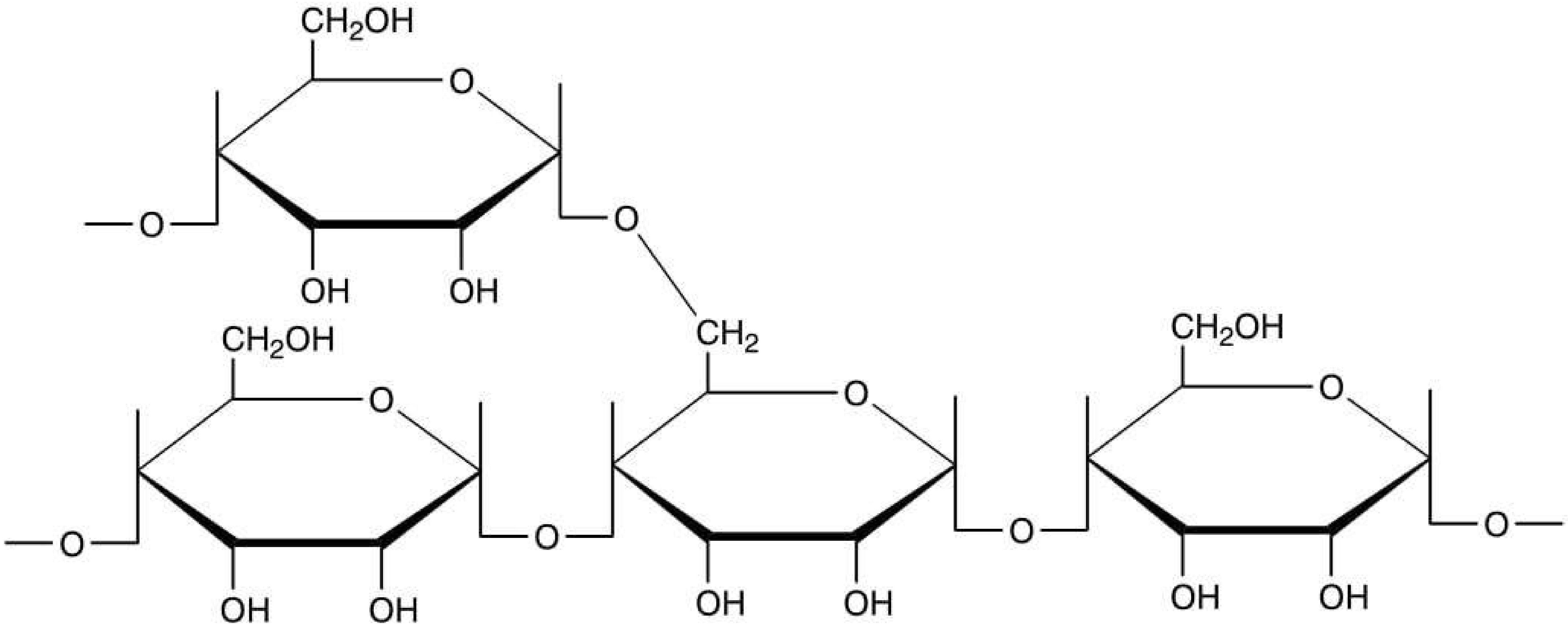
10.107

Amylose



10.108

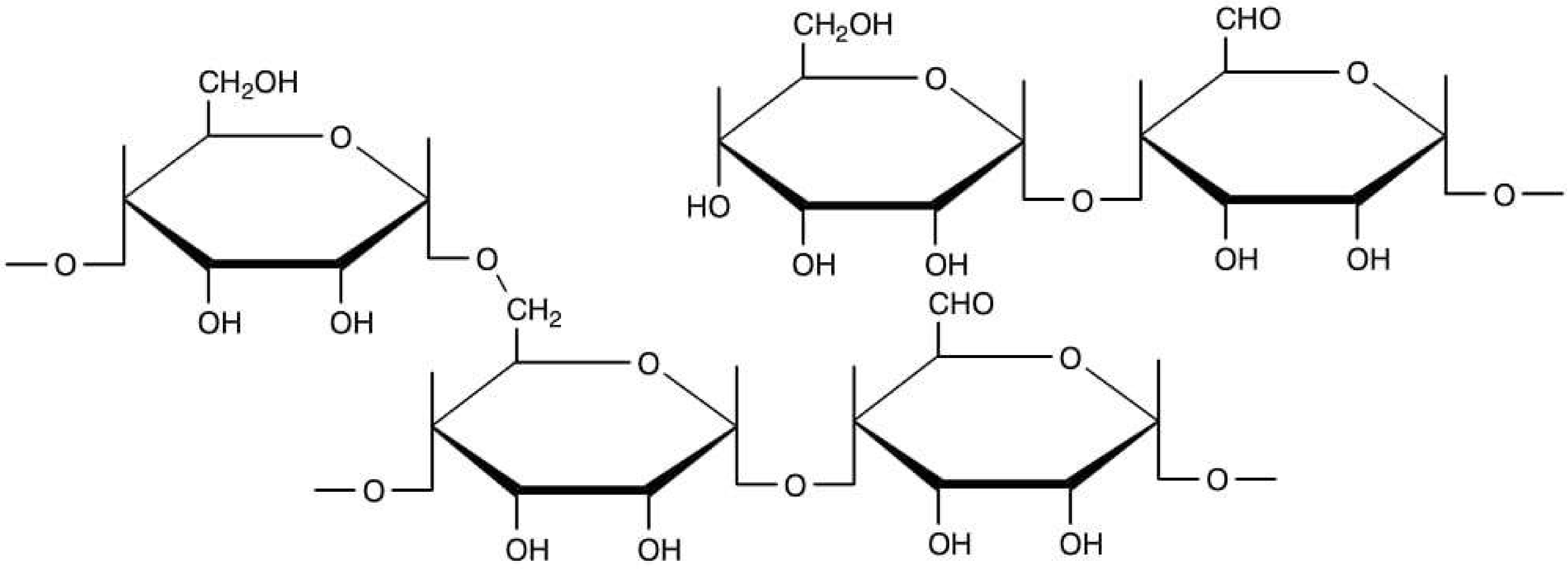
Cellulose



10.109
Amylopectin

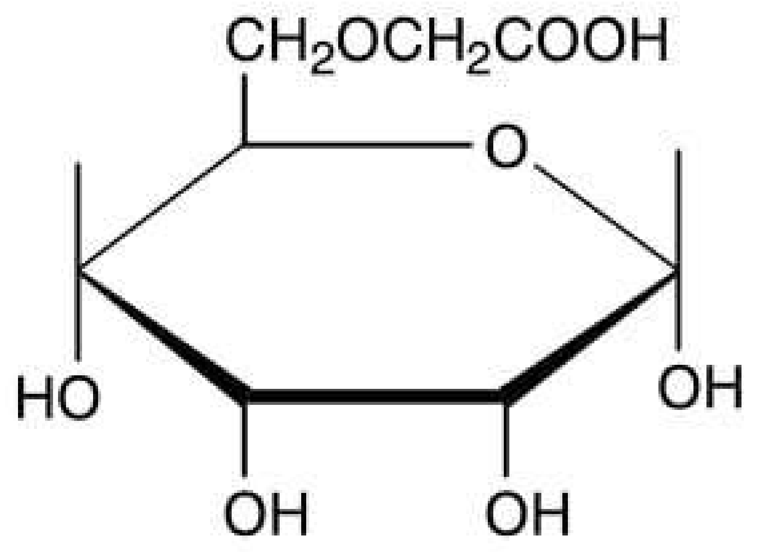
The amylose component is substantially crystalline, forming helical structures that uncoil in an aqueous solution. It can also aggregate to give a gel or precipitate, an undesirable phenomenon known as retrogradation. Amylose is completely hydrolysed by the β-amylase enzyme. Amylopectin is substantially amorphous, having a globular structure that can expand considerably in aqueous solution. Its branched chains give rise to a much more stable solution, substantially free from retrogradation, and it is much more resistant to the action of β-amylase. Starches containing little or no amylose are known as 'waxy starches'.

The properties of starch can be improved from a printing viewpoint by conversion to British Gum (10.110). This is done by a dry roasting treatment at 135–190 °C, accelerated by trace quantities of acid, to give random hydrolysis of the 1,4-links to decrease the chain length but with the formation of 1,6-links (branching). The effect is to increase the solubility and stability although reducing characteristics, which can affect certain susceptible dyes, are enhanced by formation of more aldehyde end groups. Control of the hydrolysis and branching reactions yields a varied range of products.

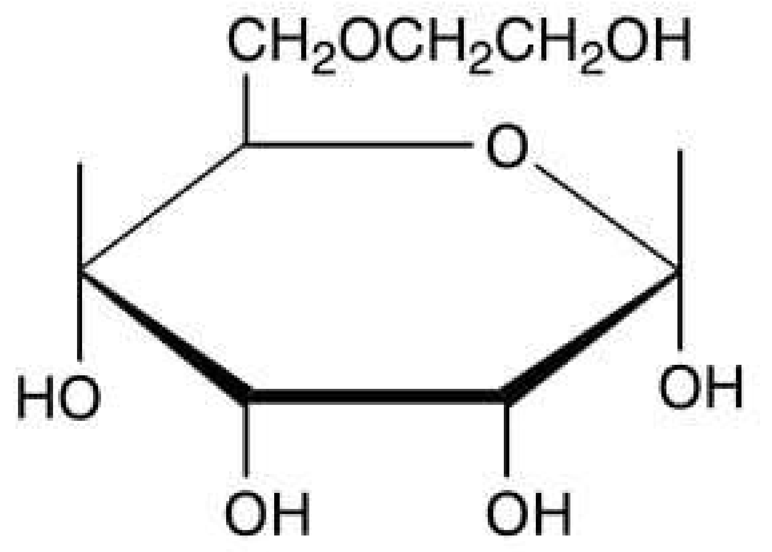


10.110
British gum

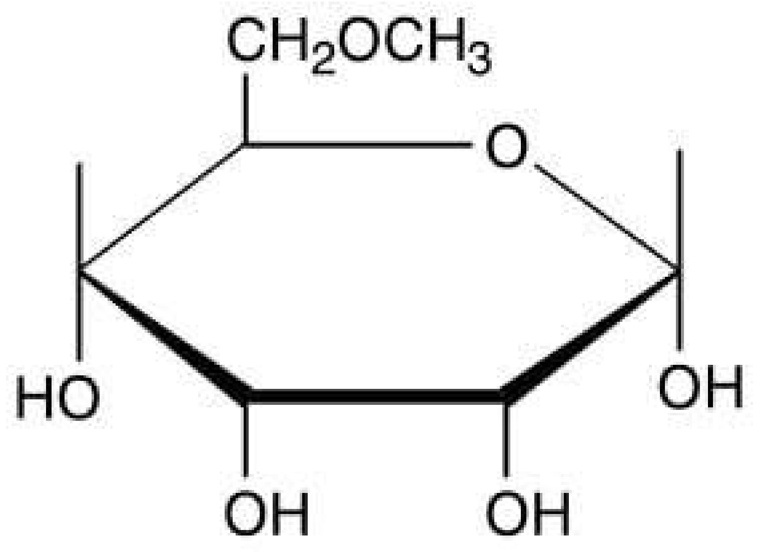
Besides roasting, other methods of modifying starch are available. Etherification and esterification, to give starch ethers and starch esters, are both practised although the ethers, being resistant to hydrolysis in acidic or alkaline media, are much the more important as thickening agents for textile printing. The starch may be first partially decomposed before etherification and the degree of etherification itself may be varied. The most important products are the carboxymethyl (10.111), hydroxyethyl (10.112) and methyl (10.113) starches (the structures illustrated use the glucose unit as a model, showing the primary hydroxy group substituted). The degree of alkylation is said to be low or high depending on whether it is less or greater than 0.3 substituents per glucose (or other) unit; the products are termed modified starches if the degree of substitution is low and starch derivatives if it is high. Crossbonded starches can be obtained by treating, for example, a starch ether of low degree of substitution with bifunctional agents such as ethylene oxide, propylene oxide, epichlorohydrin or phosphates. The corresponding derivatives of cellulose can also be made and used as thickening agents if the chain length is appropriate. The steric hindrance effect of the substituents gives thickening agents of improved all-round properties and certain derivatives have ousted their parent products in terms of commercial importance.



10.111



10.112

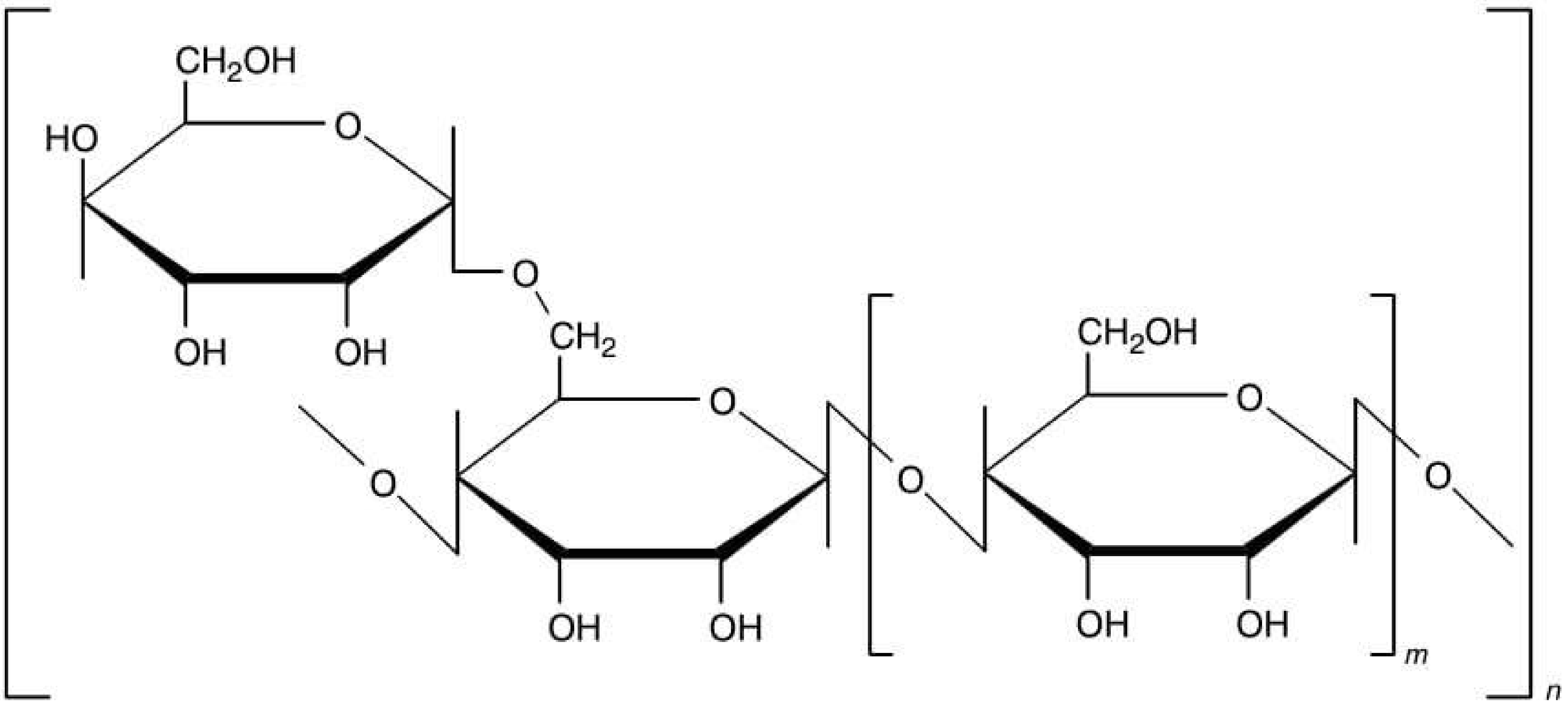


10.113

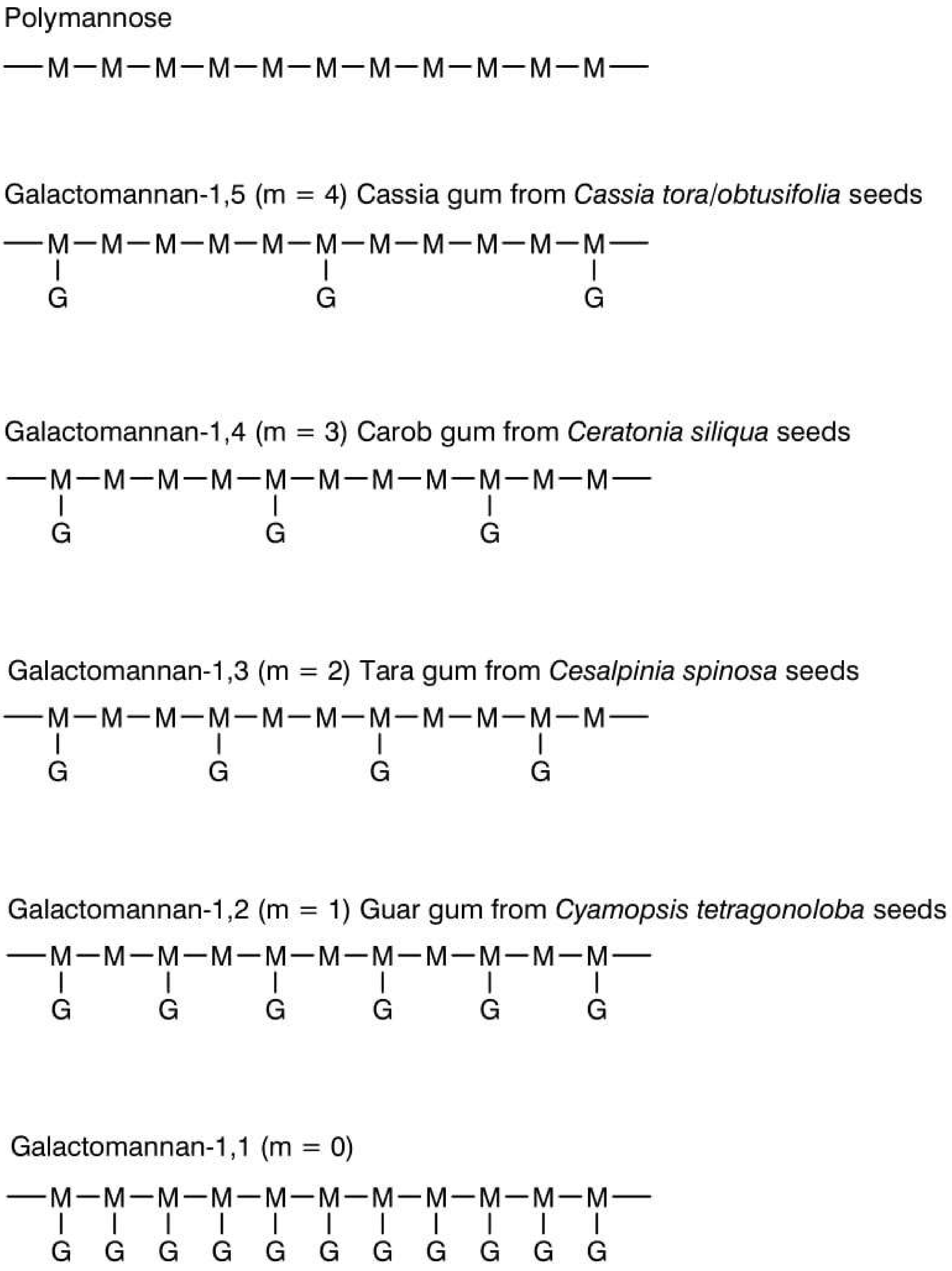
Galactomannans are another source of natural thickeners. Structurally related to starches they are polysaccharides composed of main-chain mannose and side-chain galactose units as in 10.114. Typical values are: locust bean gum (m = 3, n = 375) and guar gum (m = 1, n = 440). The distribution of galactose units varies with the source, as shown schematically in 10.115 [354]. Amongst other things, this distribution has an influence on ease of dispersibility. For example, warm water is required to effect complete dispersion of locust bean gum (the 1,4 form) but guar gum (the 1,2 form) disperses readily in cold water because of decreased molecular association arising from the greater frequency of side-chain substitution. As with the starches, modified gums can be obtained. In particular, etherification improves the cold water dispersibility of locust bean gum. In Table 10.37 various derivatives of galactomannans are listed together with their main applications [354].

Locust bean gum forms an interesting and unusual crosslinked complex by association of *cis*-dihydroxy groups in the mannose chains with borate ions, diagrammatically represented in structure 10.116. This complex forms a gel, which has been made use of in printing with vat dyes in a two-stage fixation process. The crosslinks are relatively weak, being in a state of dynamic equilibrium, and are ruptured in the presence of hydrotropes such as glycerol.

The alginates derived from seaweed are of great importance as thickening agents. These are based on alginic acid (10.117; n = 60–600) of which the major commercial salt is sodium alginate, although calcium (particularly in mixture with sodium), magnesium and ammonium alginates, as well as amine salts, are also available. Their exceptionally low



10.114
D-Galactomannoglycan


Polymannose

Galactomannan-1,5 (m = 4) Cassia gum from *Cassia tora/obtusifolia* seeds

Galactomannan-1,4 (m = 3) Carob gum from *Ceratonia siliqua* seeds

Galactomannan-1,3 (m = 2) Tara gum from *Cesalpinia spinosa* seeds

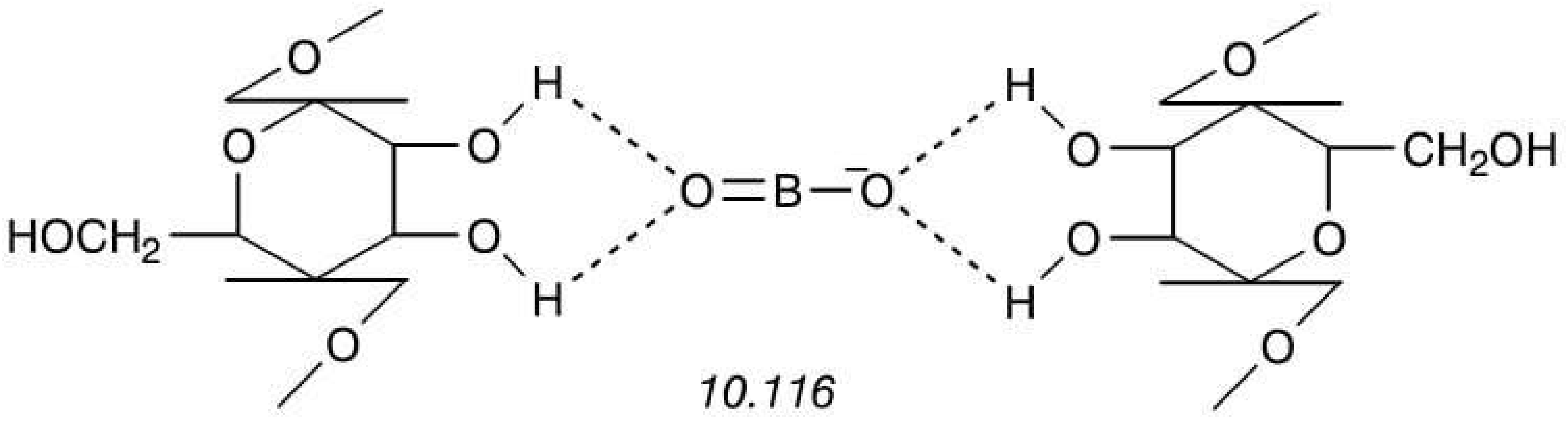
Galactomannan-1,2 (m = 1) Guar gum from *Cyamopsis tetragonoloba* seeds

Galactomannan-1,1 (m = 0)

10.115

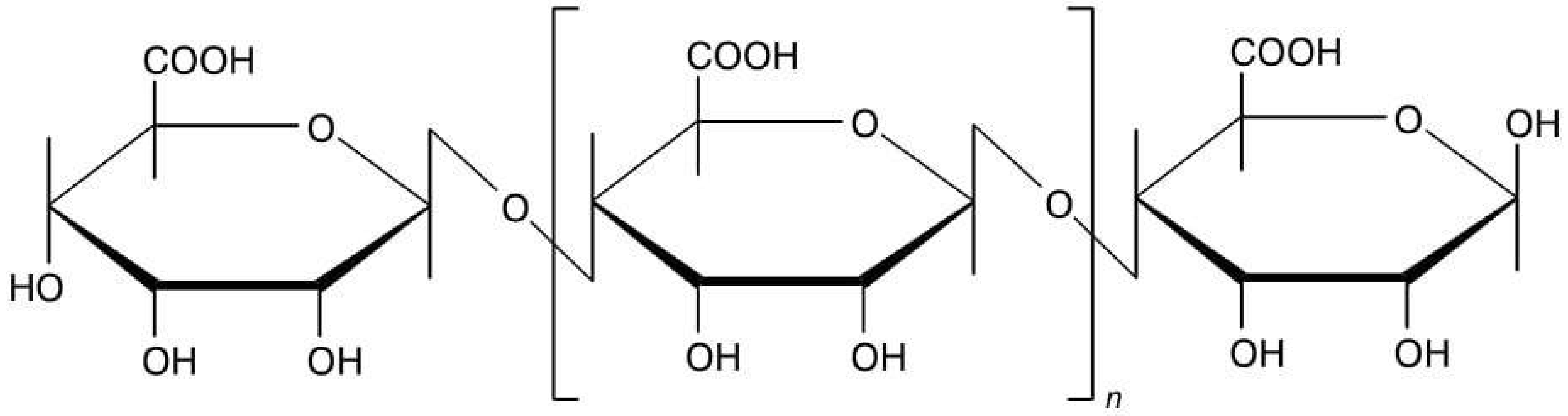
Table 10.37 Composition and applications of galactomannan derivatives [354]

Galactomannan	Chemical variant	Main applications
-1,2	Unmodified	Carpet printing/dyeing: acid, metal-complex dyes
	Depolymerised	Carpet printing/dyeing: acid, metal-complex dyes Cotton, viscose: vat, direct, azoic dyes Polyester: disperse dyes Nylon: acid, metal-complex dyes Acrylic fibres: basic dyes
	Hydroxyethylated	Carpet printing/dyeing: acid, metal-complex dyes Cotton: African prints with azoics Polyester: disperse dyes Nylon: acid, metal-complex dyes Acrylic fibres: basic dyes
	Hydroxypropylated	Carpet printing/dyeing: acid, metal-complex dyes
	Additionally depolymerised	Sizing
	Carboxymethylated	Carpet printing/dyeing: acid, metal-complex dyes Cotton: vat, limited reactive dyes
-1.4	Hydroxyethylated	Carpet printing/dyeing: acid, metal-complex dyes Cotton: African prints with azoics Polyester: disperse dyes Nylon: acid, metal-complex dyes Acrylic fibres: basic dyes Wool, silk: acid, metal-complex dyes
	Carboxymethylated	Cotton, viscose: vat dyes Wool, silk: acid dyes
-1,5	Hydroxypropylated	
	Additionally depolymerised	Sizing
	Carboxymethylated	Carpet printing/dyeing: acid, metal-complex dyes
	Additionally depolymerised	Cotton, viscose: vat dyes Wool: acid dyes



10.116

reactivity with reactive dyes is a special advantage. This is a result of replacement of the primary hydroxy groups by carboxyl groups. As well as being non-reactive towards reactive dyes, the ionised carboxylate anions repel dye anions in alkaline or neutral media. Carboxylated polymers form gels with multivalent metal ions. This behaviour, like the locust bean gum borate complex mentioned earlier, has been exploited in the two-stage flash ageing process for vat dyes in printing. Alginate esters (such as the hydroxypropyl ester) have also been used.



10.117
Alginic acid

Other natural polysaccharides used as thickening agents include gum arabic, gum tragacanth and xanthan gum, but these are of diminishing significance nowadays.

Research and development in the area of natural thickeners continues to be active. Detailed studies of the rheology of starch derivatives, alginates, cellulose ethers and vegetable gums [343,344] have shown that thickeners with low solids content form loose networks with low convolution density whilst those with a high solids content show higher convolution densities. This results in differences in tackiness, shear sensitivity and viscoelastic properties, emphasising the major influence of flow properties and viscosity on the quality of prints obtained. Starch carbamate esters and carboxymethyl carob gums of varying degrees of substitution have been evaluated in the vat printing of cotton [355,356]. As the degree of substitution of the carboxymethyl carob gum was increased, the colour strength of the prints increased. Such thickening agents, either alone or in combination with alginates, showed shear thinning behaviour that became thixotropic after storage. Alkali-modified starches have also been assessed in vat printing [357,358]. The alkali-treated starches showed higher aqueous solubility and so were more easily removed during washing off, giving a fabric with a softer handle. Improved colour yields could also be obtained.

It has been shown that carboxymethylcellulose thickeners can effectively replace emulsion systems in the application of pigments [359,360]. Research in Russia has been directed towards finding a carboxymethylcellulose thickener for reactive printing that would be efficient and economical, the latter resulting from the fact that low concentrations give excellent printing properties that cannot be achieved with other known thickeners [361]. The rheology of carboxymethylcellulose thickeners, including storage for up to seven days, has been studied in conjunction with their use in reactive printing [351], indicating suitable conditions for achieving optimum penetration, depth of colour, sharpness of outline and evenness of the prints.

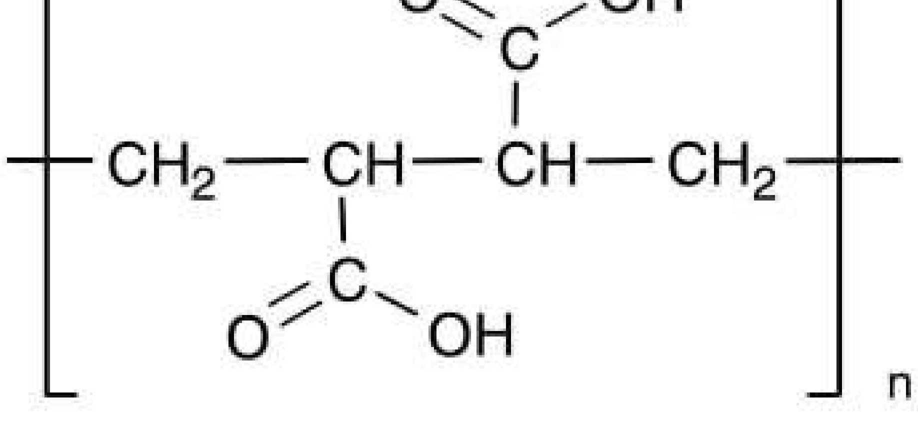
A review of uses of galactomannan thickening agents, of which some 23 000 tons were used worldwide in 1986, is available [354]. The use of borate ions to crosslink locust bean or guar mannose chains has been mentioned already. It has been shown that addition of borax to dry guar gum delays the development of viscosity, making it easier to prepare large stocks for continuous dispensing equipment [362]. The oxidative treatment of carob gum with sodium hypochlorite resulted in improved rheological properties and increased aqueous solubility [363]. No mention was made, however, of possible environmental problems arising from the use of hypochlorite.

When applying reactive dyes, it is essential to use a thickener that does not react with the dyes, alginates being by far the most used. The rheological behaviour of alginate thickeners has been studied [346], showing that the gradient rule is not obeyed across the whole range of shear rates. Alginate thickeners may deteriorate on storage, notably as a result of biological attack. The significance of this for printing performance [364] and the addition and effects of bactericidal preservatives (sodium *o*-chlorophenate or chlorinated *m*-cresol) have been investigated [364]. Certain preservatives have a marked effect on the hues obtained, this being greater with dry heat than with saturated steam fixation, but formaldehyde does not give these effects [364].

The almost exclusive use of alginates with reactive dyes is threatened by uncertainty over sourcing of raw material and by drastic fluctuations in price and quality [365]. Hence there have been sustained efforts to find alternatives. In one study of various possibilities [366] a synthetic acrylic thickener was chosen, but another investigation [367] showed that although good results can be obtained with synthetic thickeners they cannot fully replace alginates because of poor fastness to rubbing. It has been claimed [368] that carboxymethylated derivatives of cellulose, guar gum or starch are quite suitable for reactive printing and actually give better performance. Presumably the ionised carboxymethyl groups, like the carboxyl groups in sodium alginate, inhibit reaction with the reactive dyes. Indeed, it has been confirmed that carboxymethylated guar gum derivatives do not react with reactive dyes, and that both carboxymethylated and unsubstituted guar thickeners give satisfactory results with vinylsulphone reactive dyes, especially for pale grounds and fine outlines [365].

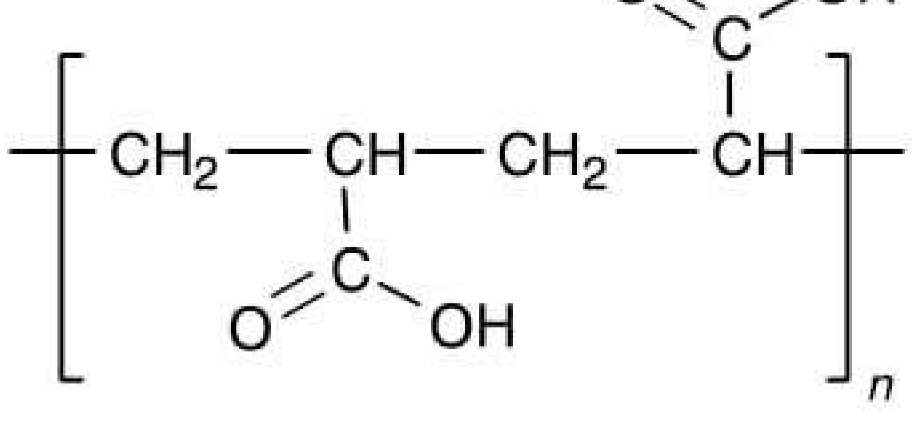
10.8.2 Synthetic thickeners

Polymers based on acrylic acid have been known since the 1930s but it was not until the late 1970s that the use of thickening agents based on them came into prominence in textile printing [369]. Typical repeat units are shown in 10.118 and 10.119. Commercial linear products represented by 10.118 can have n = 50–750 but crosslinked grades of higher relative molecular mass are also available. The products represented by 10.119 cover a range of n values from 3200 to 30 000. Only the longer-chain grades are of significant interest for textile printing in the form of their sodium or ammonium salts. However, the scope for



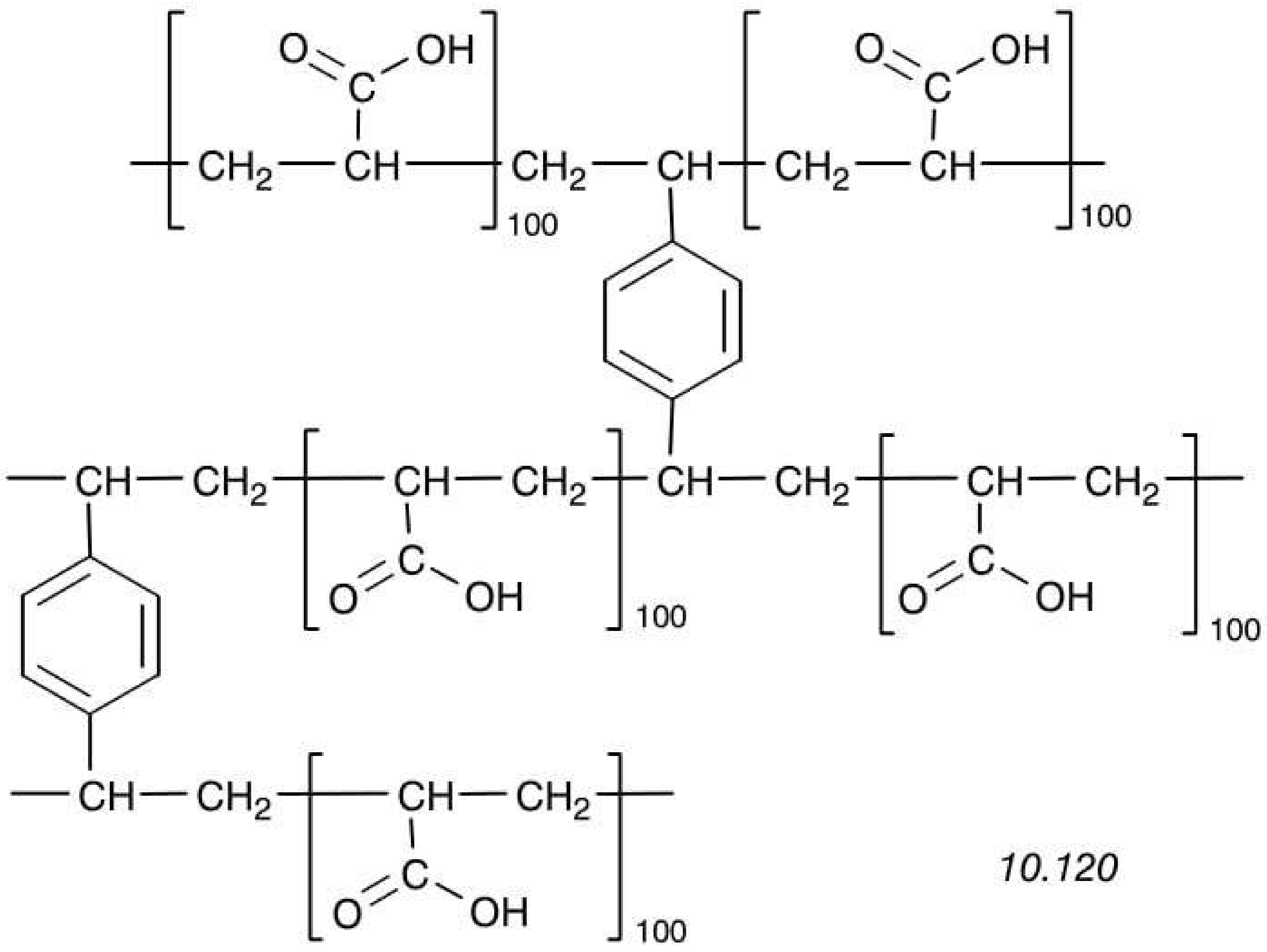
$$\left[-CH_2-CH(COOH)-CH(COOH)-CH_2-\right]_n$$

10.118



$$\left[-CH_2-CH(COOH)-CH_2-CH(COOH)-\right]_n$$

10.119



10.120

forming copolymers and crosslinked variants is virtually limitless. A schematic representation of a crosslinked copolymer, using acrylic acid and divinylbenzene at a molar ratio of 100:1, is shown in 10.120 [370].

It is important to make a clear distinction between acrylic binders used in pigment printing and acrylic thickeners. Binders are generally copolymers and usually contain an integral crosslinking agent [371]. The thickeners also find their greatest use in pigment printing. Their biggest drawback is their sensitivity to electrolytes, although this is less of a problem in pigment printing than in printing with dyes. The sensitivity of poly(acrylic acid) to electrolytes can be reduced by copolymerising with acrylamide [371], although only relatively small proportions can be incorporated before a deterioration in thickening efficiency occurs. Two important and interrelated parameters for acrylic thickeners are relative molecular mass and degree of crosslinking. Simply increasing the molecular mass of linear poly(acrylic acid) yields thickeners that give stringy pastes unsuitable for use in printing. Hence a degree of crosslinking is necessary to minimise stringiness by decreasing the water solubility and promoting dispersibility. Figure 10.50 illustrates the effect of crosslinking for three acrylic acid polymers of the same molecular mass [371]. The balance of molecular mass and degree of crosslinking influences other properties, such as degree of penetration, levelness of ground colours and sharpness of the print.

These products are usually supplied to the printer as partially neutralised polyacids. Further neutralisation is carried out by the printer when making up the print pastes. This neutralisation is often a critical process. For certain applications, as with resin-bonded pigments, neutralisation is carried out with ammonia. This has the advantage that during subsequent baking the ammonia is driven off to liberate the free polyacid, which then catalyses activation of the resin binder. In other cases neutralisation is carried out with non-volatile alkalis such as sodium hydroxide. It is particularly important to use the latter in reactive printing, since ammonia would be evaporated off during fixation leading to a lowering of pH and consequently poor fixation. Moreover, reactive dyes can be deactivated by reaction with ammonia to form their non-reactive amino derivatives.

The commercial success of acrylic thickeners in pigment printing is attributable to the

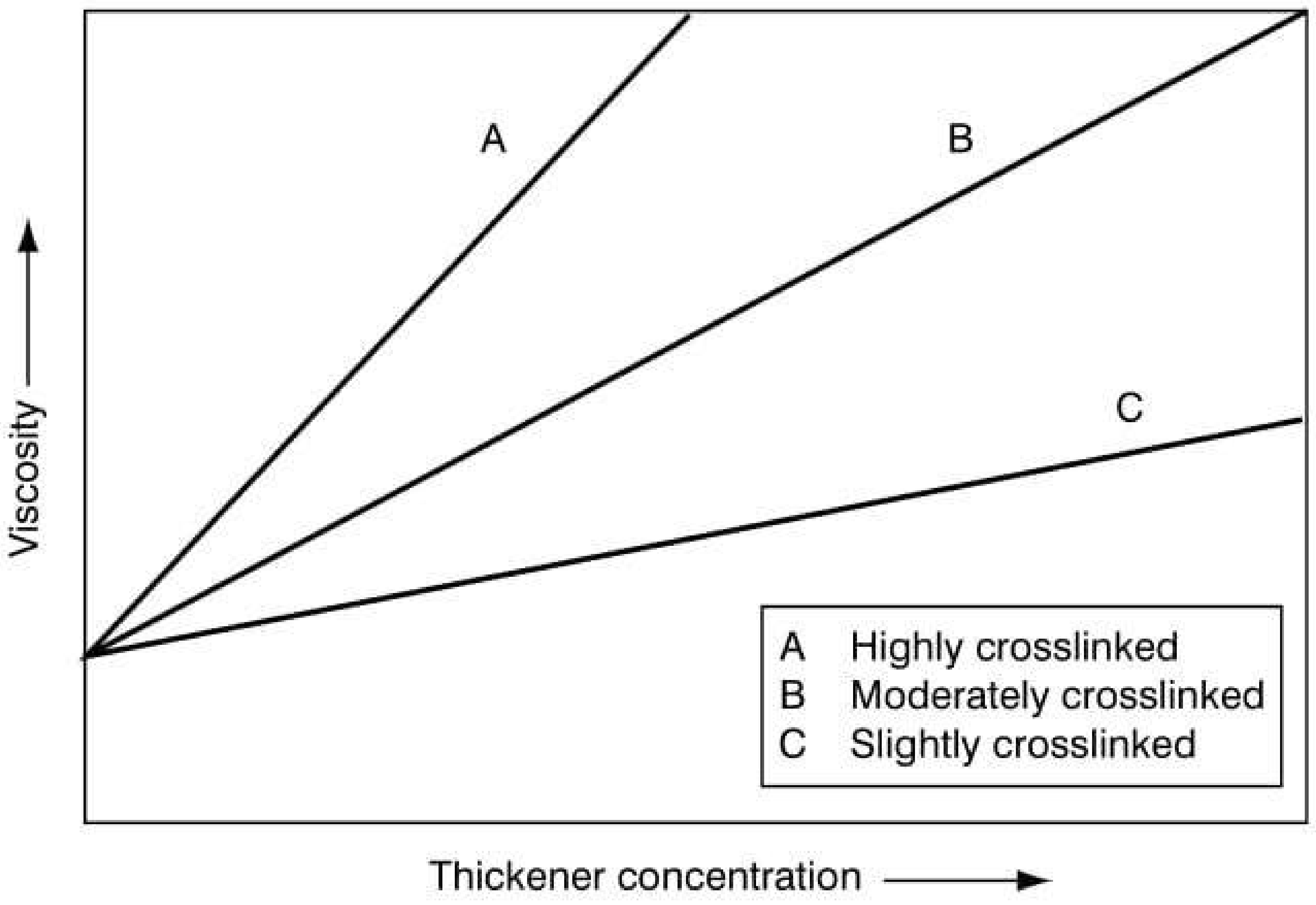
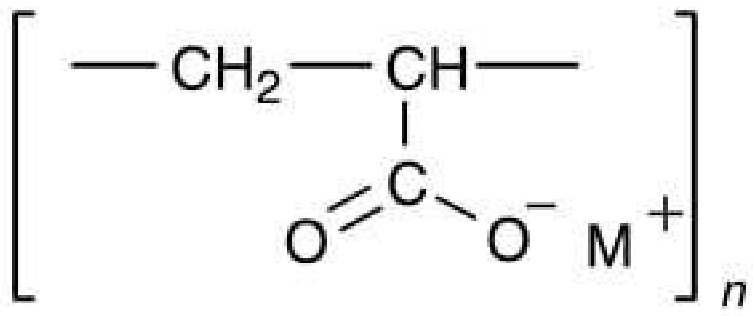


Figure 10.50 Effect of crosslinking on thickener efficiency [371]

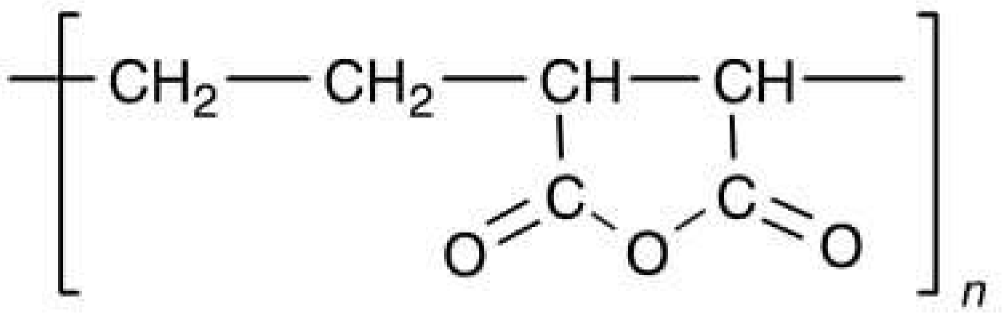
fact that they can be designed to give properties very similar to those of emulsion thickenings. These were previously the only systems used in pigment printing and they are dealt with in section 10.8.3. It is important to realise that an acrylic thickener intended for use with pigment systems may be unsuitable for use with dyes. This is because commercial thickeners, available as solutions, emulsions, liquid dispersions or powders, often contain additional chemicals to improve their stability and performance in particular systems. For pigment systems, for example, the thickener may also contain additives (surfactants or polyelectrolyte dispersing assistants), such as the ammonium or sodium salt of linear poly(acrylic acid) (10.121), which not only modify the behaviour of the acrylic thickener but also assist dispersion of the pigment [371]. Surfactant additions are undesirable with reactive dyes because they promote colour bleeding, whilst the ammonia is undesirable because of deactivation of reactive groups, the lowering of pH that occurs by its evolution during the fixation process and the subsequent difficulty in washing-off of the residual thickener, now bereft of its solubilising ammonium ions.



M = Na or NH_4

10.121

A major drawback of synthetic thickeners when used with dyes is their sensitivity to electrolytes. Most soluble dyes behave as highly ionised electrolytes and disperse dyes contain anionic polyelectrolyte dispersing agents unless they have been formulated with nonionic systems specifically for use with acrylic thickeners. Consequently there is a loss of viscosity; this can be quite pronounced although it depends on circumstances, particularly on the dye concentration. As already mentioned, this can be alleviated to some extent by copolymerisation with acrylamide during manufacture. Otherwise it is necessary to try to eliminate all electrolytes from the system or to increase the concentration of thickener. Such measures have their limitations in practice, however. Alternative synthetic thickening agents include poly(vinyl alcohol) and copolymers of maleic anhydride with alkenes (10.122).



10.122

A detailed comparative study of the rheological properties of four acrylic thickeners varying in relative molecular mass from 1.25 × 10^6 to 4 × 10^6 and of two crosslinked ethylene-maleic anhydride copolymers has been published [345]. In respect of some properties, comparisons were also made with a starch ether and an alginate. Amongst other factors, the influence of molecular mass was demonstrated (Figure 10.51), showing that the higher the molecular mass of the acrylic polymer, the less the amount of thickener required to achieve a given viscosity. Nevertheless, earlier comments in relation to the stringiness of linear acrylic polymers should be borne in mind, i.e. factors other than viscosity need to be considered. Viscosity develops as water is absorbed, causing swelling and rearrangement of the polymer chains, a process that is assisted by, indeed is critically dependent on, neutralisation. Figure 10.52 gives a schematic representation of this swelling and also illustrates the similarity in behaviour with oil-in-water emulsions [371]. It is important that the degree of crosslinking is the optimum required to maintain the polymer in this swollen state and prevent it from dissolving, which would result in loss of desirable properties.

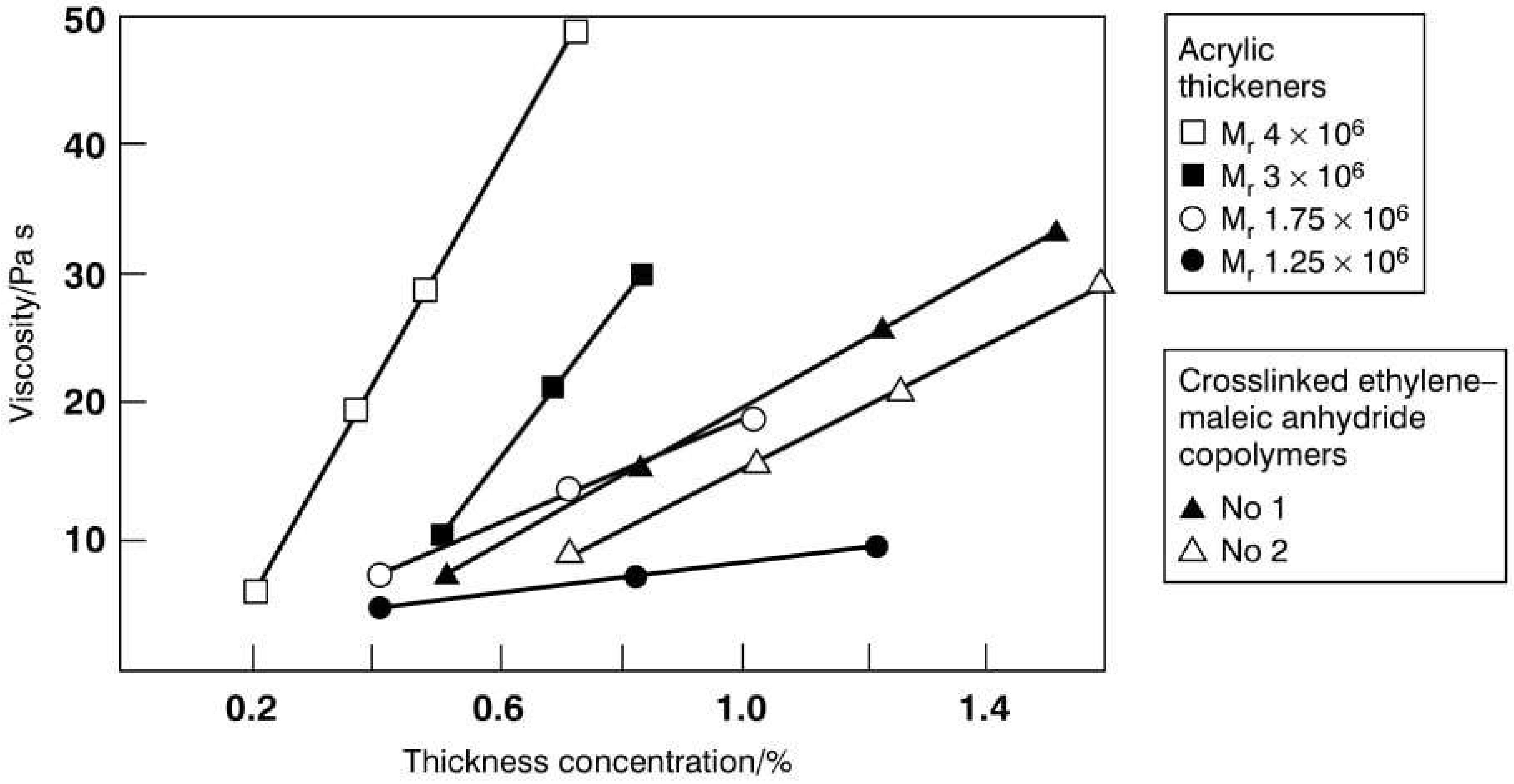


Figure 10.51 Comparison of rheological behaviour of acrylic and copolymeric thickeners [345]

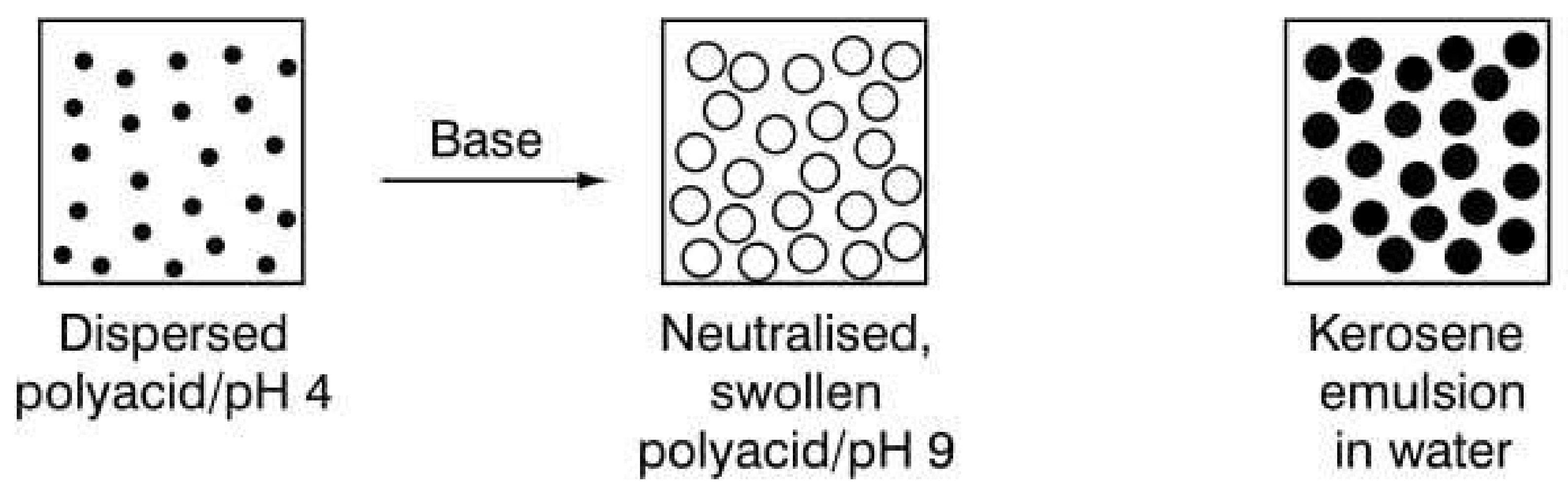


Figure 10.52 Schematic diagram illustrating swelling of polyacid thickener and comparison with oil-in-water emulsion [371]

A novel concept [371] was evaluated to seek a replacement for alginates in printing with reactive dyes. This approach utilised copolymers of poly(acrylic acid) onto which starch has been grafted by free radical polymerisation, the free radical initiator being a potassium persulphate redox system. Both native starch and starch pre-oxidised with sodium hypochlorite were included in the study. It was found that an acrylic–starch graft copolymer effectively replaced 25% sodium alginate, whilst a copolymer of poly(acrylic acid) and oxidised starch replaced 50% sodium alginate. A detailed rheological study was presented but the evaluation lacked economic analysis.

10.8.3 Emulsion thickeners

When immiscible liquids are emulsified the viscosity increases and this can be exploited to prepare thickenings for textile printing. The emulsions used contain a hydrocarbon solvent (usually white spirit), surfactant(s) and water; the oil phase must account for at least 70% of the total volume [342]. The first pigment printing systems introduced in the late 1930s were water-in-oil emulsions (that is, at least 70% of the product was water) in which typical surfactants were ethoxylated alcohols, acids or amides with a low degree of ethoxylation, perhaps 5–8 oxyethylene units per molecule, morpholine/oleic acid or lauric, palmitic and stearic acid esters of sorbitol. Later, manufacturers developed oil-in-water emulsions for which appropriate surfactants are higher ethoxylated alcohols, acids or amides, or a wide variety of alkylaryl types. For any type of emulsion, the HLB of the emulsifying agent(s) is clearly of great importance.

The size of the droplets in an emulsion is inversely related to its viscosity, typical diameters ranging from 100 to 7000 nm. Theoretically no more than 75% of oil can be incorporated in an aqueous emulsion, assuming uniformly spherical droplets, but distortion due to packing allows significantly higher proportions of oil phase to be added. Presumably the oil droplets are stabilised by a surrounding layer of like charges, the type and strength of the charge depending on the surfactant(s) used. Consequently the stability of the emulsion tends to be impaired by any additions that reduce the charge on the droplets.

Emulsion thickeners can be mixed with low concentrations of either natural or synthetic thickeners, especially when applying fibre-substantive dyes rather than pigments; these additions act as film formers, taking the place of the binder used with pigments to increase retention of the dye by the substrate prior to fixation.

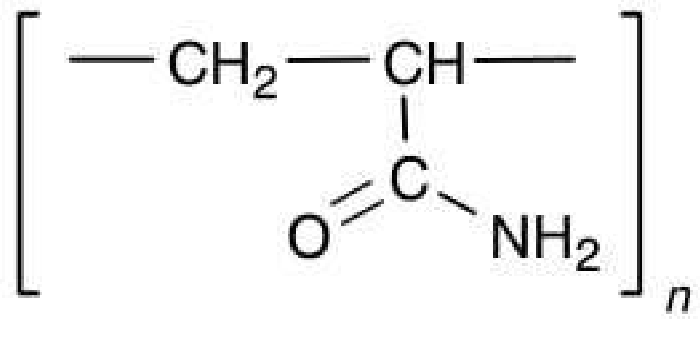
10.8.4 Continuous dyeing

The foregoing discussion has concentrated on the use of thickening agents in textile printing. Similar types of product are used to thicken pad liquors in continuous dyeing processes, although then they are normally described as migration inhibitors rather than thickening agents. All polysaccharides mentioned previously, especially the alginates, locust bean, guar and xanthan gums, modified starches and celluloses, can be used in continuous dyeing, but by far the most widely used are the alginates. Concentrations tend to be significantly lower than in printing since the dyeing process requires a lower viscosity, permitting rapid and complete penetration into the fabric during padding. In addition to the alginates, polyacrylates (10.8.2), polyacrylamides and polyethoxylates are also used [373]. Polyethoxylates are mixed polyglycol ethers of fatty alcohols with ethylene oxide (or propylene oxide), the nonionic block copolymers described in section 9.6 that operate by virtue of a low cloud point (about 25 °C). The functions of these products are two-fold: (a) they should favour the uniform application of dye by padding; and (b) they should effectively inhibit any tendency of the dye to migrate during the subsequent intermediate drying process. In the absence of an inhibitor, dye liquor tends to migrate towards hotter regions of the fabric during drying, causing either patchiness or an undesirable two-sided effect. Whilst viscosity plays an important part in facilitating the uniform absorption of dye liquor, it is less effective than coagulation for inhibiting migration. The polyacrylates are particularly effective [373].

In continuous dyeing agents to assist rapid wetting and even penetration of the fabric are invariably added to pad liquors along with the migration inhibitor. Many types of surfactant can be used, including phosphate esters (which are particularly effective [373]), sulphonates, sulphates, sulphosuccinates and sulphated ethoxylates. Care should be taken to ensure that the type and concentration of product chosen do not depress the degree of fixation of the dyes. Wetting agents are rarely used in printing since they would tend to promote bleeding or haloing of printed areas.

Methods available for assessing migration inhibitors have been reviewed [374,375]. Factors influencing dye migration during the drying phase include fibre type, liquor pick-up, drying temperature, running speed, type of dyes and the various pad liquor additives present. Those additives intended to increase substantivity and agglomeration of the dyes tend to inhibit migration. Interaction between dyes is demonstrated by the finding [376] that, using an alginate migration inhibitor on 50:50 polyester/cotton, the migration of an individual dye can be inhibited by the presence of other dyes in the mixture that have larger particle sizes or a greater tendency to flocculate. However, increasing the concentration of migration inhibitor progressively neutralises this tendency. When the concentration is high enough, specificity of particulate migration is eliminated as the migration of dyes in the mixture approaches zero.

Polyacrylamides (10.123) of chain length (n) 7000 to 14 000, which is higher than normally suitable for migration inhibitors, are useful pad liquor additives [373] in that they increase liquor pick-up and sometimes colour yield, notably with pigments. When used with azoic dyes on cellulosic fabrics, they can eliminate the need for the intermediate drying process. In a study [377] using polyacrylonitrile saponified with alkali to form amide groups capable of being crosslinked with formaldehyde, it was found that migration during drying decreases as the degree of crosslinking is increased, this being attributed to the increased structural density of the polymer films.



10.123

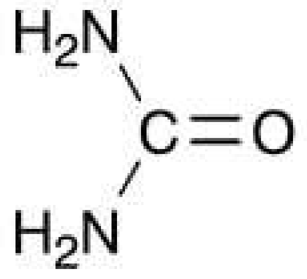
The continuous dyeing of polyester/cotton blends inevitably results in staining of the cotton by disperse dyes, this effect being greatly influenced by the chemical nature and concentration of the migration inhibitor, the dyebath pH and the chemical nature and concentration of the dyes, whereas the presence of wetting agent or neutral electrolyte does not have much influence [378]. Normally in the dyeing of polyester/cotton blends a higher dyeing temperature minimises staining of cotton, since the higher temperature facilitates migration of disperse dye from the cotton to the polyester. Migration inhibitors can negate this effect, however, so it is important to establish the optimum agent concentration necessary to prevent migration but avoiding excessive concentrations that could lead to increased staining of the cotton.

It has been shown that xanthan gum is an effective migration inhibitor for the application of water-soluble chemicals, leading to uniform distribution and more reproducible fixation [379]. Although this work was specifically concerned with the application of a soluble flame retardant to polyester, suitability for the application of reactive dyes or resin finishes is also claimed.

10.8.5 Hydrotropic agents

In many printing and some continuous dyeing processes the colour yield of dyes can often be improved, sometimes markedly, by the use of an auxiliary that tends to increase the aqueous solubility of the dye, particularly when using highly concentrated pastes or liquors that tend to lose moisture under adverse conditions. There is clearly an analogy here with the mechanism of solubilisation discussed in section 10.6.2, since the hydrotrope acts as an amphiphilic bridge between the dye solubilisate and the aqueous medium. Surfactants can therefore function as hydrotropes and are sometimes used as such in continuous dyeing processes. Hydrotropes with much less powerfully surface-active properties are more suitable for use in printing, where surfactants are normally avoided because their concomitant powerful wetting properties would promote bleeding and haloing of the print.

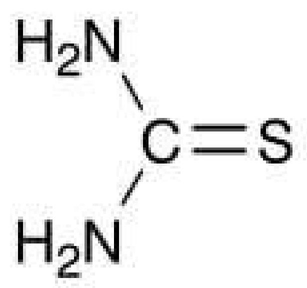
By far the most important of these compounds are urea (10.124) and thiourea (10.125). However, dye–fibre systems are so varied that many hydrotropes are of interest under specific conditions. Typical examples that have been mentioned [380] include: triethanolamine (10.126), *N*,*N*-diethylethanolamine (10.127), sodium *N*-benzy1sulphanilate (10.128), sodium *N*,*N*-dibenzy1sulphanilate (10.129), ethanol, phenol (10.130), benzyl alcohol (10.131), resorcinol (10.132), cyclohexanol (10.133), ethylene glycol, glycolic acid (10.134), 2-ethoxyethanol (10.135), diethylene glycol (10.136), 2-ethoxyethoxyethanol (10.137), 2-butoxyethoxyethanol (10.138), thiodiethylene glycol (10.139) and glycerol (10.140), the last-named in particular being useful with practically all classes of dyes.



$(\mathrm{H_2N})_2\mathrm{C{=}O}$

10.124

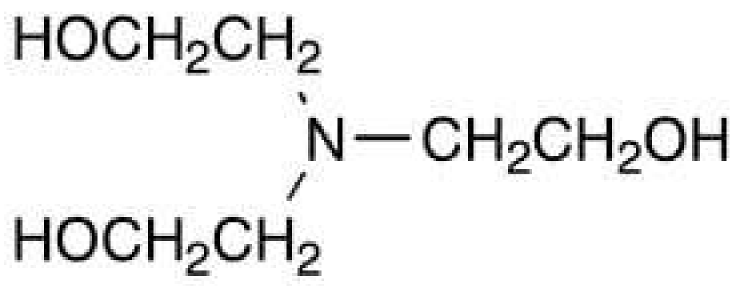
Urea



$(\mathrm{H_2N})_2\mathrm{C{=}S}$

10.125

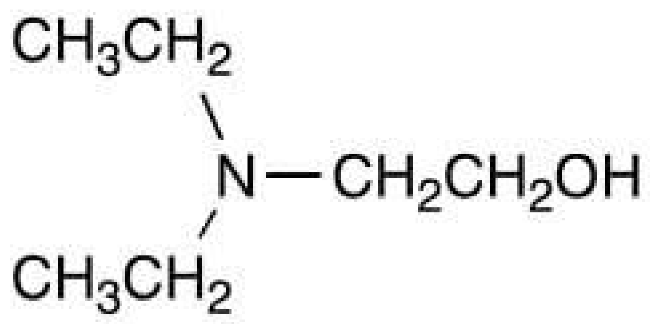
Thiourea



$(\mathrm{HOCH_2CH_2})_2\mathrm{N{-}CH_2CH_2OH}$

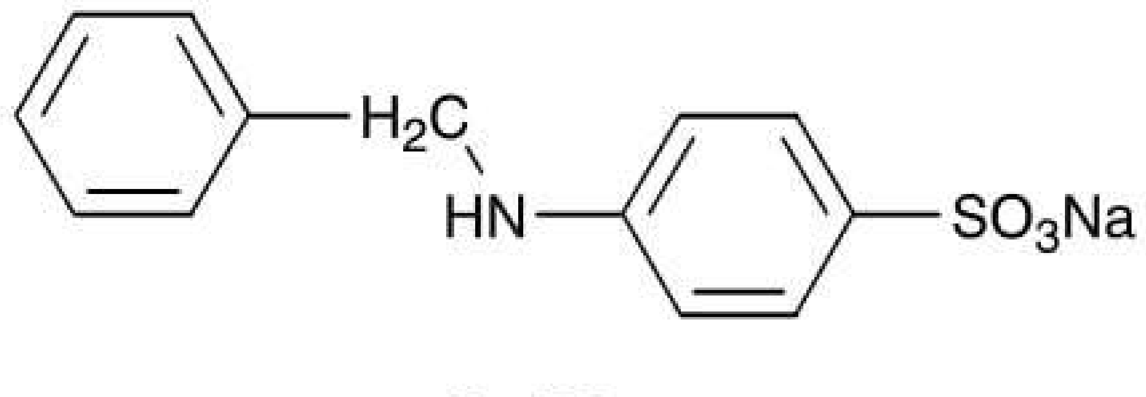
10.126

Triethanolamine

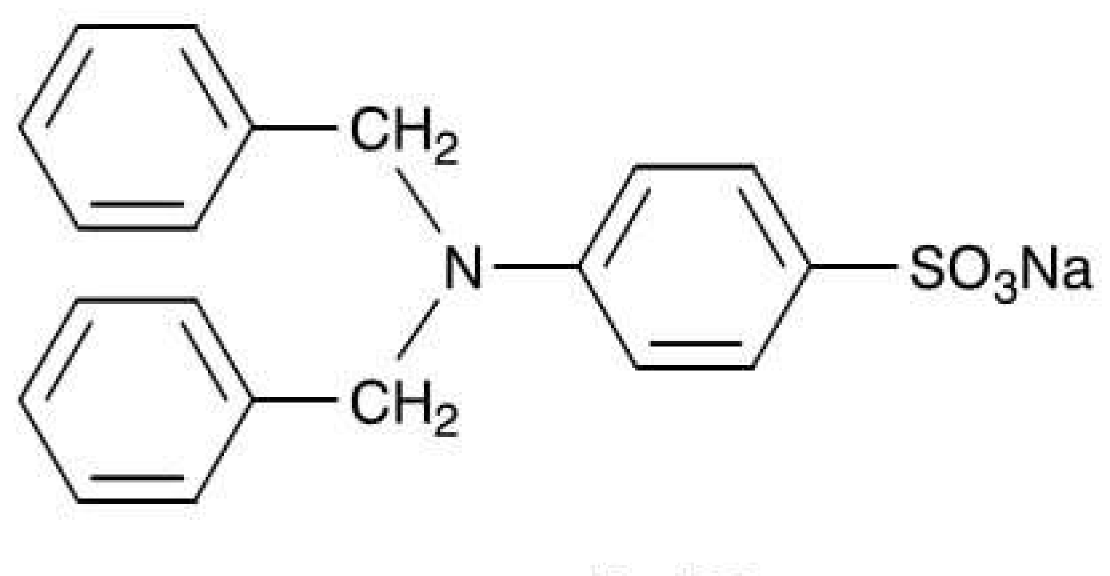


$(\mathrm{CH_3CH_2})_2\mathrm{N{-}CH_2CH_2OH}$

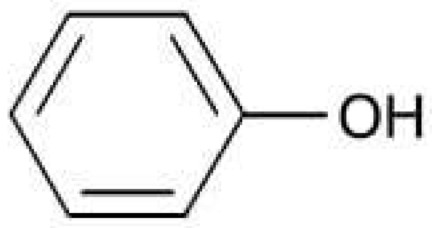
10.127



10.128

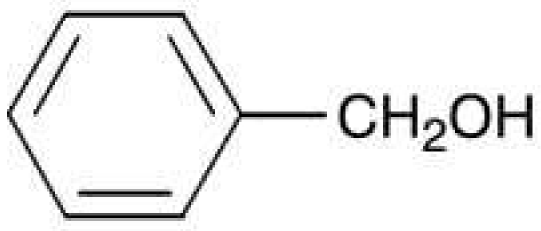


10.129

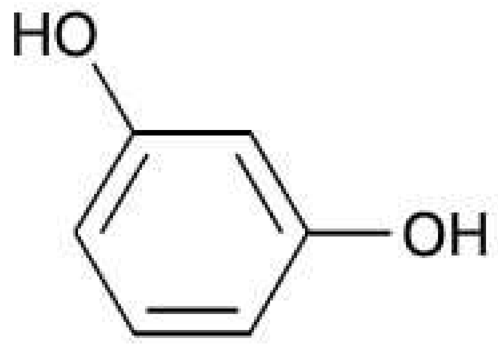


10.130

Phenol

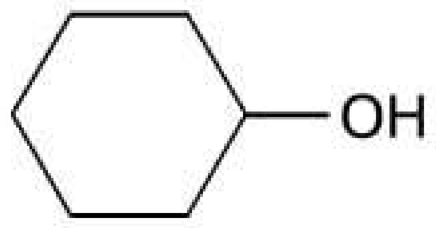


10.131



10.132

Resorcinol



10.133

Cyclohexanol

$HOCH_2COOH$

10.134

$CH_3CH_2OCH_2CH_2OH$

10.135

$HOCH_2CH_2OCH_2CH_2OH$

10.136

$CH_3CH_2OCH_2CH_2OCH_2CH_2OH$

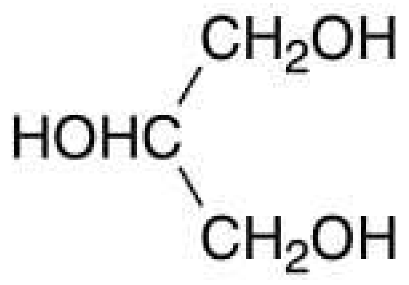
10.137

$CH_3CH_2CH_2CH_2OCH_2CH_2OCH_2CH_2OH$

10.138

$HOCH_2CH_2SCH_2CH_2OH$

10.139

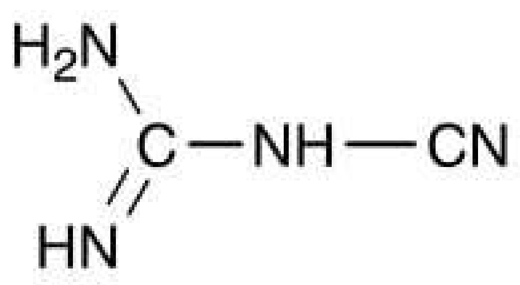


$HOHC(CH_2OH)_2$

10.140

Glycerol

Most hydrotropic agents, though not surfactants in the usual sense of the word, do significantly lower the surface tension of water and this is an important prerequisite for their solubilising action. Hydrogen bonds, together with weaker dipolar and van der Waals forces, contribute to this interaction, the active centres in the hydrotropic molecules being proton-donating groups (such as hydroxy, amino and amido groups) and proton-accepting atoms (such as the nitrogen atom of a tertiary amine). For this reason hydrotropes can also be added to the diluent system in the manufacture of certain dyes, particularly liquid brands, in which they not only increase the apparent solubility of the dye but also help to prevent the formation of surface skin. Another compound that has entered this area is 1-cyanoguanidine (10.141) popularly known as dicyandiamide. The main mechanisms whereby hydrotropes are believed to function have been mentioned above. However, there has been a good deal of discussion regarding possible mechanisms, mainly in connection with the interaction of urea with reactive dyes. Useful reviews of this topic are available [381,382].



$H_2N(HN{=})C{-}NH{-}CN$

10.141

Dicyandiamide

The growth of environmental awareness has certainly impinged on this area, restricting the use of hydrotropes that are volatile during steaming or dry heat treatments, as well as those suspected of endangering health. These problems are particularly acute with urea, widely used for a long time and considered an essential hydrotropic assistant in printing and continuous dyeing with reactive dyes. This is considered in more detail in section 12.7.1.

10.8.6 Environmental aspects

Reference to Table 10.10 in section 10.5.2 indicates printing to be responsible for some 10–20% of the total pollution load from the textile wet processing of cotton. Other substrates, as well as continuous dyeing, also make significant contributions. Useful reviews of the environmental aspects of textile printing generally [383,384] and of pigment printing in particular [385,386] are available. There are two aspects to be considered:

(1) airborne pollution from volatile components during steaming and dry heat treatments
(2) aqueous effluent pollution from washing-off and washdown procedures.

In both cases there are two basic methods of control:

(1) elimination or minimisation of offending products, which may involve total or partial substitution by more benign products, or a redesigned process that does not require that type of auxiliary
(2) remedial treatment of exhaust gases or effluent.

In any case, it is always sound practice to optimise the concentration of an auxiliary so that no more than necessary is applied. This aim of using minimum quantities is assisted by the trend towards more efficient thickeners. For example, in the 1960s it was common for thickeners to be made up to a 20–30% concentration, whereas today 10% is more common and it is predicted that this will fall to an average of about 5% within the next decade [383].

Airborne pollution can arise from volatile fractions during drying, as well as dry heat curing or heat setting treatments. This aspect has been associated mostly, but not exclusively, with the use of emulsion thickeners in pigment printing, considerable volumes of organic compounds being released during drying and curing. Consequently, emulsion printing is now seldom carried out in the major developed countries [383]. Those acrylic thickeners that contain organic solvents or hydrocarbons are also sources of airborne pollution, but thickeners free from such additives are now available [386]. One method of dealing with the volatile emissions is incineration, but this is very costly. Scrubbing is highly efficient with water-soluble volatiles but not with hydrocarbons: hence it is best to avoid using polluting materials. A detailed account of the ecological factors in pigment printing is available [385], indicating the obligation to minimise or eliminate emissions of residual monomers, formaldehyde and unwanted solvents. Furthermore, alkylphenol ethoxylates formerly used as emulsifiers can be replaced by fatty alcohol ethoxylates or, to some extent, by anionic surfactants. Pigment printing also offers ecological benefits over other systems in that it saves time and energy, and washing-off is unnecessary [385].

In general (excluding pigment printing), however, the thickeners or migration inhibitors are present in waste waters, both from washing-off the dyeings or prints and from washing-down of equipment. The usual three methods of treatment (chemical degradation, bioelimination and recycling) have to be considered for dealing with them. Natural thickeners are not toxic in themselves but, in parallel with the analogous sizing agents (Table 10.11 in section 10.5.2), they show high chemical and biological oxygen demand [354,383,387]. Galactomannans [216,217,354] in particular are thought to have a good future in respect of environmental impact. Since the naturally occurring polymers present the least difficulties in environmental terms, it is thought that their derivatives will become less important [383].

The treatment and disposal of these wastes is not only expensive but entails the loss of potentially useful materials. Thus, as with sizing agents, recycling is an attractive consideration [388,389]. The basic principle is precipitation of the thickener in a suitable aqueous solvent system followed by isolation, often by ultrafiltration. Dyes can be separated from the thickener either continuously or discontinuously [388]. In a detailed study [389], the efficiency of precipitation of high-, moderate- and low-viscosity alginate thickeners in four solvent systems was compared with that of carboxymethylated galactomannans or celluloses and four synthetic thickeners, giving the results in Table 10.38. Thus all types of alginate thickener can be isolated quantitatively from the wash water and recycled without difficulty. These recycled thickeners are claimed [388,389] to give rheological properties and printing results equivalent to those of the original products. Pure acrylic thickeners can also be precipitated almost quantitatively [389].

Table 10.38 Precipitation (%) of printing thickeners using solvents [389]

Thickener	Methanol	Ethanol	Acetone	Aqueous methanol
Low-viscosity alginate	100	100	100	100
Moderate-viscosity alginate	100	100	100	100
High-viscosity alginate	100	100	100	100
Carboxymethylgalactomannan				
Low-viscosity	>90	>90	>90	70–90
High-viscosity	>90	>90	>90	70–90
Carboxymethylcellulose				
Low-viscosity	>90	>90	>90	55–90
High-viscosity	>90	>90	>90	55–90
Synthetic thickener 1	70–90	70–80	70–95	<20
Synthetic thickener 2	50	50	50–70	<20
Synthetic thickener 3	0	0	0	0
Poly(acrylic acid)	>90	>90	>90	>90

Natural thickeners are prone to biological attack and degradation, leading to a loss of thickening efficiency. It is common practice to add a small amount of a bactericide to protect against attack during storage [383,387,390]. About thirty classes of compounds have been listed as bactericides [387], but phenol derivatives (including chlorinated phenol, *m*-cresol or *o*-phenylphenol) and formaldehyde have proved particularly suitable, added either by the manufacturer of the thickening agent or by the printer during formulation of the stock thickener. As bactericides, such compounds are by definition toxic and hence environmentally undesirable if not actually prohibited in some countries. However, it has been pointed out [383] that they are used only at very low concentrations (usually below 0.1%) that are just about sufficient for bacterial efficiency. Together with the thickener they are then washed out with copious amounts of water, entering the effluent at such high dilution that they no longer have bactericidal action and can even be biologically eliminated during effluent treatment.

Mention has already been made of the environmental undesirability of many hydrotropes (section 10.8.5) and this particularly applies to urea, the most widely used. This is discussed in more detail in section 12.7.1 in connection with reactive dyes. Suffice to note that the efficiency of urea as a hydrotrope is proving difficult to equal in every respect with substitutes that are environmentally acceptable [382].

10.9 TREATMENTS TO ALTER DYEING PROPERTIES OR ENHANCE FASTNESS

Treatments to improve the intrinsic fastness of dyeings have a long and prolific history. Most of these are aftertreatments, although some are concurrent with the dyeing process as in the application of UV absorbers to enhance light fastness. The treatments described in this section are essentially concerned with improving fastness properties or fibre stability. Treatments to modify the handle or other fibre properties are excluded, these being dealt with in section 10.10. Furthermore, such treatments are not an essential integral part of the dyeing process, thus excluding the afterchroming of chrome dyes and the oxidation of sulphur and vat dyeings. Many processes have been developed for improving fastness but relatively few are still in commercial use today. Their efficacy has to outweigh the extra processing cost and time. The emphasis will be on processes of current commercial or research interest. An excellent comprehensive review covering the period 1880–1980 is already available [391]. Of growing interest, at least in the research sector, are fibre pretreatments aimed primarily at modifying dyeing properties, although these may have secondary benefits in terms of improved fastness. There has always been a good deal of interest in pre- and aftertreatments amongst textile chemists and colourists, largely on account of the innate interest of the chemistry and the challenges involved. Commercial processors have been less enthusiastic, however, since these variations involve additional costs and scheduling difficulties.

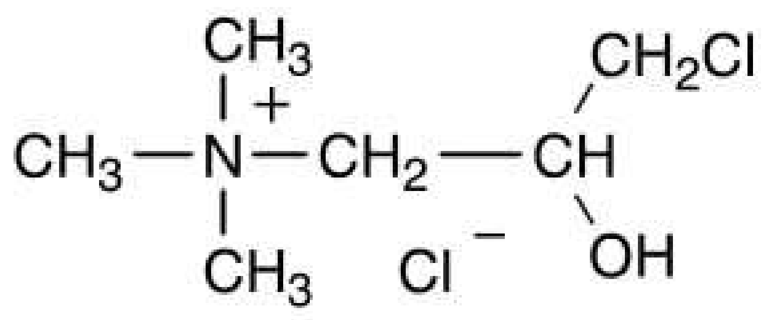
10.9.1 Pretreatments

One of the earliest fibre pretreatments for improving the dyeability of cotton is of course mercerisation (section 10.5.4). However, more recent research interest in this area has been generated by environmental concerns about reactive dyeing, aiming to enhance substantivity for the modified fibre so that higher absorption and fixation are obtained. This results in less dye (hydrolysed or still active) in the effluent. A further objective is to minimise the usage of electrolyte in the application process. This area has been thoroughly reviewed [392,393].

At the risk of over-simplification, most of the pretreatments covered by Lewis and McIlroy will be summarised in Tables 10.39 to 10.42. Their review [393] and the original works cited in it should be consulted for details, of course. The great majority of processes involve increasing the nitrogen content (i.e. the basicity) of the cellulose, there being an analogy here with the better dye-sorption properties of wool that naturally contains such built-in nitrogen. Table 10.39 presents structural modifications of cellulose not entailing the application of a polymer. Most of these reactions involve amination in one form or another. In fact interest in the amination of cellulose began in the 1920s, long predating current environmental concerns regarding reactive dyes. Hence it is not surprising that some of the earliest processes are environmentally suspect. Nevertheless, more acceptable processes have evolved, making cellulose more substantive to anionic dyes and enabling much less electrolyte and non-alkaline fixation conditions to be adopted for reactive dyeing.

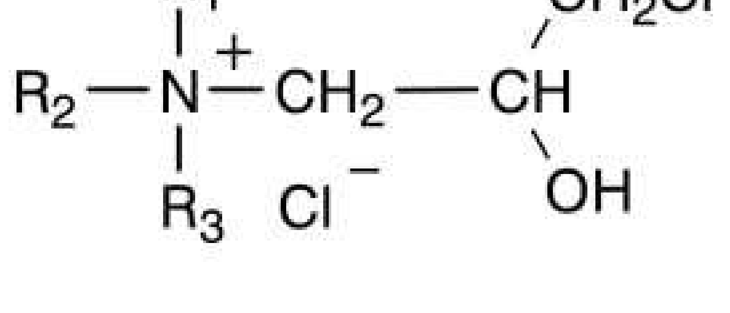
It has been pointed out that aminoethylcellulose produced by a two-stage dry process using 2-aminoethylsulphuric acid can even react covalently with hydrolysed vinylsulphone dyes, thus enhancing fixation and making washing-off easier [394]. Another cationic quaternary compound that has been used [395] is 3-chloro-2-hydroxypropyltrimethylammonium chloride (10.142). This compound and four analogous reactive cationic agents (10.143) have been proposed [396], prepared by reaction of the appropriate amine with epichlorohydrin.

The cationisation of cotton cellulose using these agents takes place in two stages (Schemes 10.49 and 10.50), although from a practical viewpoint these occur concurrently in a single process by exhaustion for 20 minutes at 80 °C in the presence of sodium hydroxide as the base catalyst. In the first stage an epoxide is formed in the presence of alkali. In the second stage this epoxide reacts with a hydroxy group in the cellulose. The cationised cotton could be dyed with anionic dyes; only CI Acid Red 127 was used in this research. The degree of substitution of the cellulose and the amount of dye absorbed both decreased as the length of the hydrocarbon chains attached to the nitrogen atom was increased. Regardless of hydrocarbon chain length, the light fastness was slightly higher on cotton than on nylon or wool dyed with the same dye. Fastness to washing decreased with increasing length of the hydrocarbon chains. The cationised cotton showed enhanced antibacterial properties, the potency increasing with increasing hydrocarbon chain length [396].



$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|+}{\underset{|}{N}}}}-CH_2-CH(CH_2Cl)(OH)\quad Cl^-$$

10.142



$$R_2-\overset{R_1}{\underset{R_3}{\overset{|+}{\underset{|}{N}}}}-CH_2-CH(CH_2Cl)(OH)\quad Cl^-$$

10.143

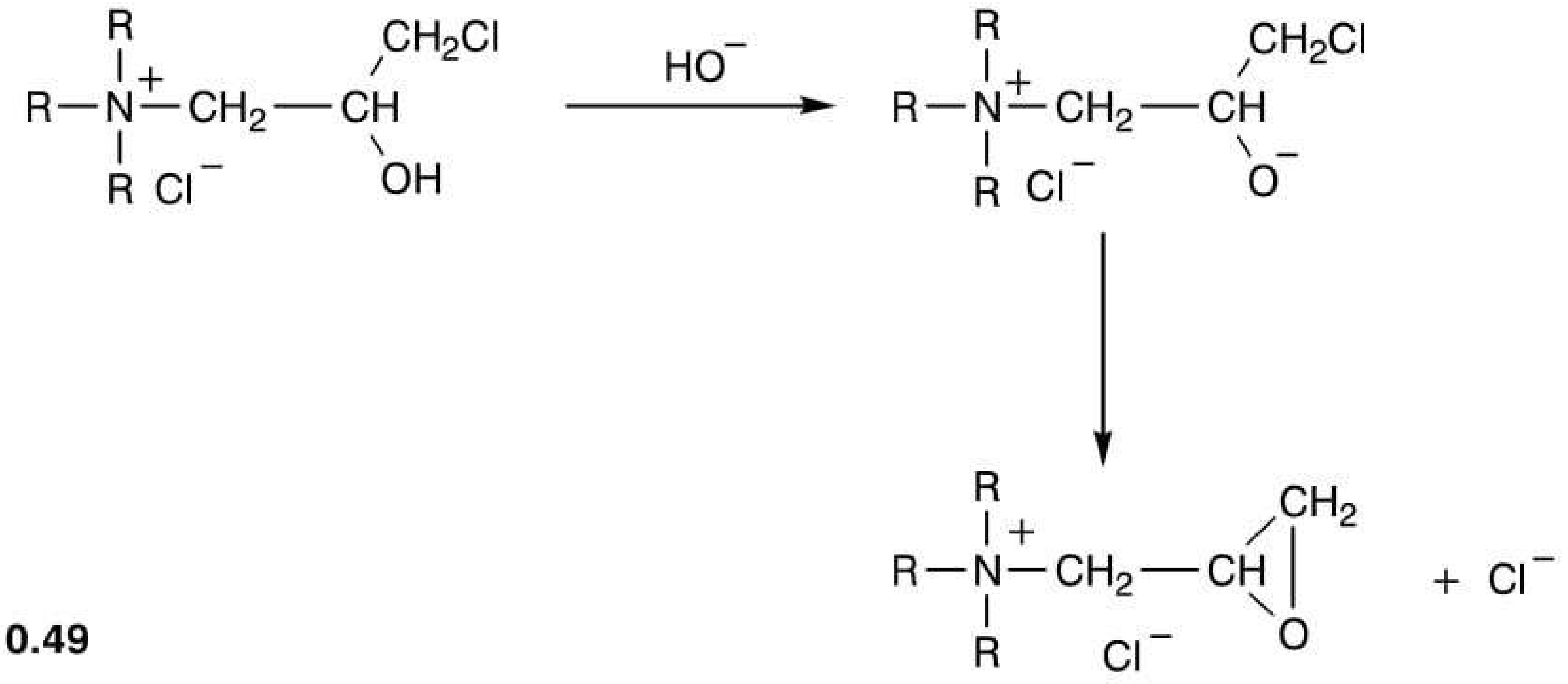
Trimethylamine: $R_1 = R_2 = R_3 = CH_3$

Triethylamine: $R_1 = R_2 = R_3 = CH_3CH_2$

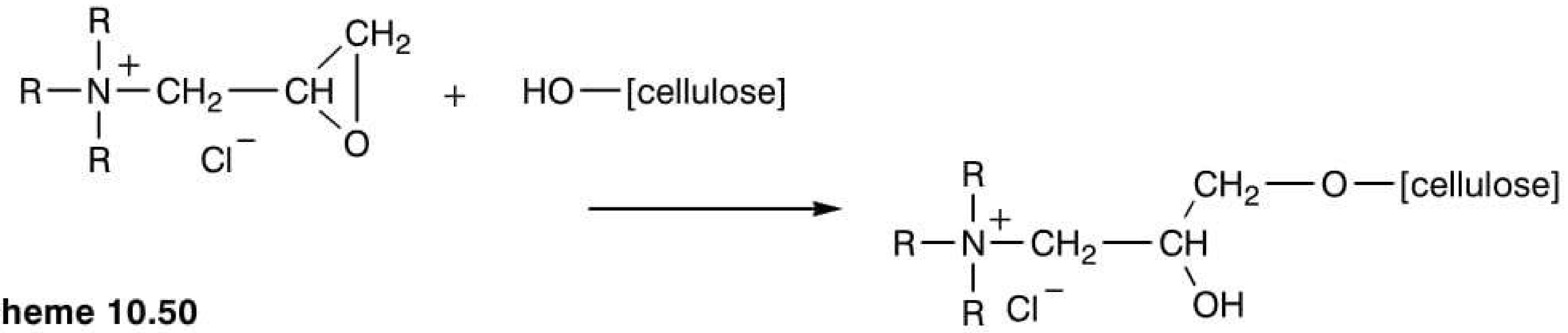
Tripropylamine: $R_1 = R_2 = R_3 = CH_3CH_2CH_2$

Tripentylamine: $R_1 = R_2 = R_3 = CH_3(CH_2)_4$

Dimethyltetradecylamine: $R_1 = R_2 = CH_3$
$R_3 = CH_3(CH_2)_{13}$



Scheme 10.49



Scheme 10.50

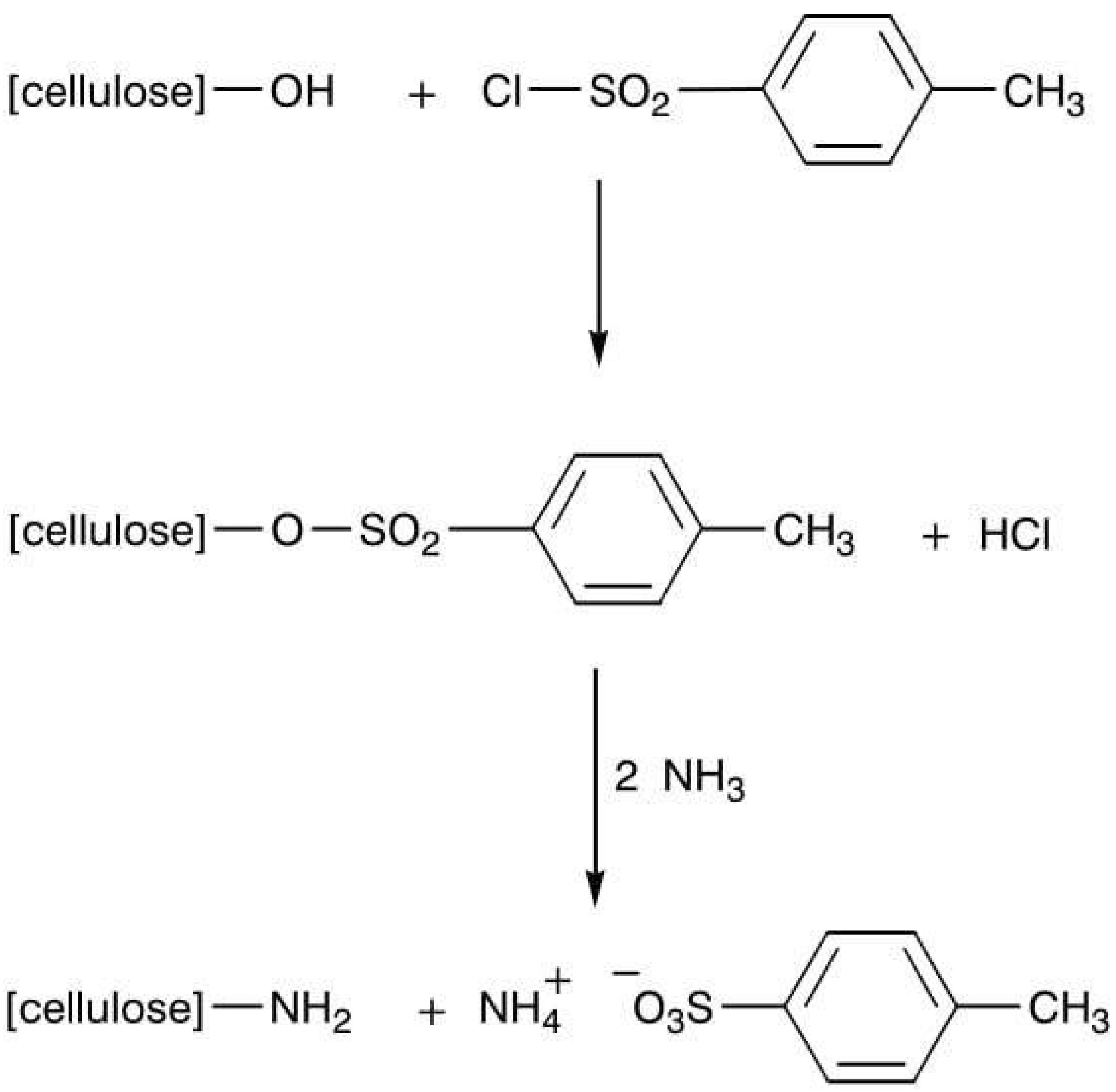
Table 10.39 Pretreatments to modify cotton cellulose by substitution reactions [393]

Pretreatment reaction	Method	Comments
Amination	Tosylation, followed by treatment with amines (Scheme 10.51)	All amination treatments give improved dyeability
	p-Nitrobenzoyl chloride, followed by reduction of nitro (Scheme 10.52)	
	Acetylaminobenzenesulphonyl chloride in nitrobenzene or chloroform, followed by hydrolysis of the amide (Scheme 10.53)	
	2-Chloroethylamine and alkali-treated cellulose (Scheme 10.54)	
	Sodium 2-aminoethylsulphate in aqueous alkali (Scheme 10.55)	More efficient in producing 2-aminoethylated cellulose. Relatively inexpensive and doesn't require organic solvent
	Sodium borohydride added to a sodium 2-aminoethylsulphate pad liquor	Gives white aminated cotton. Borohydride reduces yellow Schiff bases formed by reaction of aldehyde groups with amino groups
	Polymerisation of ethyleneimine on fibre by various methods	Improved dyeability
Diethylaminoethylation	2-Chloroethyldiethylamine hydrochloride (Scheme 10.56)	Dyeable in absence of salt with direct, reactive or acid dyes

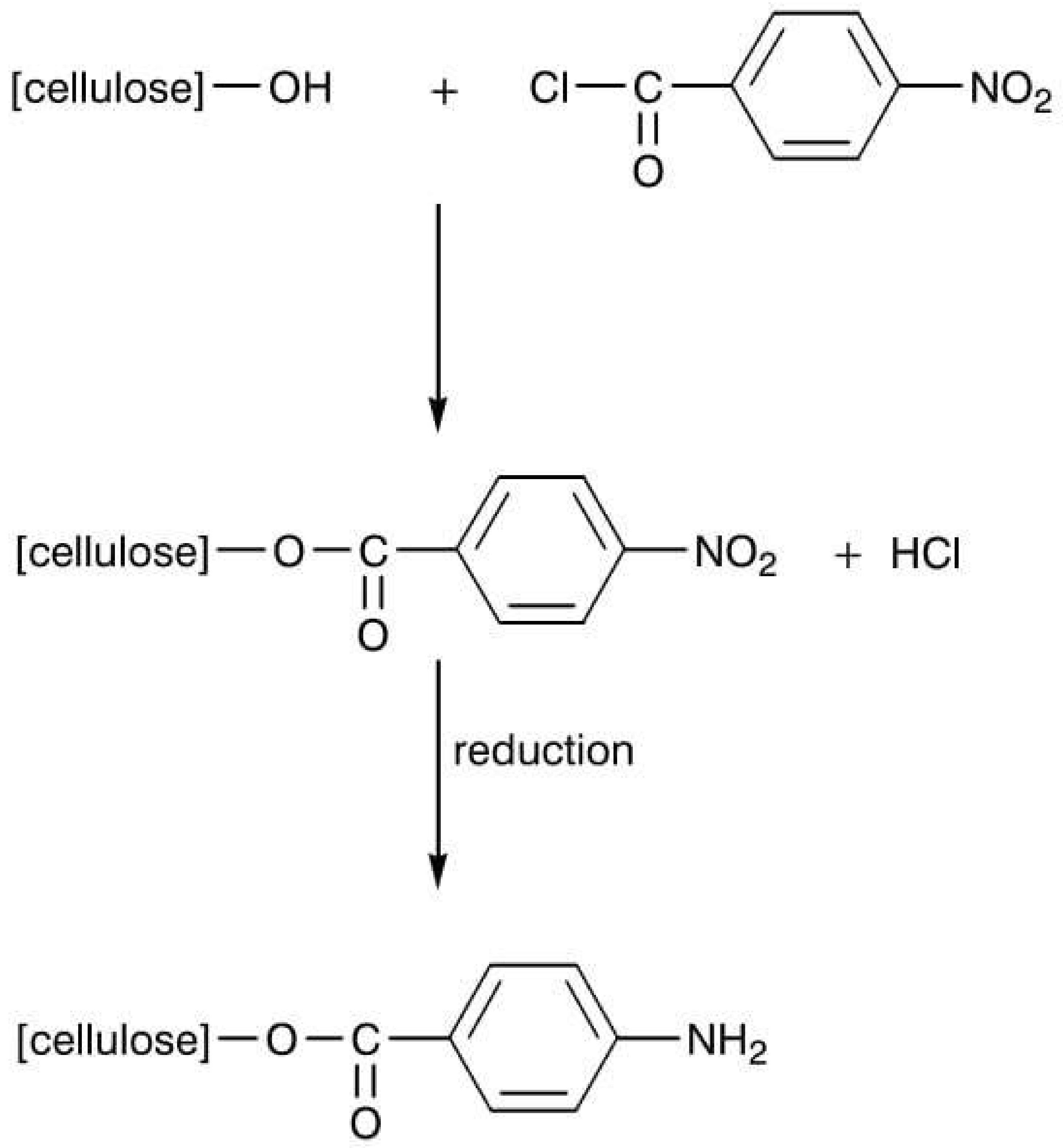
Continued on next page

Table 10.39 *Continued*

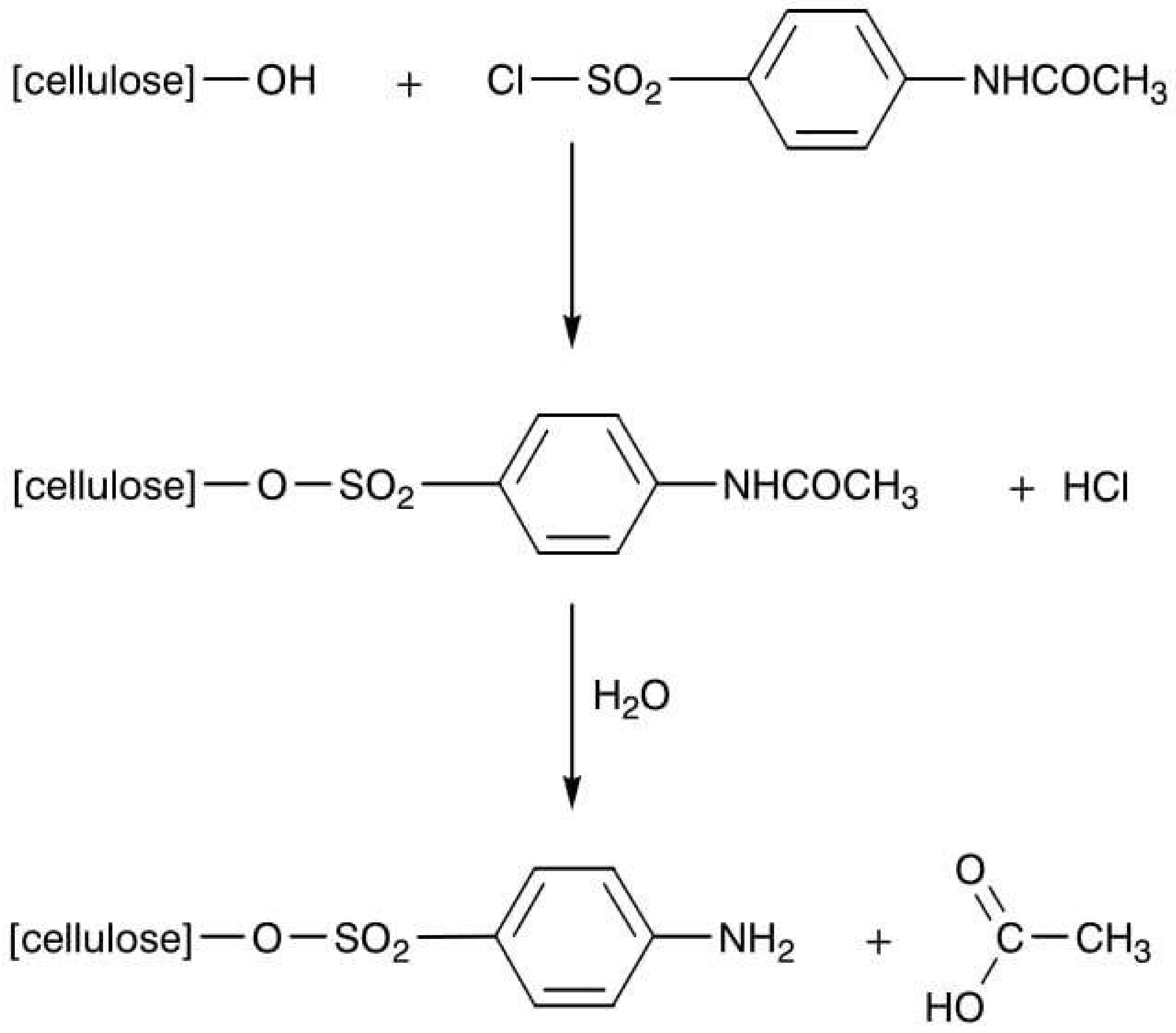
Pretreatment reaction	Method	Comments
Esterification	Inorganic or organic acids	Improved dyeability
Esterification and amination	3-Chloropropionyl chloride, followed by amine (Scheme 10.57)	Primary, secondary, tertiary and quaternary derivatives can be produced. Dyeable with reactive dyes, neutral to slightly acidic without salt
Amination	Epoxides in alkali, including ethylene oxide, propylene oxide, glycidol (2,3-epoxypropan-l-ol). Scheme 10.58 shows glycidyltrimethylammonium chloride	Glycidyltrimethylammonium chloride marketed to enhance dyeability with direct and reactive dyes
Introduction of quaternary N groups	1,1-Dimethyl-3-hydroxyazetidinium chloride in presence of strong alkali by pad–bake (Scheme 10.59)	Dyeable with reactive dyes at pH 7 without salt, giving extremely high fixation
Acylation	Nicotinoyl-thioglycolate and alkali by pad–bake (Scheme 10.60)	Dyeable with monochlorotriazine reactive dyes at pH 3 without salt
Amination	*N*-Methylolacrylamide in presence of Lewis acid catalyst. Further modifications possible by addition to double bond (Scheme 10.61)	Improved dyeability with dichlorotriazine dyes at pH 5 without salt, giving 99% fixation
	Amines with durable press resins	Some improvements in dyeability, especially with direct dyes, but light fastness can be a problem



Scheme 10.51



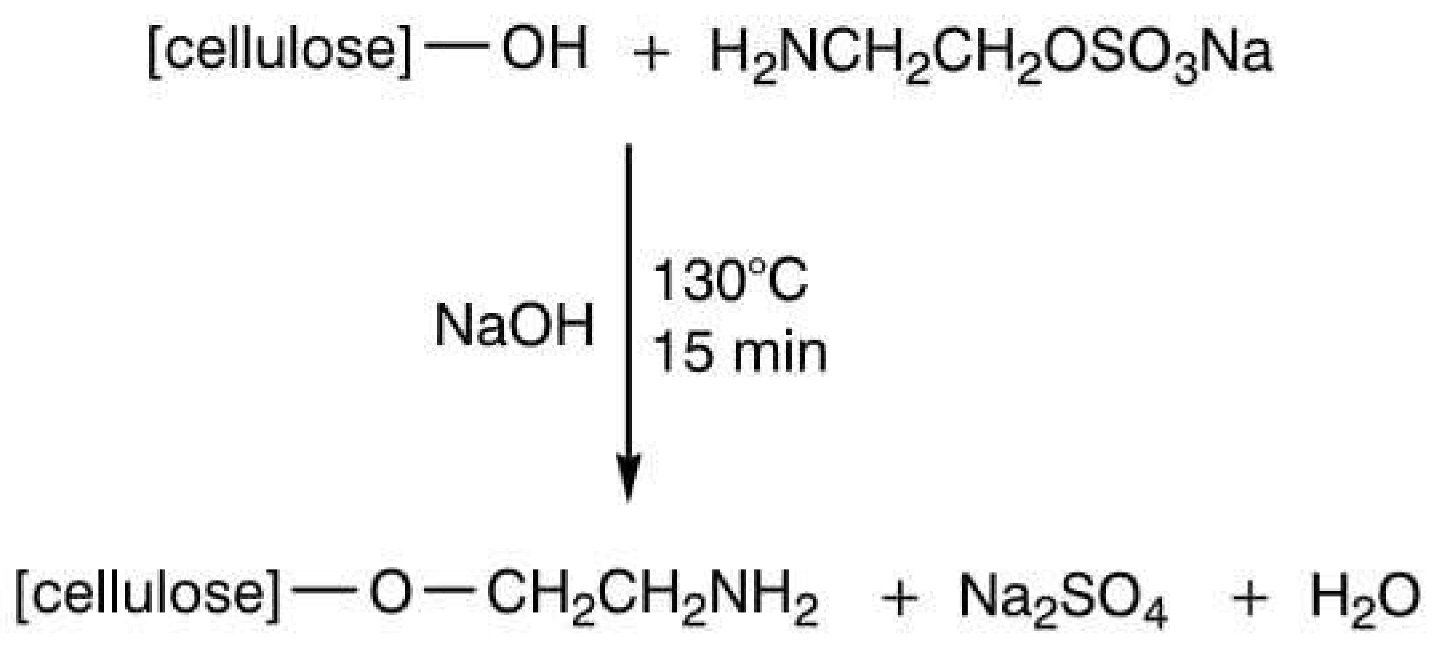
Scheme 10.52



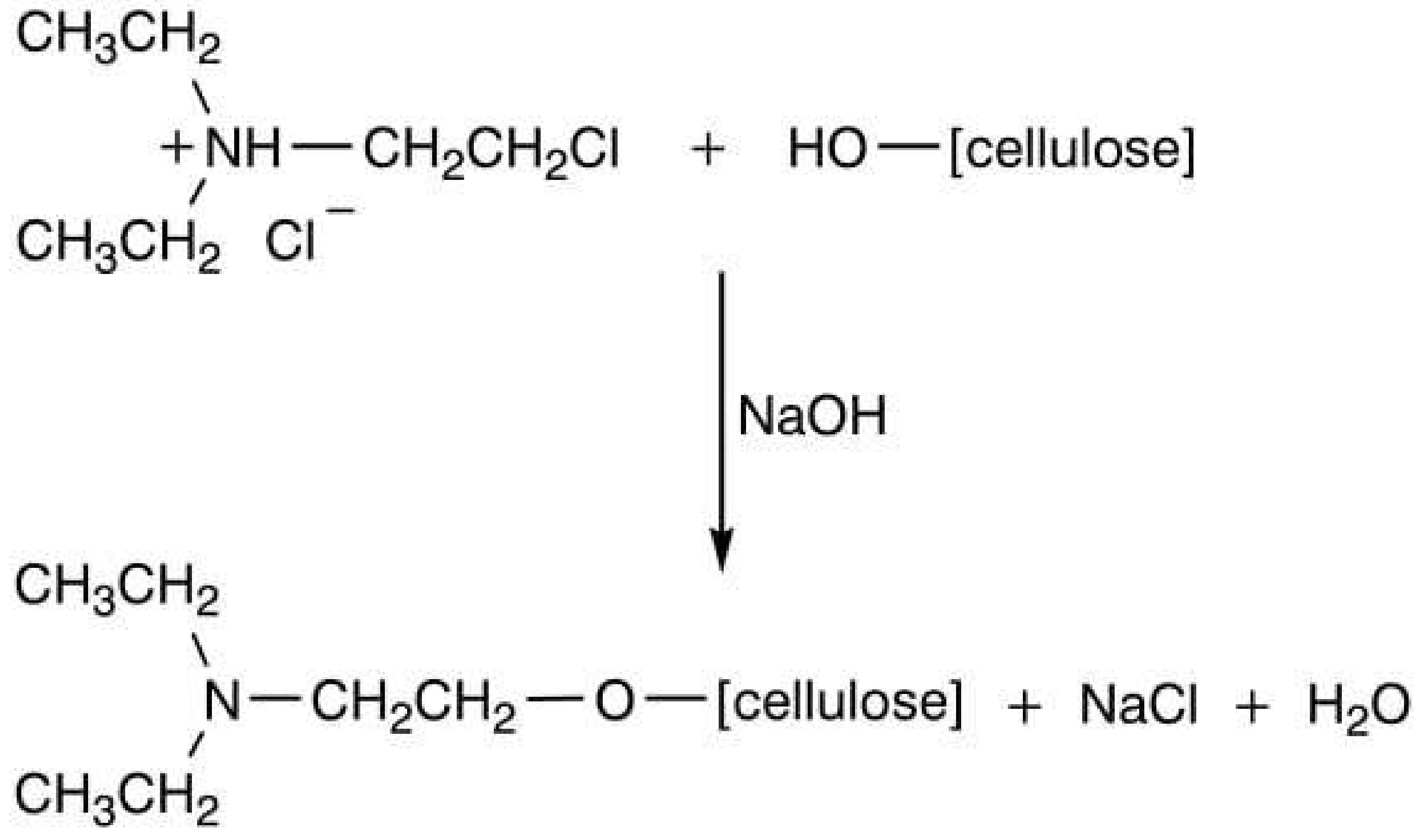
Scheme 10.53

$$[\text{cellulose}]\text{—OH} + \text{ClCH}_2\text{CH}_2\text{NH}_2 \longrightarrow [\text{cellulose}]\text{—O—CH}_2\text{CH}_2\text{NH}_2 + \text{HCl}$$

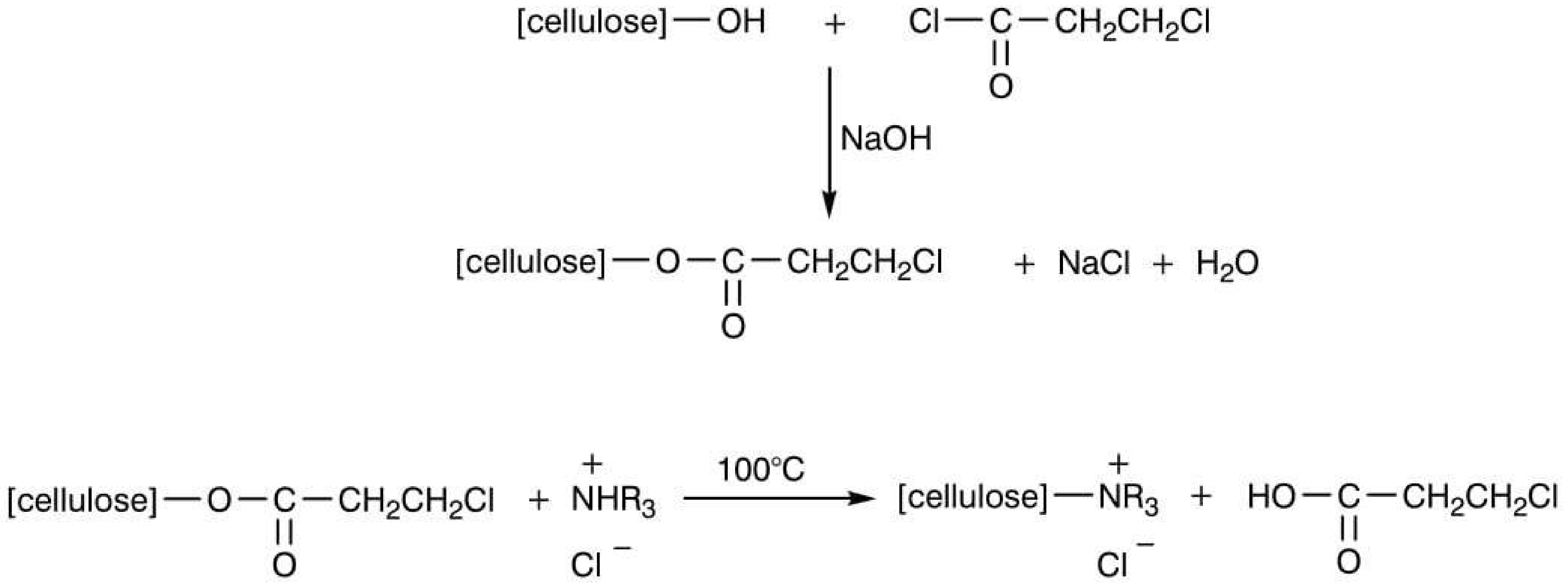
Scheme 10.54



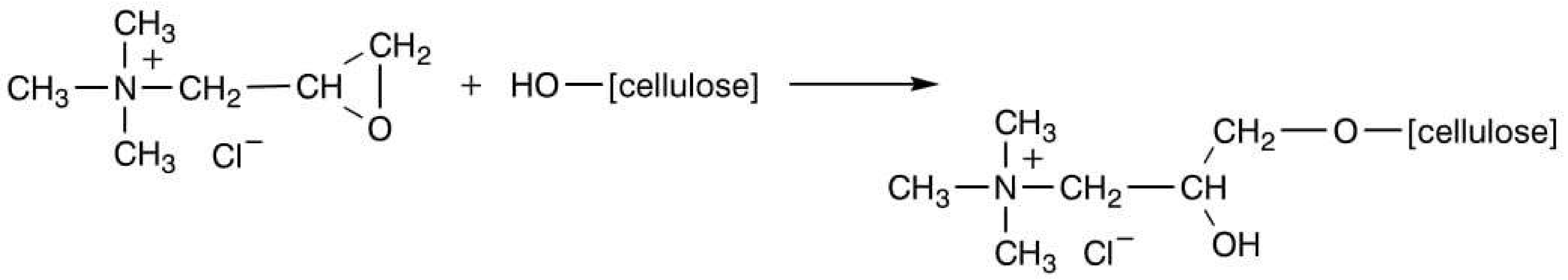
Scheme 10.55



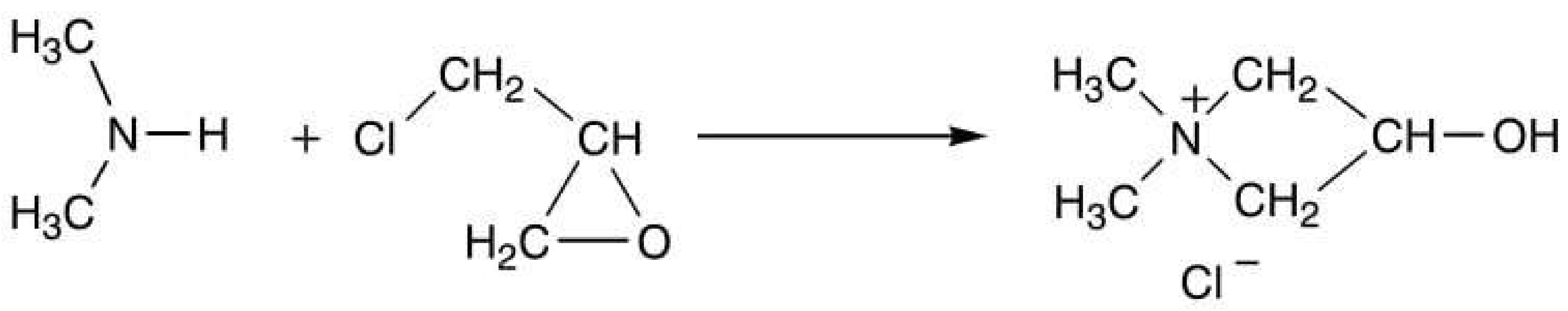
Scheme 10.56



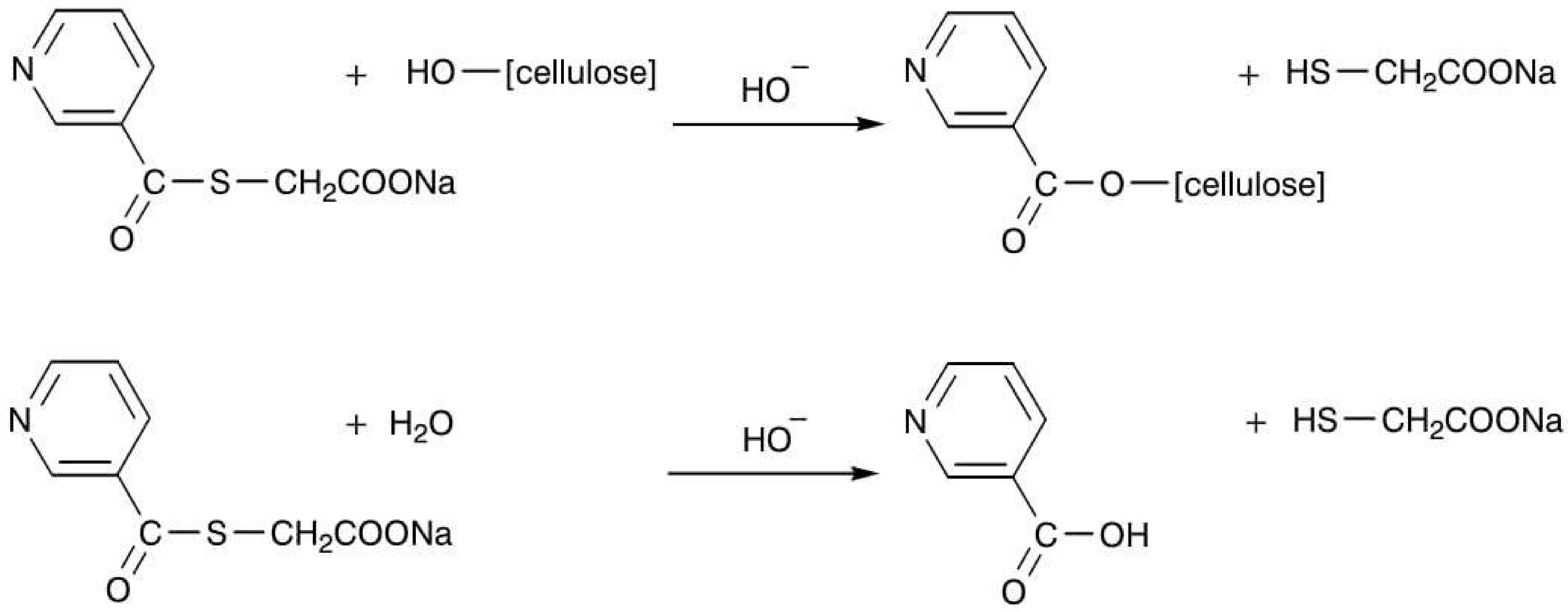
Scheme 10.57



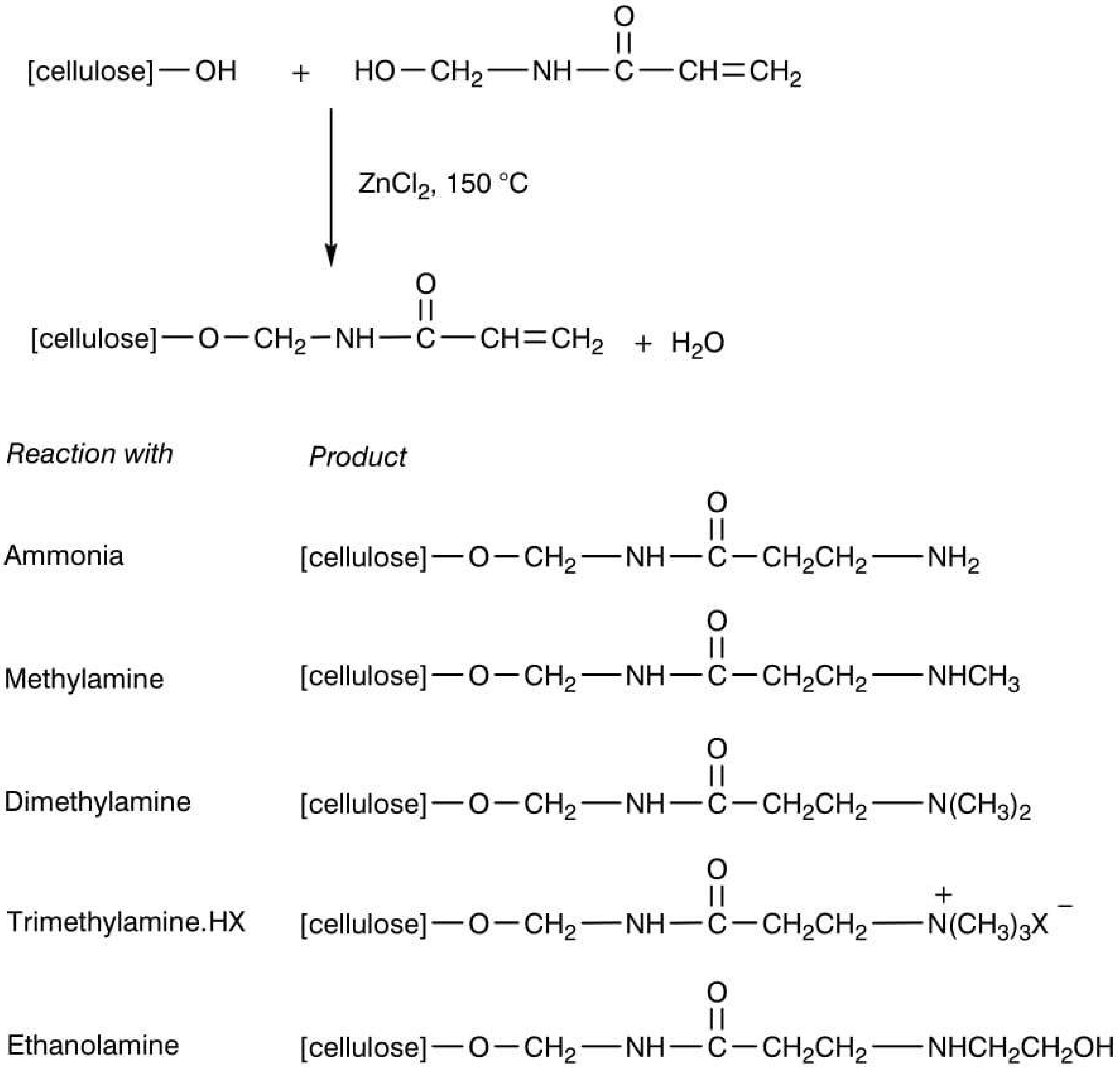
Scheme 10.58



Scheme 10.59



Scheme 10.60



$$[\text{cellulose}]\text{—OH} + \text{HO—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—CH=CH}_2 \xrightarrow{\text{ZnCl}_2,\ 150\ ^\circ\text{C}} [\text{cellulose}]\text{—O—CH}_2\text{—NH—}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{—CH=CH}_2 + \text{H}_2\text{O}$$

Reaction with	*Product*
Ammonia	$[\text{cellulose}]\text{—O—CH}_2\text{—NH—}\overset{\overset{O}{\|}}{\text{C}}\text{—CH}_2\text{CH}_2\text{—NH}_2$
Methylamine	$[\text{cellulose}]\text{—O—CH}_2\text{—NH—}\overset{\overset{O}{\|}}{\text{C}}\text{—CH}_2\text{CH}_2\text{—NHCH}_3$
Dimethylamine	$[\text{cellulose}]\text{—O—CH}_2\text{—NH—}\overset{\overset{O}{\|}}{\text{C}}\text{—CH}_2\text{CH}_2\text{—N(CH}_3)_2$
Trimethylamine.HX	$[\text{cellulose}]\text{—O—CH}_2\text{—NH—}\overset{\overset{O}{\|}}{\text{C}}\text{—CH}_2\text{CH}_2\text{—}\overset{+}{\text{N}}\text{(CH}_3)_3\text{X}^-$
Ethanolamine	$[\text{cellulose}]\text{—O—CH}_2\text{—NH—}\overset{\overset{O}{\|}}{\text{C}}\text{—CH}_2\text{CH}_2\text{—NHCH}_2\text{CH}_2\text{OH}$

Scheme 10.61

A somewhat different substitution reaction involved treating cotton with an aqueous solution containing 10 ml/l carbon disulphide, 1% sodium hydroxide and 0.5% wetting agent [397]. This thiocarbonate pretreatment was followed by dyeing with a direct dye in the presence of ammonium persulphate as free radical initiator, giving higher wet fastness than on alkali-treated or untreated cotton. This was explained in terms of involvement of the thiocarbonate groups in the formation of covalent bonds between cellulose and the direct dye by a free radical mechanism.

Table 10.40 represents those pretreatments requiring application of a polymer, the fundamental objective again being to increase basicity by incorporation of amino groups. A point of interest is use of the cationic polymer Hercosett 125 (Hercules), formed by condensation of adipic acid and diethylenetriamine to give a polyamide subsequently partially crosslinked with epichlorohydrin, a resin more commonly associated with shrink-resist treatments of wool. Once again, improvements in dyeability are usually claimed but retaining good light fastness appears to be a common problem. Fibre-reactive quaternary ammonium compounds with chlorohydrin functionality have also been evaluated as epoxide pretreatments for wool/cotton blends in an attempt to facilitate union dyeing using anionic dyes for wool [398]. Since alkaline conditions were required, the integrity of the wool was preserved by treatment at ambient temperature for 3 hours at pH 11.

Cotton grafted with 2-vinylpyridine followed by quaternisation using an excess of an alkyl bromide or epichlorohydrin showed markedly increased exhaustion with direct dyes [399]. Grafting alone gave a substantial effect, with further slight improvements being conferred by the quaternisation. Improved fastness to washing was also claimed.

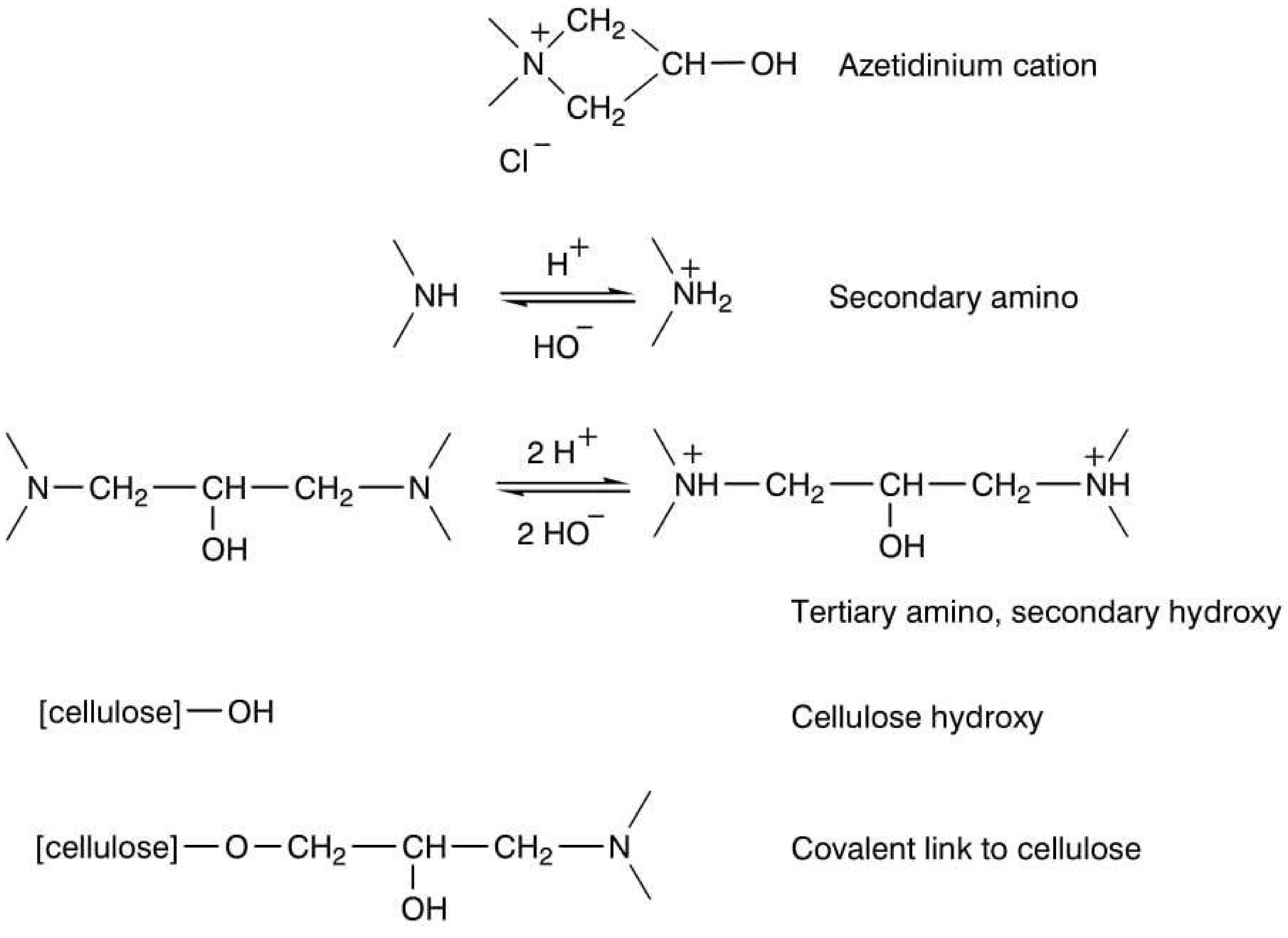
Table 10.40 Pretreatments to modify cellulose using amino-containing polymers [393]

Pretreatment polymer	Method	Comments
Chitosan	Cationic polymer applied by exhaustion from acidic solution	Improved coverage of immature fibres, increased exhaustion but decreased fastness unless further treated with fibre-reactive quaternary compound
Sandene (Clariant)	Cationic polymer applied by exhaustion under alkaline conditions	Enhanced dyeability with anionic and reactive dyes, the latter applied under neutral or slightly acidic conditions. Reduced light fastness and marked dulling with some dyes
Hercosett 125 (Hercules) reactive cationic polymer formed by condensation of adipic acid and diethylenetriamine, then partially crosslinked with epichlorohydrin	Pad-dry-cure for 3 min at 100 °C. Scheme 10.62 represents the reactive and nucleophilic sites that may exist on the surface of the treated fibre	Dyeable neutral without salt; good results with some high-reactivity dyes (dichlorotriazine and difluoropyrimidine) but not with some other types (monochlorotriazine and dichloroquinoxaline). Washing fastness very good but light fastness lower

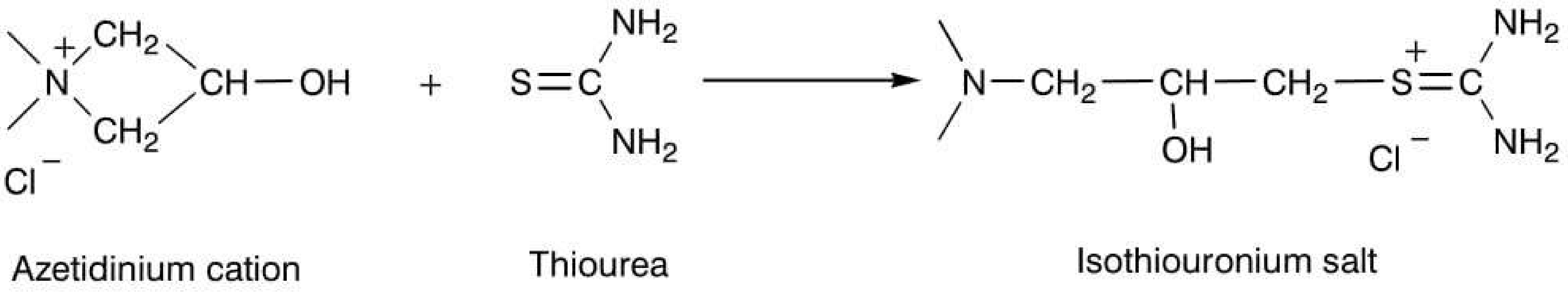
Continued on next page

Table 10.40 *Continued*

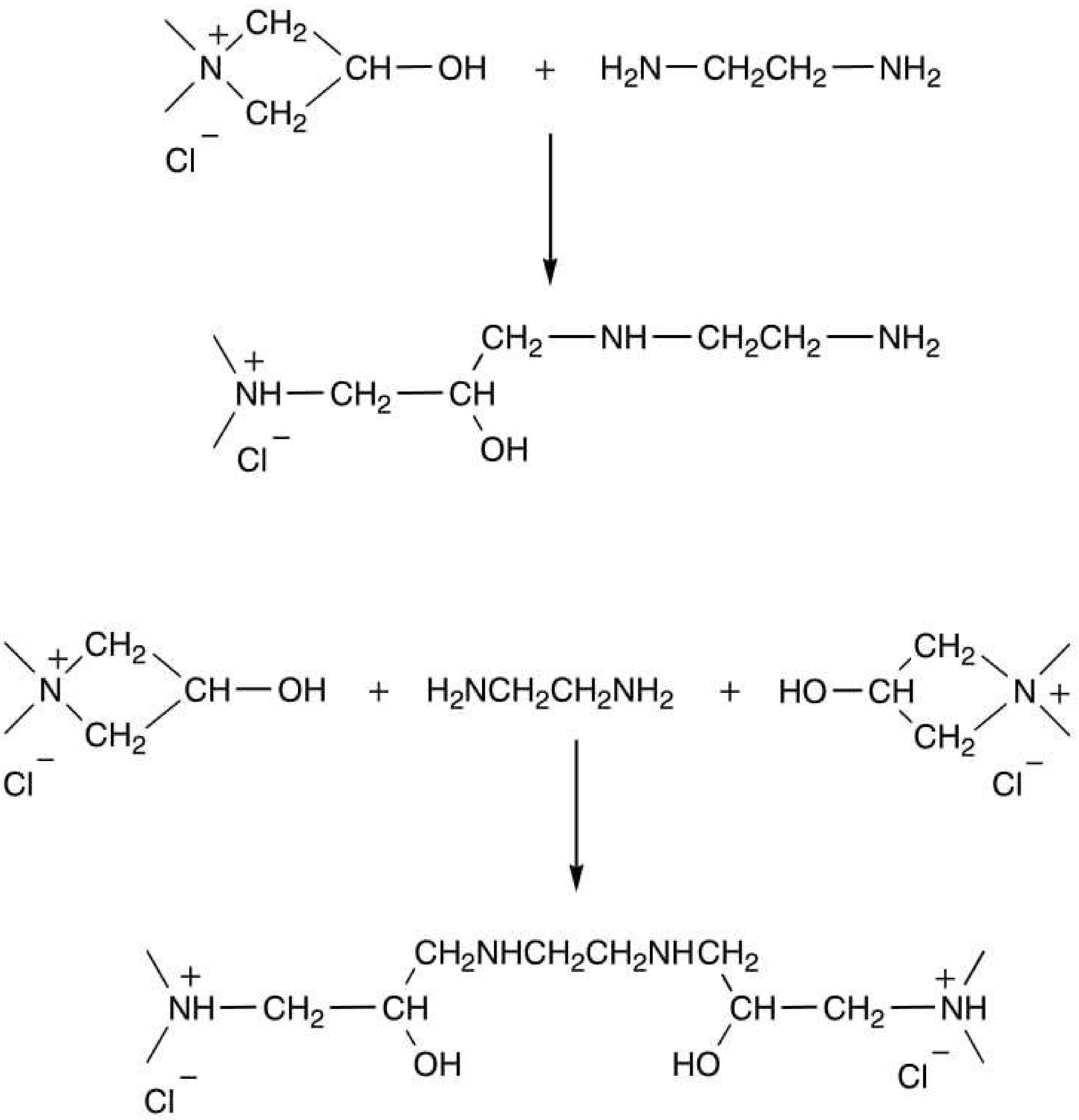
Pretreatment polymer	Method	Comments
Thiourea derivative of Hercosett (isothiouronium salt)	Scheme 10.63	Build-up good for dichlorotriazine dyes. Dyes of other types gave good results up to about 2% applied depths
Ethylenediamine derivative of Hercosett	Scheme 10.64	About 95% fixation of low- or high-reactivity dyes under slightly acidic conditions without salt, but light fastness still inferior
Polyepichlorohydrin and dimethylamine	Polymerisation of epichlorohydrin in carbon tetrachloride with boron trifluoride/ether catalyst, then reaction with dimethylamine. Applied to cotton by exhaust method or pad–dry. Scheme 10.65	Good yields with direct dyes using only 2 g/l salt. Excellent build-up with most reactive dyes; only 10% of normal salt usage needed for low-reactivity dyes and none for highly reactive types. Washing fastness very good but light fastness impaired.



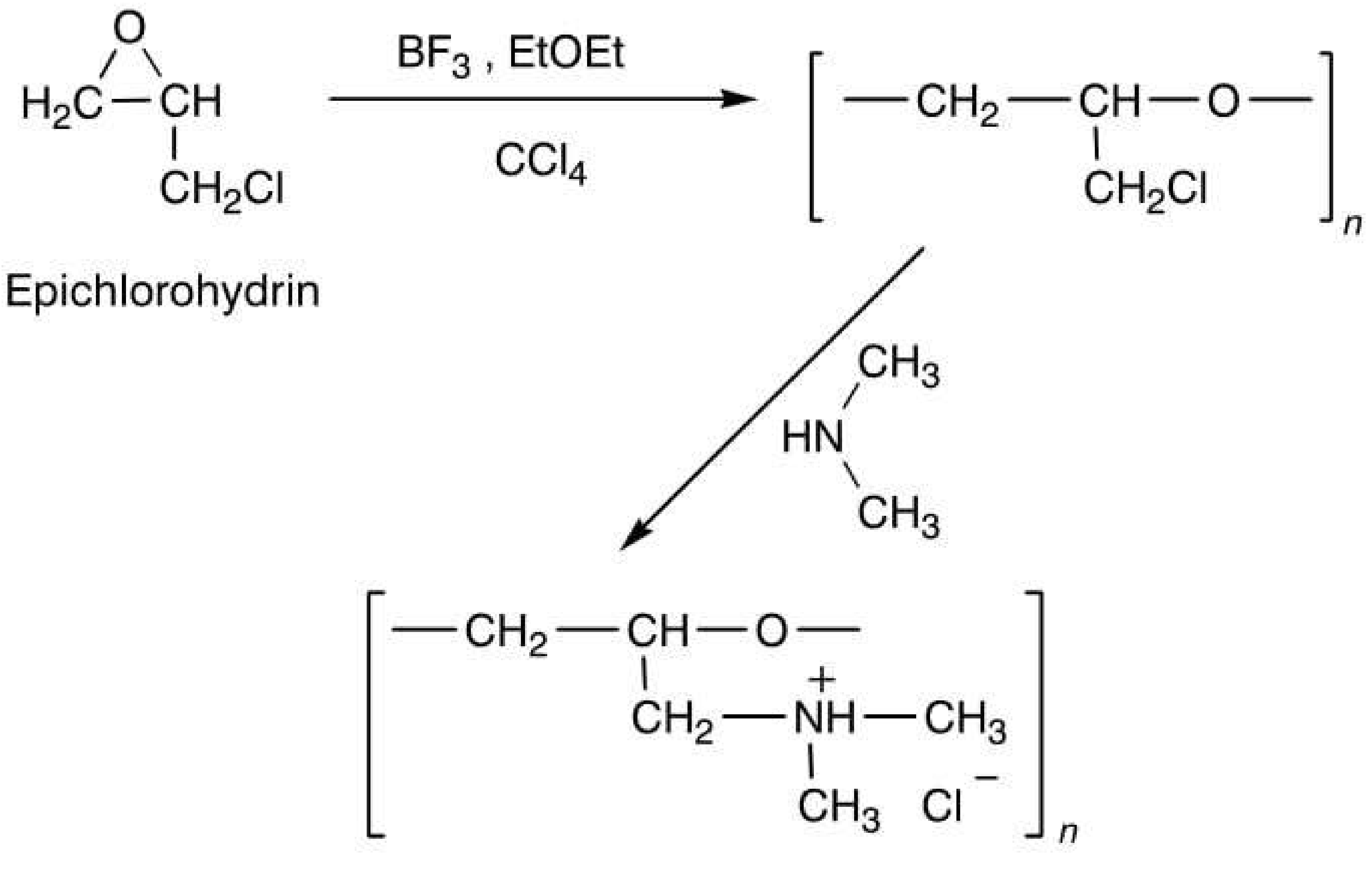
Scheme 10.62



Scheme 10.63



Scheme 10.64



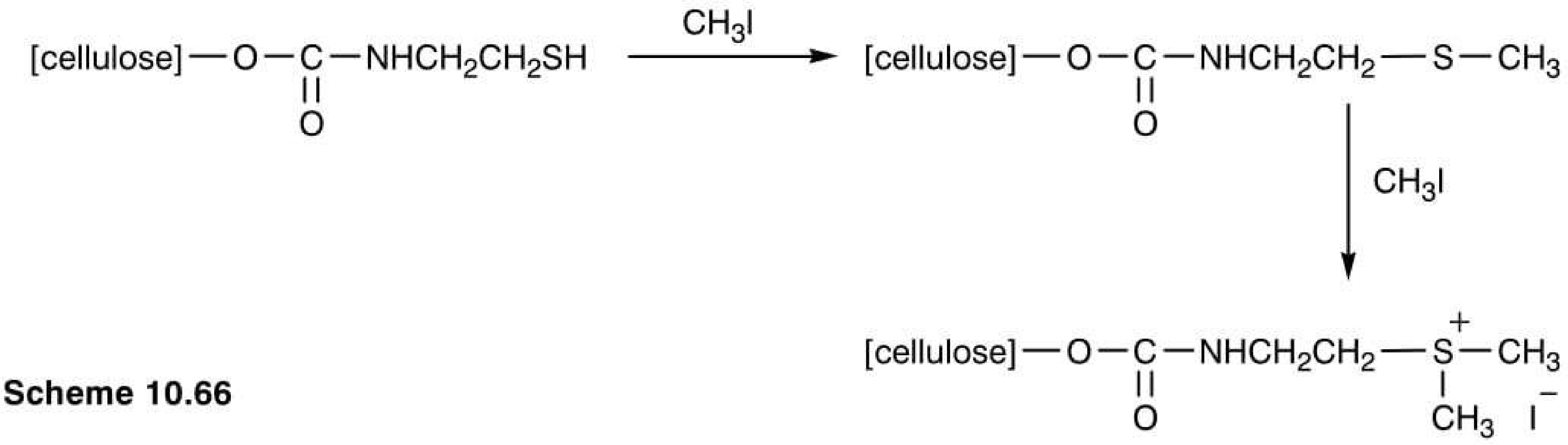
Scheme 10.65

Certain pretreatments depend on introducing sulphur rather than nitrogen, these being summarised in Table 10.41. So far these appear to have been much less successful than nitrogenous treatments.

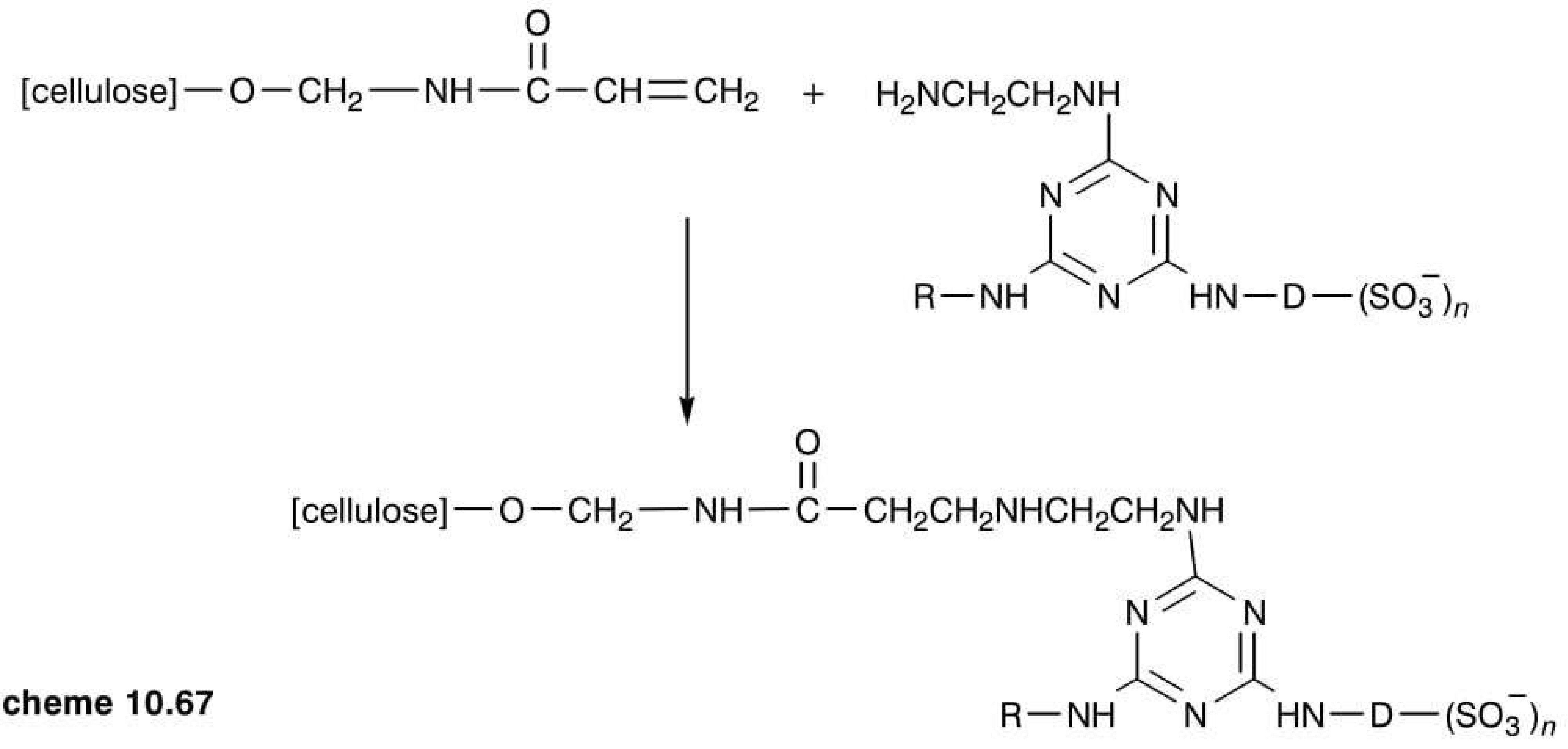
A more radical approach to pretreatment reverses the conventional reactive dyeing concept by preparing a reactive cotton cellulose capable of reacting covalently with suitable dyes containing, for example, aliphatic amino groups. In an initial attempt, cotton was

Table 10.41 Pretreatments to modify cellulose using sulphur-containing agents [393]

Pretreatment reaction	Comments
Cotton treated with bis(2-isocyanatoethyl) disuphide in dimethylformamide at 80 °C, followed by reduction with tri-n-butylphosphine in methanol containing 10% water. This gives the 2-mercaptoethylcarbamyl ester, which is treated with methyl iodide to form sulphonium salts. (Scheme 10.66).	The greater the sulphonium content, the greater the uptake of direct dyes. Not an environmentally acceptable pretreatment, however.
Alkali-treated cellulose immersed in an arylsulphonium salt solution.	Dyeings with direct, reactive, sulphur and disperse dyes at pH 5 showed improved colour strength but detailed results were not reported.
Linen esterified with thioglycolic acid to incorporate thiol groups, these being more strongly nucleophilic than hydroxy groups.	Increased colour yields obtained with reactive dyes, but not enough to give adequate solidity on linen/wool blends.



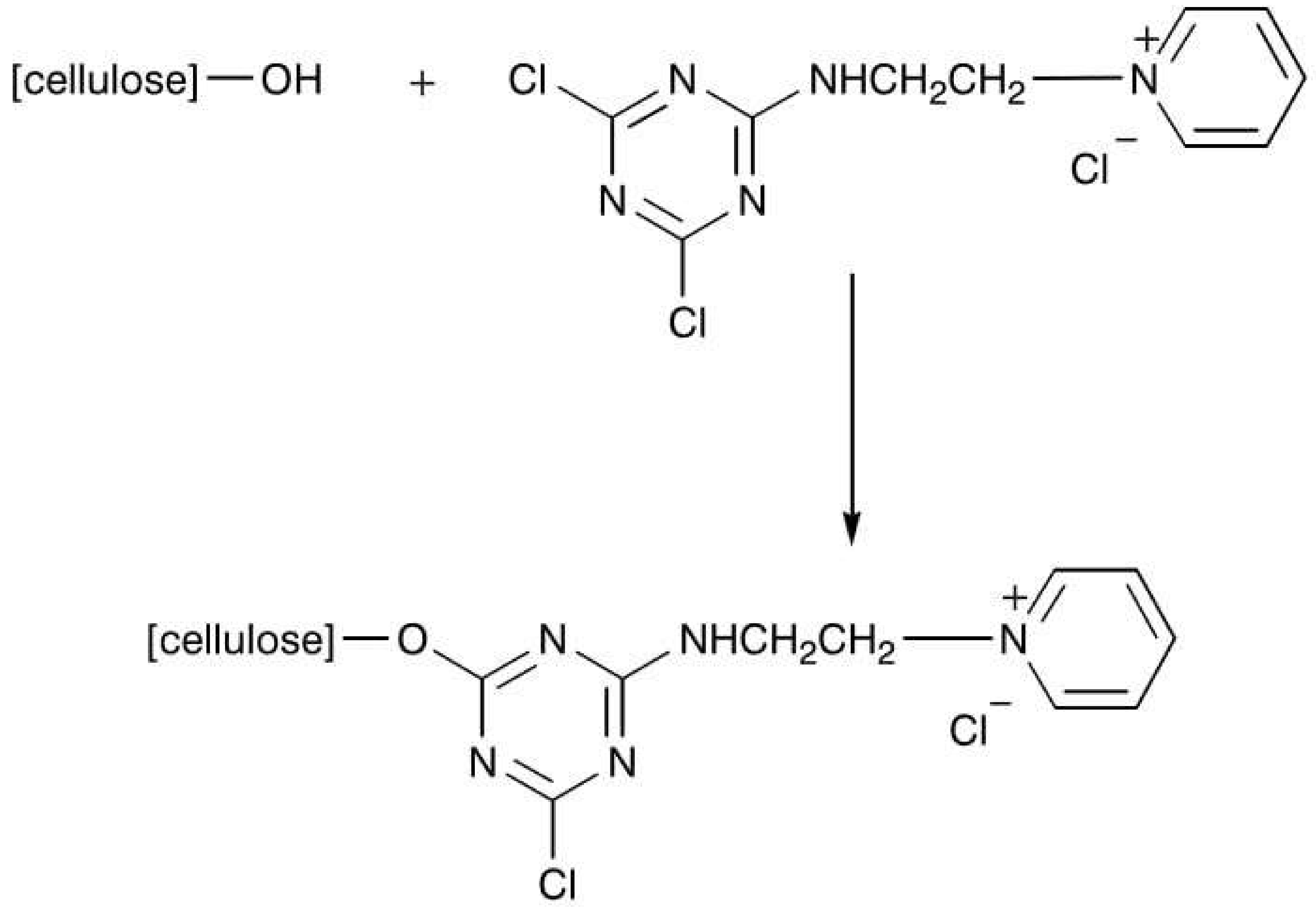
Scheme 10.66



Scheme 10.67

treated with *N*-methylolacrylamide (Scheme 10.61). This is capable of Lewis acid catalysed etherification of hydroxy groups in cellulose and alkali-promoted Michael addition to nucleophiles [393]. The modified cotton was reacted with aminoalkylated triazine dyes (Scheme 10.67) at pH 10.5 in the presence of 80 g/l salt. In contrast to conventional halotriazine reactive dyes, these are stable to hydrolysis under these conditions. However, build-up proceeded only up to a limit, beyond which the absorbed dye appeared to act as a resist agent, preventing further uptake. In any case, this process still required the addition of a high concentration of salt.

This approach was subsequently improved considerably by treating cotton with 2,4-dichloro-6-(2′-pyridinoethylamino)-*s*-triazine (Scheme 10.68). One of the chloro substituents reacts under mild conditions with cellulose and the reactivity of the other chloro is reduced [393], giving a fibre containing monochlorotriazine residues that can react covalently with aminoalkylated dyes. Pad–batch pretreatment gave better results than exhaustion, enabling application of the dye at pH 9 in absence of salt and giving similar fastness to conventional dyeing. A highly significant advantage is that full use is made of the dye applied because no dye hydrolysis can occur, resulting in shorter washing-off times and a reduction in coloured effluent. However, the process requires special dyes and at present no commercial range of these exists. Furthermore, there could be hydrolysis problems with the pretreating agent or with the pretreated fibre. Any unlevelness in the pretreatment process would clearly be disastrous in commercial terms.



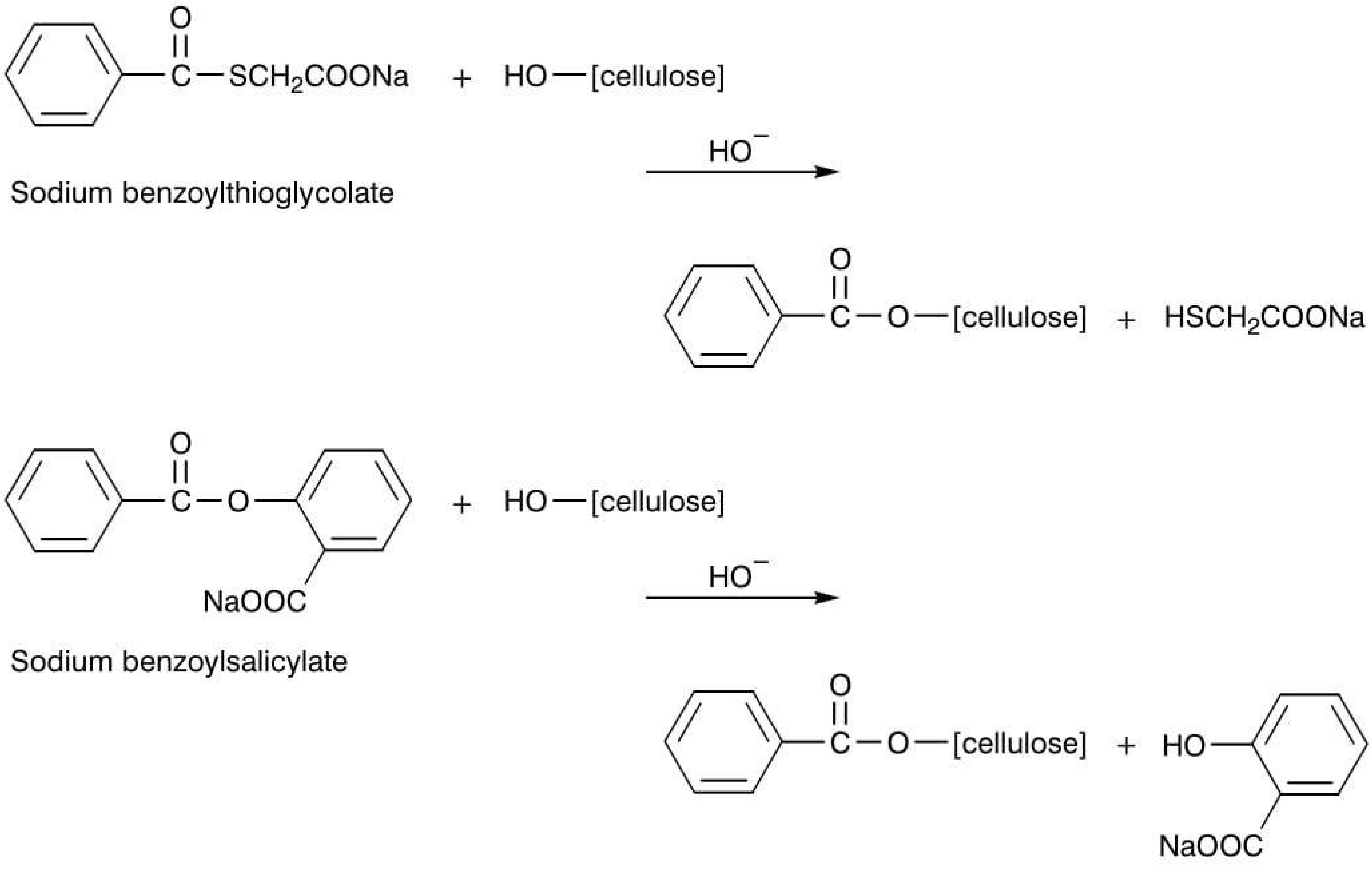
Scheme 10.68

A rather more perverse activity of researchers concerns their attempts to make cotton dyeable with disperse dyes so that, for example, polyester/cotton blends could be dyed or printed with a single dye class. This inevitably means invoking symbiotic chemistry; if cotton is to become dyeable with hydrophobic disperse dyes, it must itself be made more hydrophobic. This carries with it the risk that the very physical properties that make cotton so desirable, and for which it is incorporated into blends with hydrophobic fibres, are negated. Thus the moisture regain of a blend of polyester with hydrophobic cotton may be such that it has no advantage over a fabric made entirely from polyester microfibre. It is perhaps significant that moisture regain is hardly mentioned by researchers devising treatments for making cotton more hydrophobic. Little is also said regarding light fastness, although good fastness to washing is sometimes claimed [400].

Processes devised to make cotton hydrophobic are summarised in Table 10.42. These processes are undoubtedly successful in conferring substantivity for disperse dyes but attaining compatibility within a range of dyes across the entire colour gamut and on fibre blends of various blend ratios could be a problem. In addition, ester bonds can be saponified during washing, typically losing 30% of the effect after one wash and 60–70% after five washes. Hence commercial exploitation is subject to severe limitations.

Table 10.42 Pretreatments to make cotton more dyeable with disperse dyes [393,400]

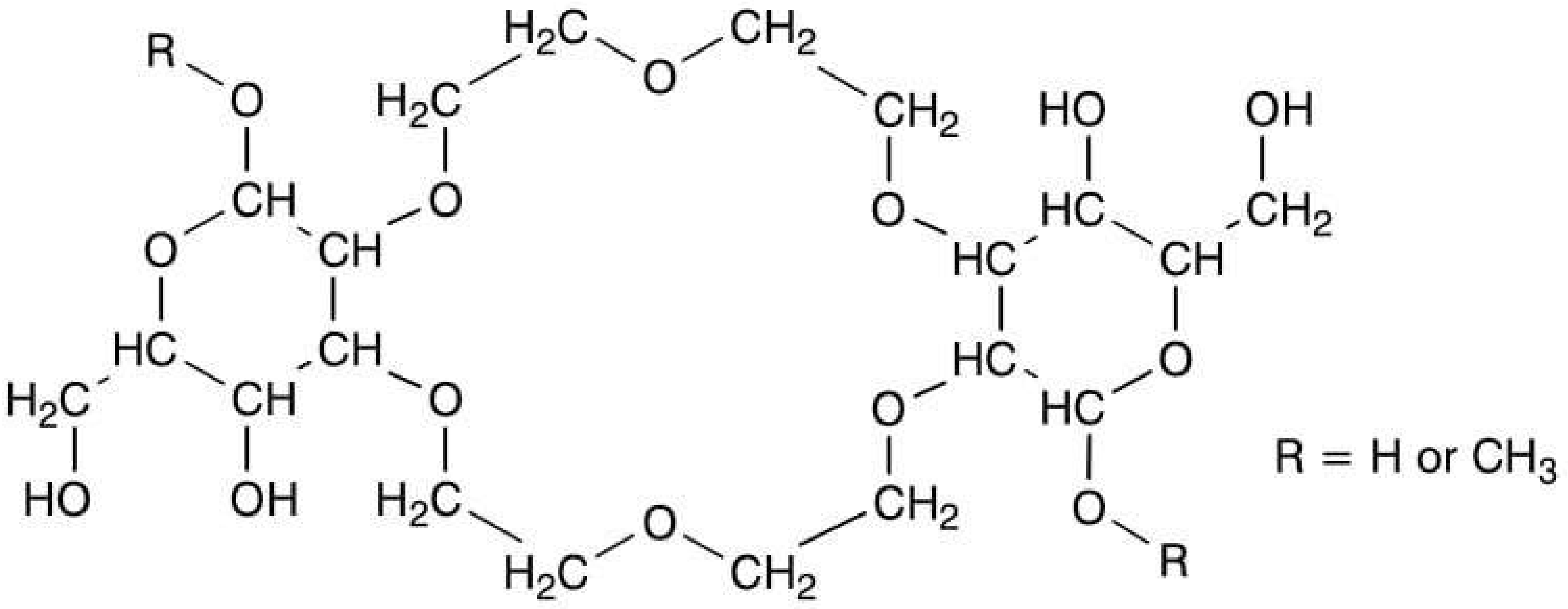
Pretreatment reaction	Comments
Benzoylation with benzoyl chloride.	Proposed in the 1920s to confer easy-care properties. In 1976 process patents introduced for making cotton acceptable to disperse dyes in transfer printing.
Water-soluble acylating esters sodium benzoylthioglycolate and benzoylsalicylate (Scheme 10.69).	Applied by padding with alkali and baking at 200 °C. More acceptable for health and safety reasons than the lachrymatory agent benzoyl chloride.
Aliphatic acid chlorides.	Increasing the length of the aliphatic chain increased uptake of disperse dyes; maximum uptake needed at least eleven C atoms per molecule.
Aromatic substituents in cellulose confer greater disperse dye substantivity than aliphatic substituents.	Benzoylation required a degree of substitution of 15–25% for optimum substantivity; 30–40% was needed to give good fastness to washing.
Graft copolymerisation of styrene on partially carboxymethylated cotton using gamma radiation.	Higher graft yields of polystyrene gave higher colour yields with disperse dyes.



Scheme 10.69

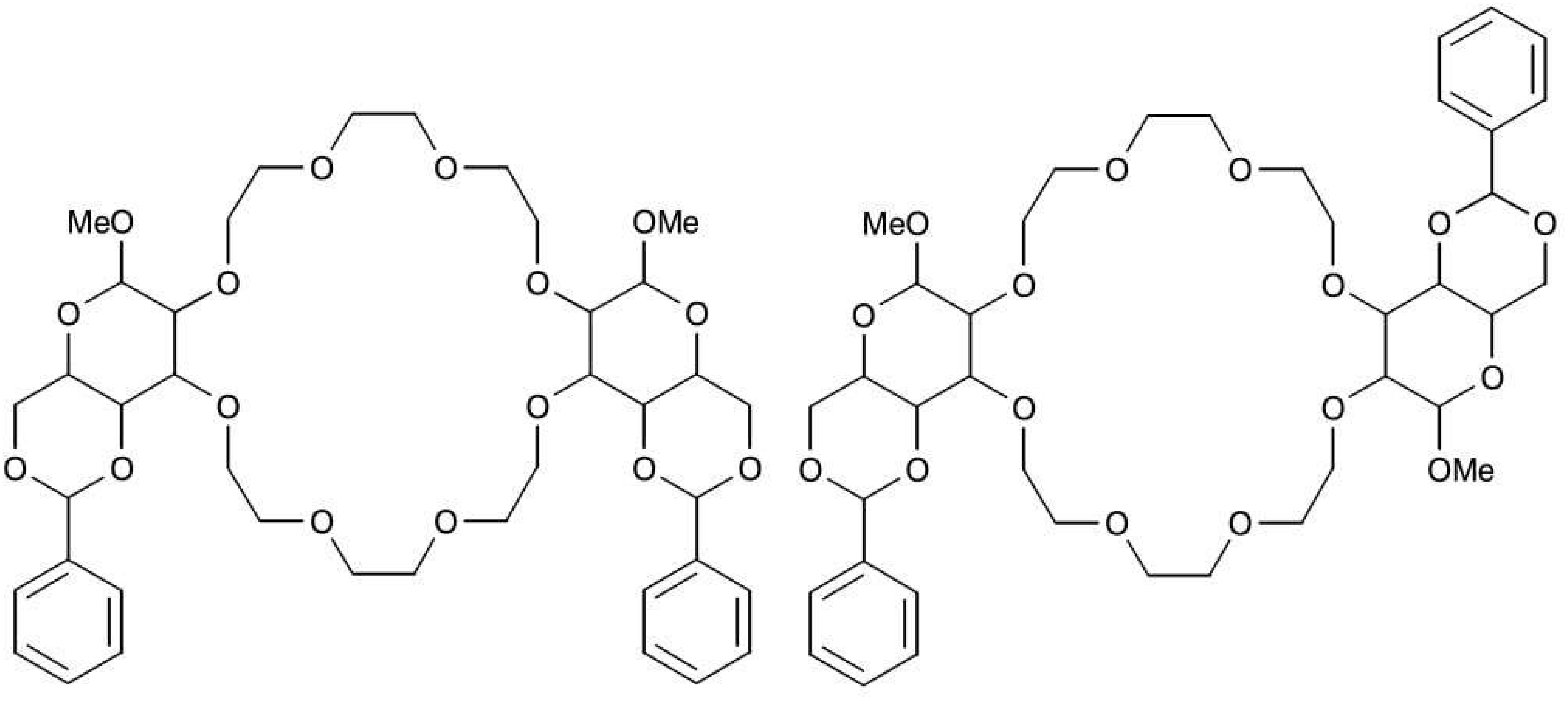
Since wool dyeing is characterised by much higher levels of exhaustion than are typical for the dyeing of cellulosic fibres, as well as much lower concentrations of electrolytes, interest in pretreatments for wool is less concerned with the environmental aspects of dyeing processes. The motivation to modify wool is usually to increase or decrease dye absorption so that, for example, differential dyeing effects can be obtained [401]. As well as overdyeing fabrics containing some predyed wool, possibilities in this area include the use of prechromed and unchromed wool, pretreatment with a cationic agent to give increased dye uptake or pretreatment with a syntan (section 10.9.4) to give a dye-resist effect. Attempts around 1970 to commercialise the prechromed/unchromed system faltered as a result of poor reproducibility. In any case, nowadays there would be environmental questions to be addressed regarding chromium in the effluent. Pretreatment with a cationic agent or syntan has economic benefits over the spinning of predyed wools in the production of heather-effect yarns.

Wool has been pretreated with glucose-derived crown ethers of the type shown in 10.144 and 10.145 [402]. Crosslinking occurs by interaction of amino groups in wool keratin with the glucosidic hydroxy groups in the crown ether. Increased dyeability with reactive dyes was achieved (Figure 10.53), a primary objective of the research being the low-temperature dyeing of wool.



10.144

Bis-glucopyranoside-18-crown-6 ethers



10.145

Bis-glucopyranosido-24-crown-8 ethers

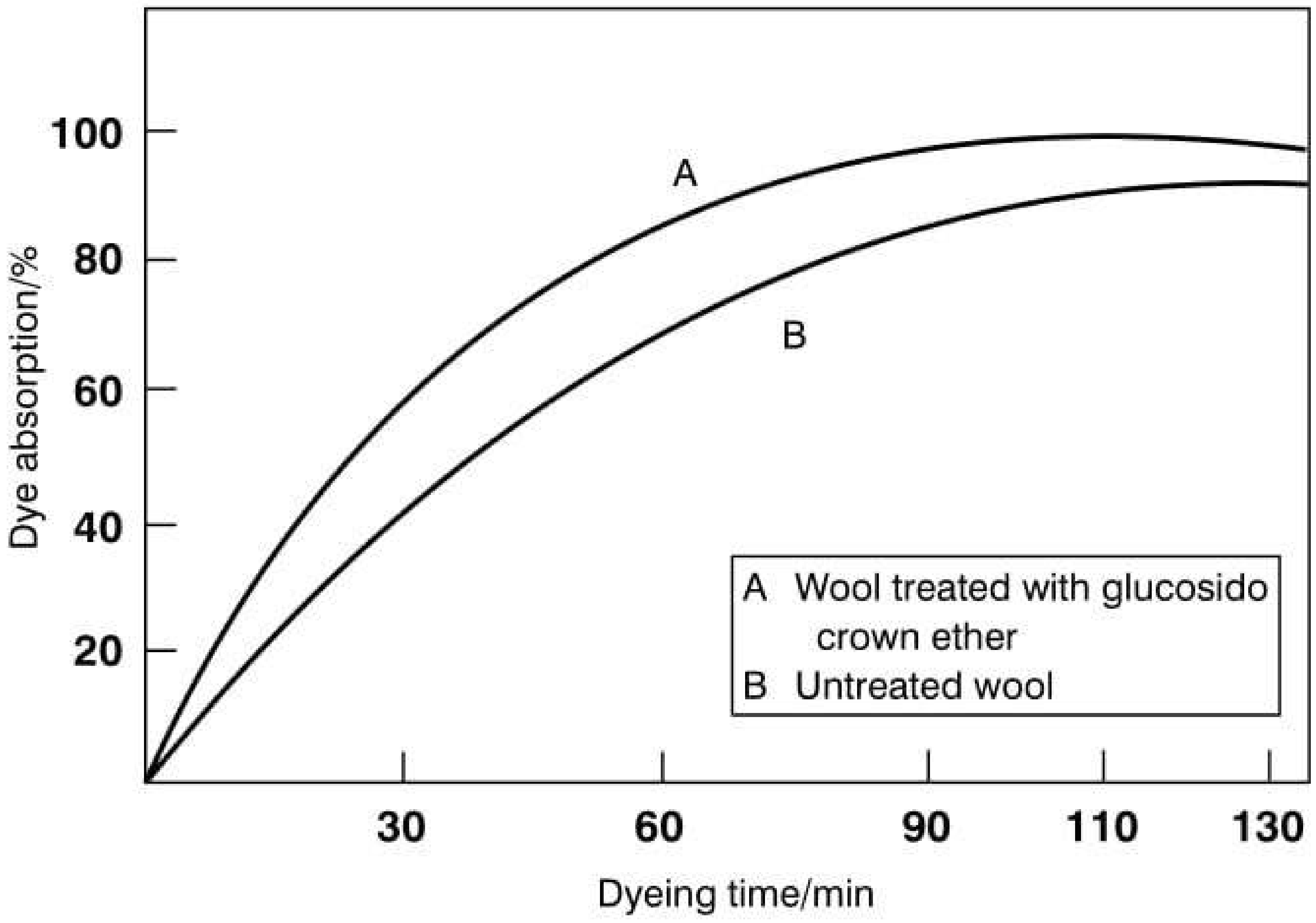
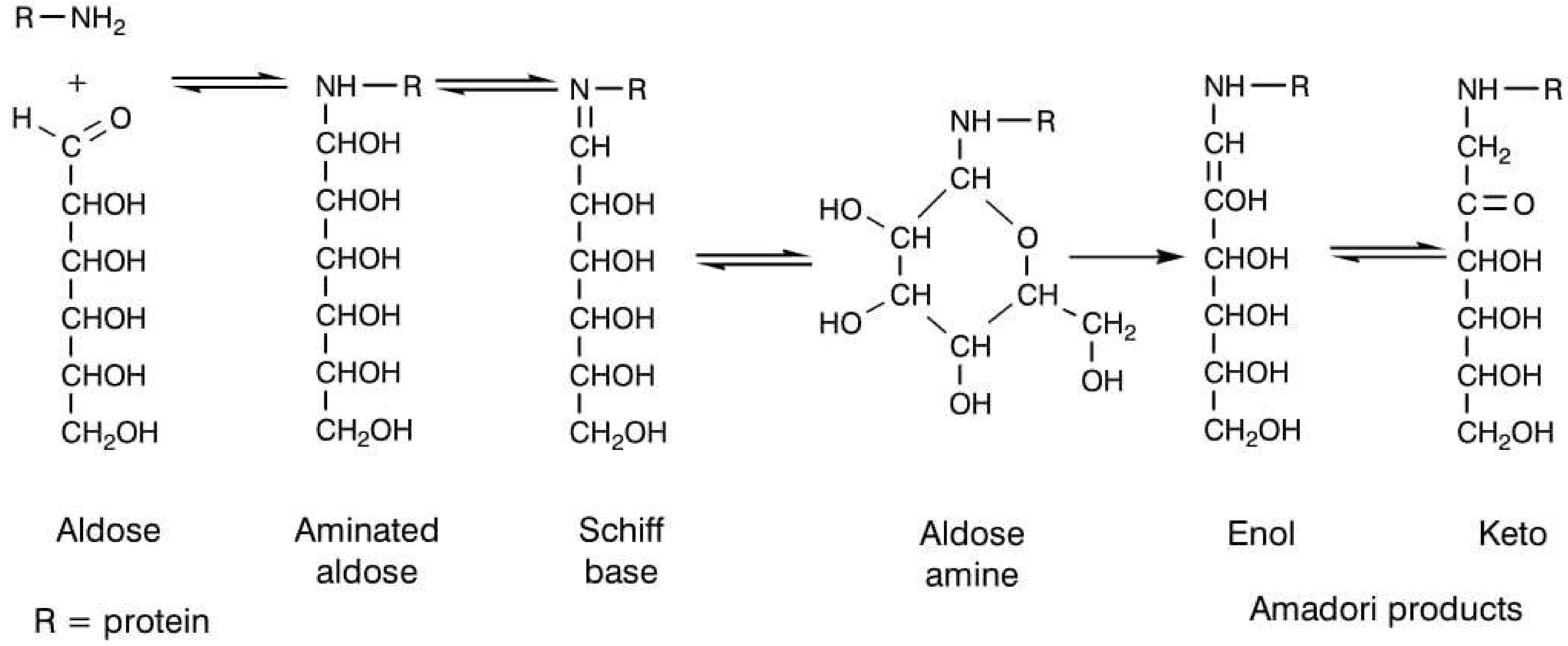
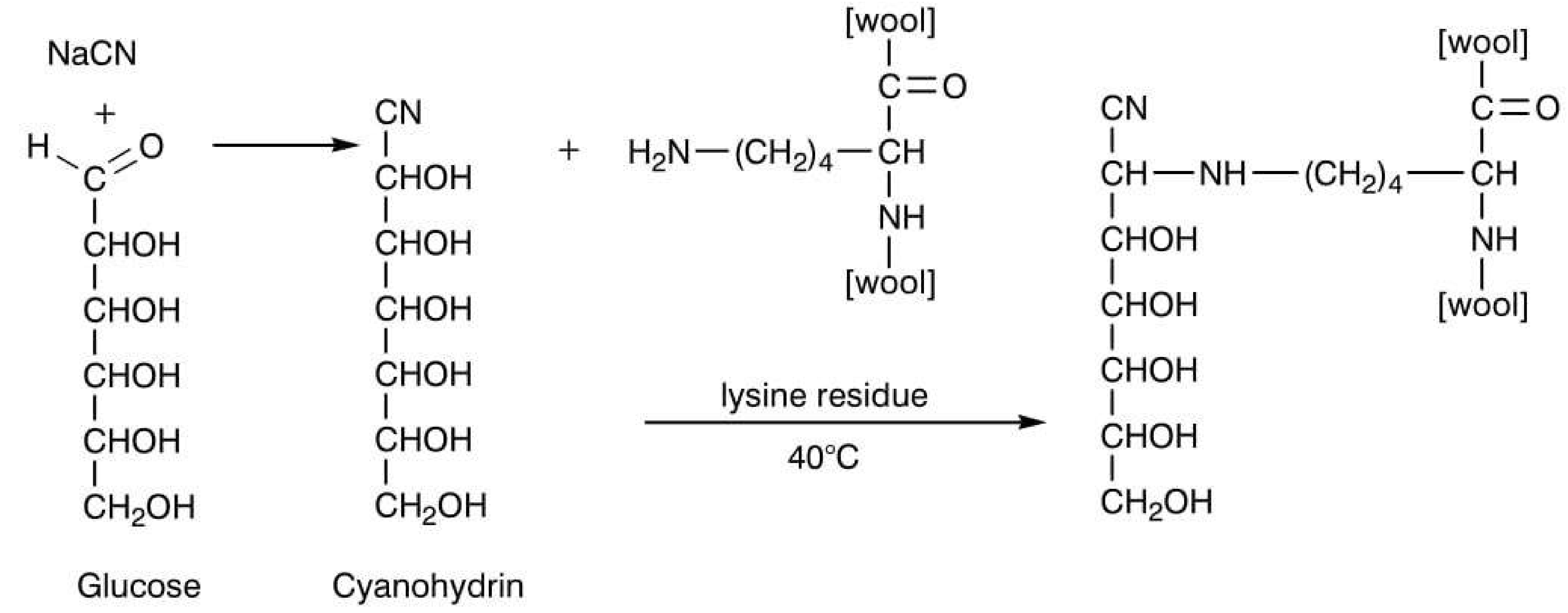


Figure 10.53 Rate of absorption of Lanasol Red G (Ciba; CI Reactive Red 83) by wool [402]

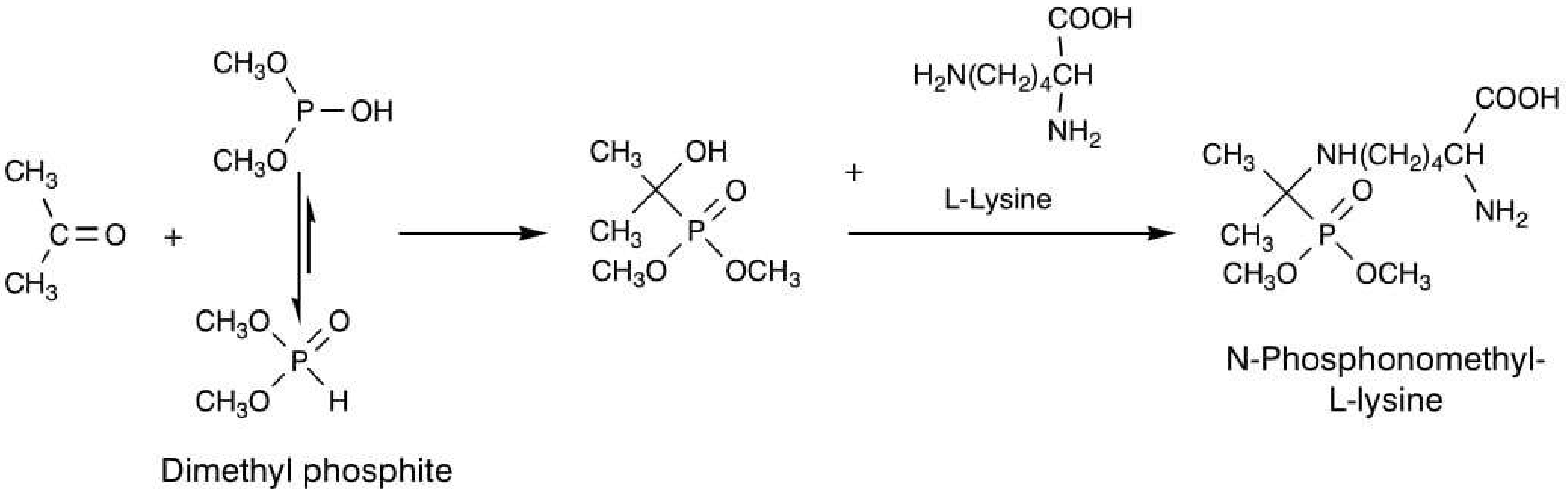
Wool dyeing at low temperatures has been enhanced by utilising the Maillard, Strecker and modified Strecker (P-Mannich) reactions as pretreatments [403,404]. In a sense, the interaction of wool with the glucose crown ethers already mentioned made use of the Maillard reaction. This is the reaction between the oxo group of an aldose molecule and the freely accessible amino groups of an amino acid or protein molecule, leading to the ultimate formation of the tautomeric forms of an *N*-substituted 1-amino-1-deoxy-2-ketose via the series of reactions shown in Scheme 10.70 [403]. This reaction is associated with the browning observed when cooking saccharide-containing foods. Hence it is necessary to control the conditions of application to wool so that yellowing or browning does not occur; 30 minutes at 90 °C gave satisfactory results [404]. The Strecker reaction is similar except that a glucose-cyanohydrin is used (Scheme 10.71). The modified Strecker or P-Mannich reaction typically uses dimethyl phosphite in place of the cyanohydrin [404], thus being more acceptable on health and safety grounds for use in a dyehouse (Schemes 10.72 and 10.73).



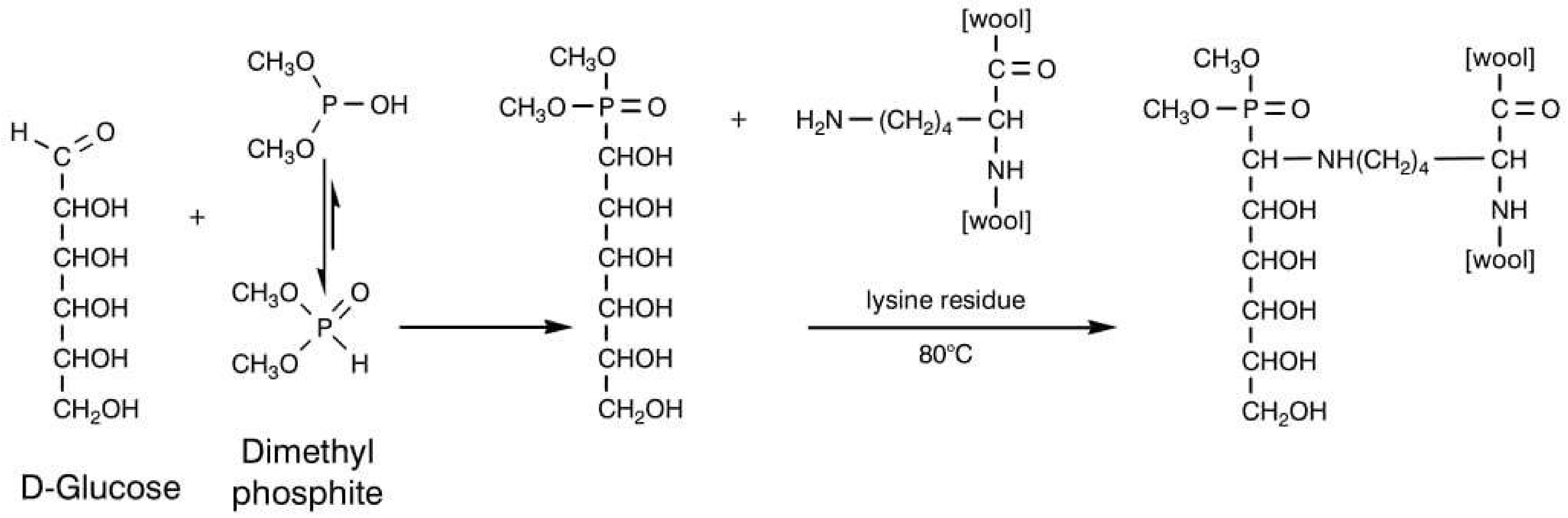
Scheme 10.70



Scheme 10.71



Scheme 10.72



Scheme 10.73

When the Maillard reaction was evaluated using 10 g/l glucose for 30 minutes at 90 °C and 20:1 liquor ratio the fibre diameter increased by 3.5%; xylose gave an increase almost twice as much but showed some yellowing. In this process accessibility of the fibre for dye molecules is increased, since the glucose molecules penetrate between the peptide chains. The reaction also introduces primary alcoholic groups, making the wool more dyeable with the reactive dyes normally used on cellulosic fibres, as well as with bromoacrylamide reactive dyes. Satisfactory dyeing was achieved at pH 5 and up to 80 °C on glucose-treated wool. Penetration was rapid, enabling the dyeing time or temperature to be decreased. The build-up and fixation of reactive dyes were increased. The Strecker reaction utilising glucose–cyanohydrin required only 20 minutes at 40 °C, whereas the modified Strecker reaction using glucose–dimethyl phosphite needed 30 minutes at 80 °C. All treatments gave improved dyeability, the order of efficacy being:

Modified Strecker > Strecker > Maillard

although differences were relatively slight. Dichlorotriazine dyes showed increased yield after the modified Strecker reaction. There was no decrease in light fastness. Treatment with dimethyl phosphite alone also improved dyeability but not to the same extent as glucose–dimethyl phosphite. Penetration of the peptide chains by glucose–dimethyl phosphite is shown in Scheme 10.74. The process is thought to occur in the following stages [404]:

(1) Penetration of dimethyl phosphite into the fibre, accompanied by decomposition of salt linkages and elimination of structural water in a multi-step hydration process. New salt linkages are formed between cationic groups in wool keratin and anionic dimethyl phosphite.
(2) Penetration of glucose molecules into the loosened structure, causing further increase in accessibility of the reactive sites.
(3) Formation of covalent bonds between dimethyl phosphite, glucose and amino groups in wool keratin, stabilising the loosened fibre structure.

Imaginative use has been made of triazine and sulphatoethylsulphone reactive dye chemistry in the application of pretreatments to nylon [405]. The concept resembles that used to make cotton cellulose reactive before dyeing with aminoalkylated dyes, as discussed earlier (Schemes 10.67 and 10.68). In this case, nylon becomes the reactive partner by pretreatment with a reactive multifunctional crosslinking agent:

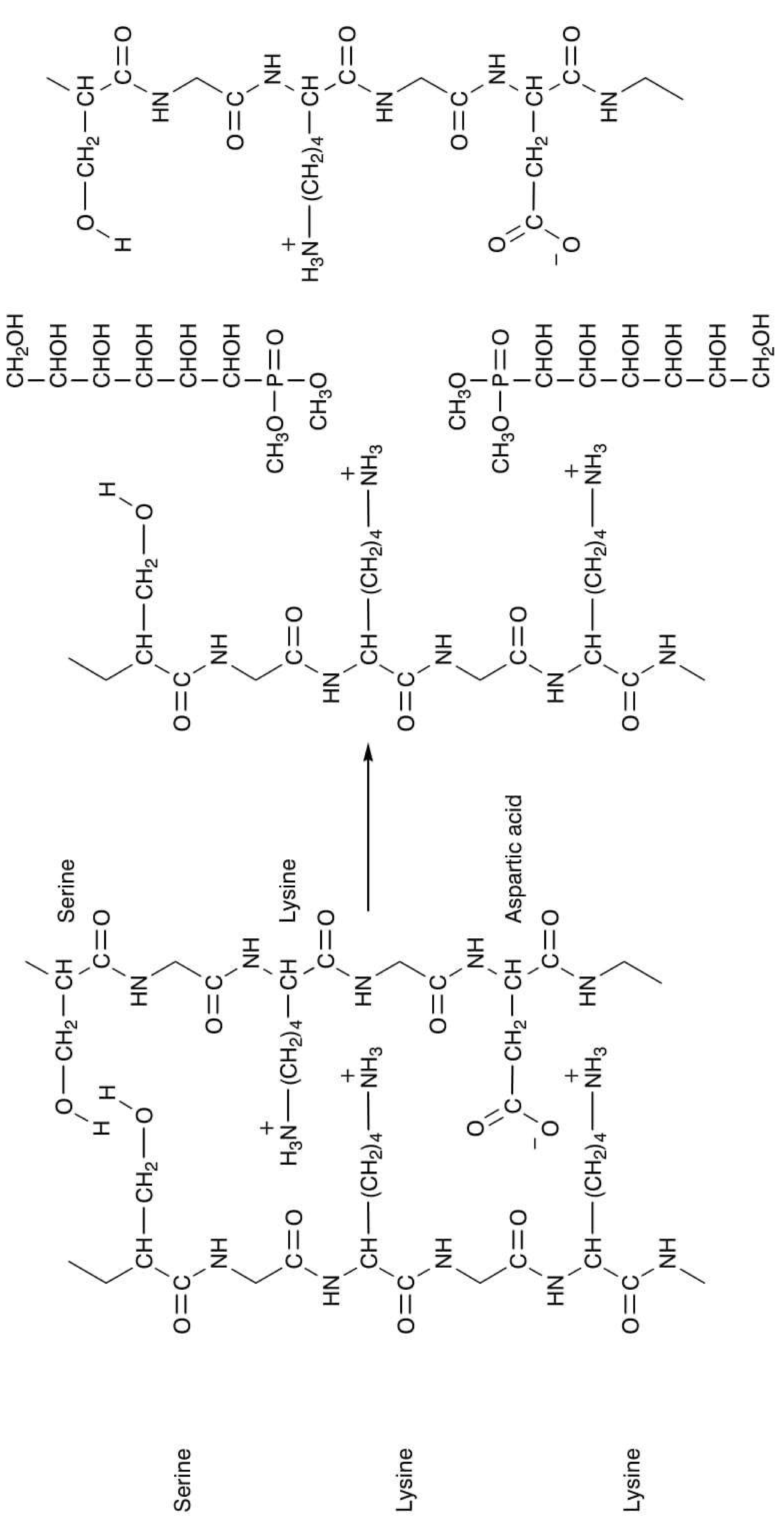
(a) 1,3,5-tris(acryloyl)hexahydro-*s*-triazine (10.146) or
(b) the trifunctional reactive compound XLC (10.95), already discussed as a shrink-resist reactant for wool (section 10.5.5).

The pretreated nylon then undergoes covalent fixation of dyes containing aminoalkyl groups. Interestingly, nylon treated with XLC showed markedly lower substantivity and reactivity with conventional dyes. If the pretreated nylon was reacted with ammonia, however, creating amino functionality at the reactive sites, normal reaction with a conventional reactive dye was restored [405].

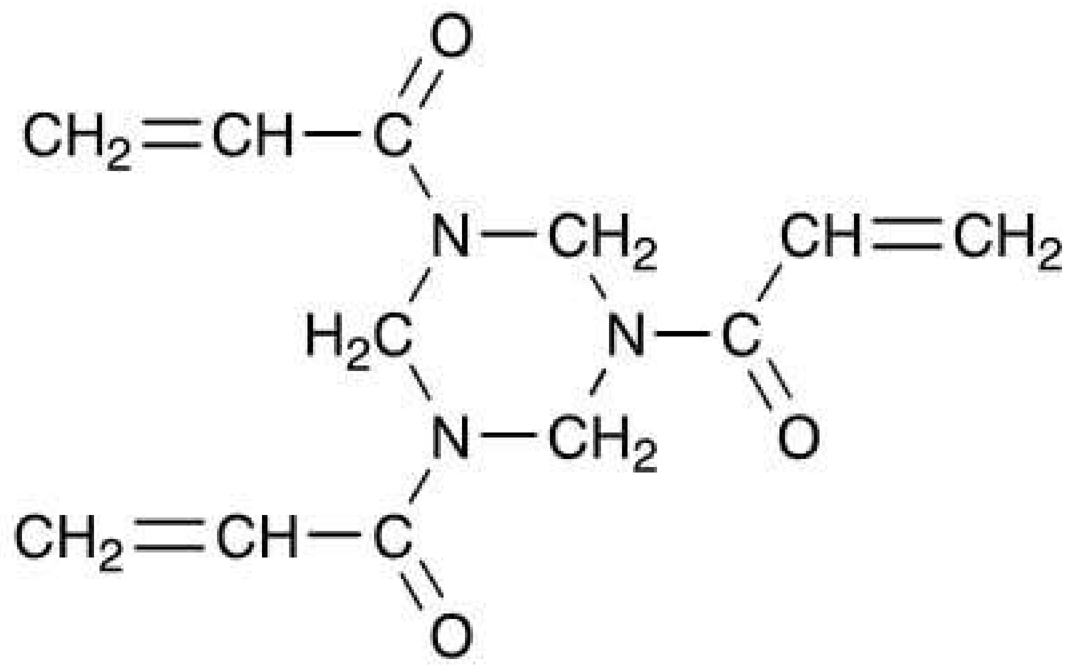
Many of the syntan aftertreatments described in section 10.9.4 can be applied as pretreatments instead, mainly to confer dye-resist effects. This aspect is dealt with in section 10.9.4 rather than here.

10.9.2 Ultraviolet absorbers

The use of polyester and nylon upholstery fabrics in automobiles results in their prolonged exposure to sunlight at high temperatures and humidities. This has created a demand for dyeings of very high light fastness and for these dyed fibres to have exceptional resistance to photodegradation. Although the selection of dyes of suitably high fastness under these



Scheme 10.74



10.146

extreme conditions is of primary importance, additional protection can be achieved using so-called ultraviolet absorbers, these being colourless aromatic compounds with a high propensity to absorb the troublesome UV radiation. Such products are usually applied during dyeing and confer protection to both dyes and fibres. Although the main interest in UV absorbers centres on polyester and nylon, they are also recommended for use on other fibres, e.g. polypropylene, silk, wool (particularly bleached wools that have a tendency to photoyellowing) and cotton. More recently, due to the increased incidence of skin carcinomas induced by excessive exposure to sunlight, UV absorbers are being used together with modifications of fabric construction to give increased resistance to the passage of harmful rays through the fabric to the skin [406–408].

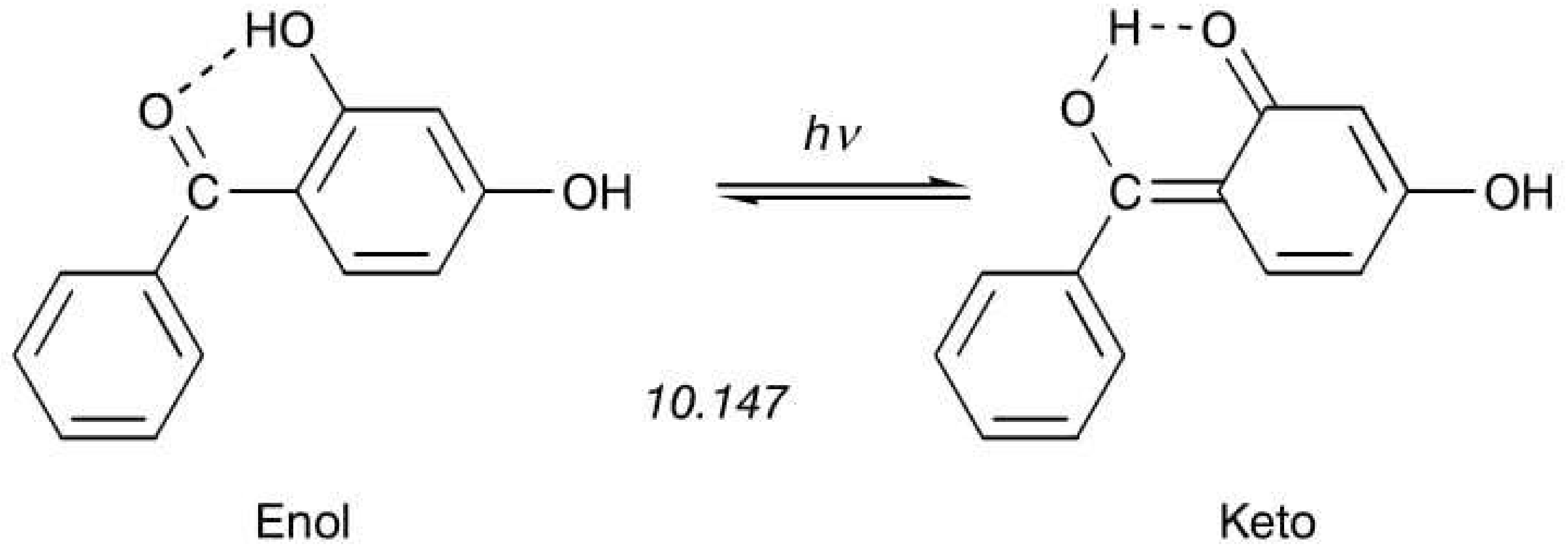
The principle involved is the same as that used in skin protection creams (that go under the commonly used misnomer of sun protection screens), as well as finding extensive use in plastics and surface coatings to enhance their durability to sunlight exposure. Two useful reviews are available [409,410]. Table 10.43 gives a comparison of the components of solar radiation. This illustrates very clearly the apparent paradox that those components present in least quantity nevertheless pack the greatest punch in terms of photon energy. Thus out of a total photon energy value of 1328 kJ/mol UV radiation of wavelengths 280–400 nm accounts for 1065 kJ/mol (80%), despite the fact that it represents only 6% of the total radiation intensity. This is the radiation that is primarily responsible for the degradation of fibres and colorants. This is also the region, or at least part of it, in which UV absorbers have to function. A useful definition [410] states that a UV absorber is a molecule that may be incorporated within a host polymer in order to absorb ultraviolet radiation efficiently and convert the energy into relatively harmless thermal energy, without itself undergoing any

Table 10.43 Intensity of global radiation (sum of direct and scattered radiation) at the earth's surface and its classification (summer, vertical incidence) [409]

Regions of solar radiation	Wavelength (nm)	Radiation intensity (W/m^2)	Radiation intensity (%)	Mean photon energy (kJ/mol)
UV-B	280–320	5	0.5	400
UV-A	320–360	27	2.4	350
	360–400	36	3.2	315
Visible	400–800	580	51.8	200
Infrared	800–3000	472	42.1	63

irreversible chemical change or inducing any chemical change in the host macromolecules. Thus UV absorbers do not simply scavenge UV radiation preferentially and become themselves expended in the process, in the way that gas-fume fading inhibitors operate (section 10.9.3). UV absorbers convert electronic excitation energy into thermal energy by a rapid but reversible intramolecular proton transfer mechanism [410].

The fundamental nuclei of most of these compounds are represented by *o*-hydroxybenzophenone (10.147), *o*-hydroxybenzotriazole (10.148) or *o*-hydroxybenzotriazine (10.149). All of these structures exhibit keto–enol tautomerism, the keto form being favoured on irradiation. The characteristics of these skeletal structures can be modified by introducing substituents to make them more suitable for specific purposes. For example water-insoluble UV absorbers are preferred for application with disperse dyes for polyester, whereas water-soluble sulphonated derivatives are more suitable for use with anionic dyes on nylon. Thermal stability will be required if such agents are to be incorporated into molten polymers or intended for pad–thermosol application to polyester. Typical variants, together with other types of protective agents, will be mentioned later when dealing with specific fibres. Even certain dyes can act as UV protective agents, particularly in heavy depths, but other dyes may catalyse fading or fibre degradation [411]. Derivatives of certain dyes with built-in UV absorber moieties have been produced specifically with the aim of obtaining dyes of exceptionally high light fastness. For example, CI Disperse Yellow 33 (10.150; R = H) can be converted to a benzophenone derivative (10.151) and a benzotriazole analogue (10.152) of the important polyester dye CI Disperse Yellow 42 (10.150; R = Ph) is also readily available [410]. In some instances there is also a need for an antioxidant; these are discussed below in connection with nylon additives.



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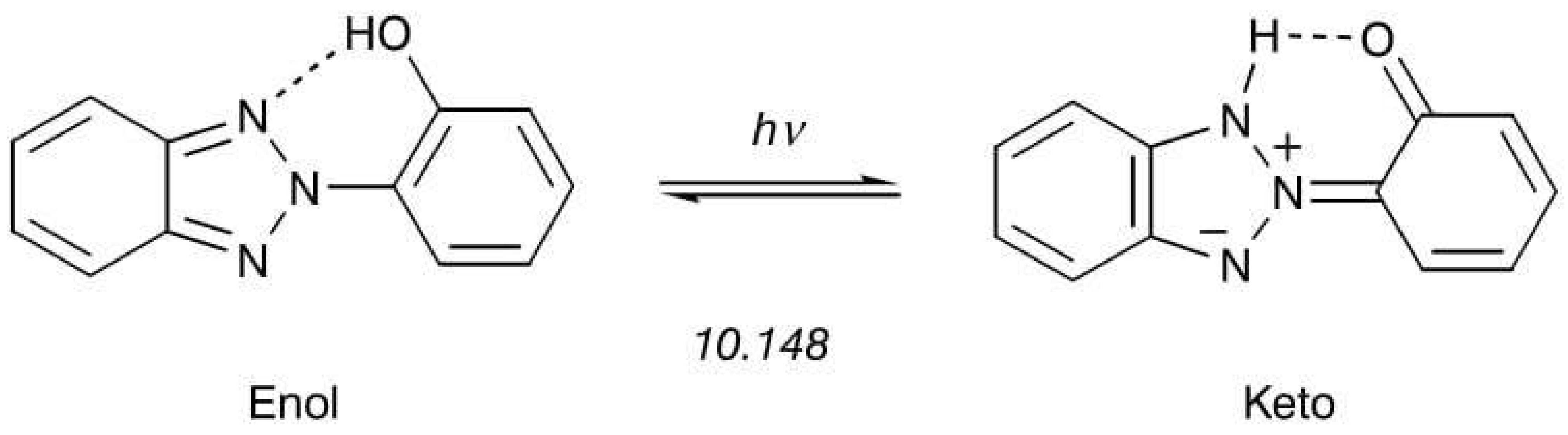
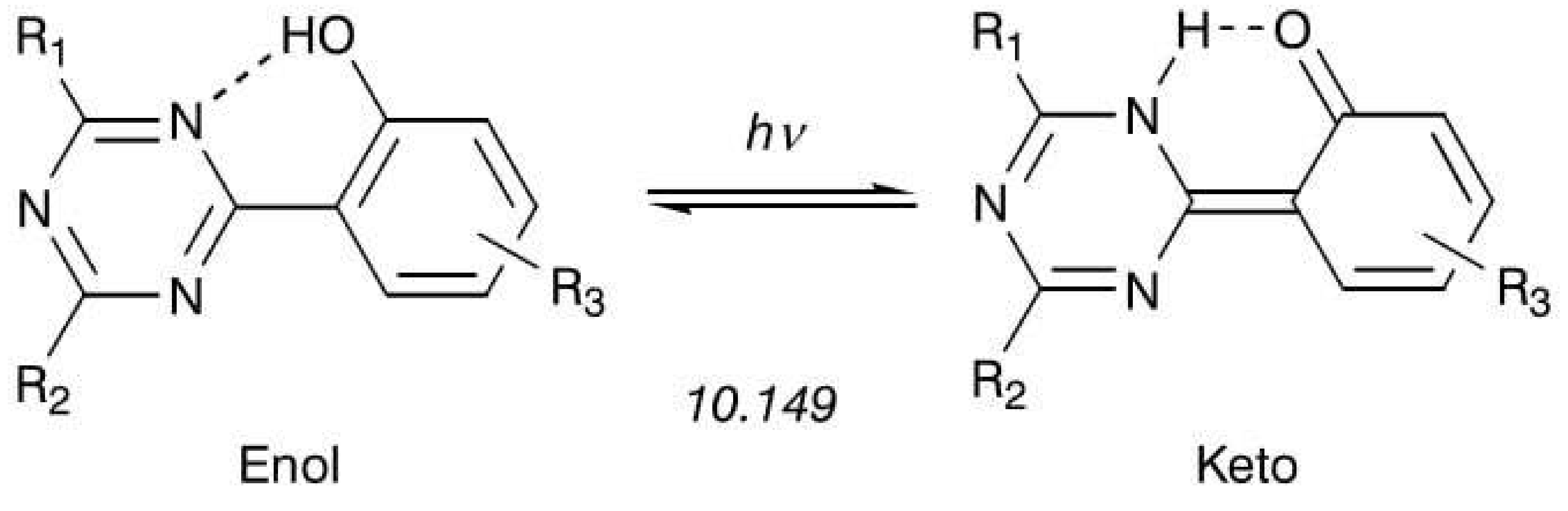


10.148



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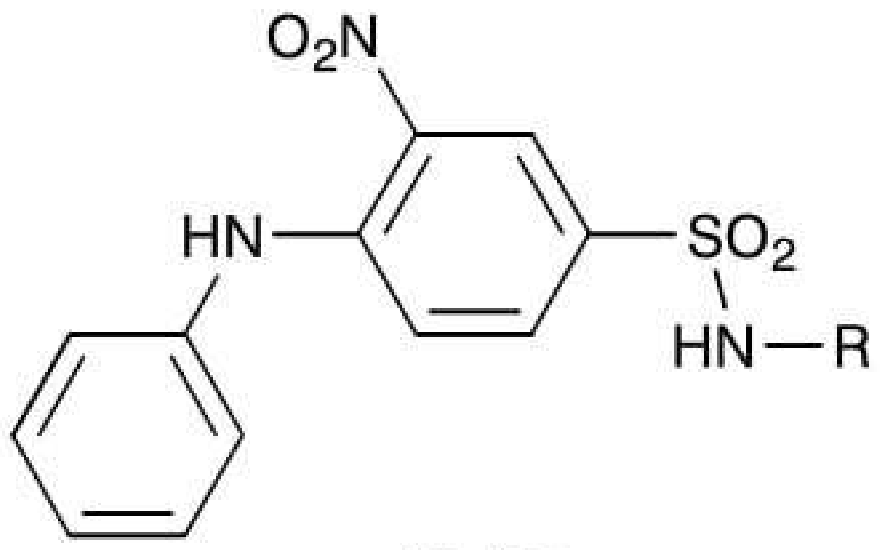
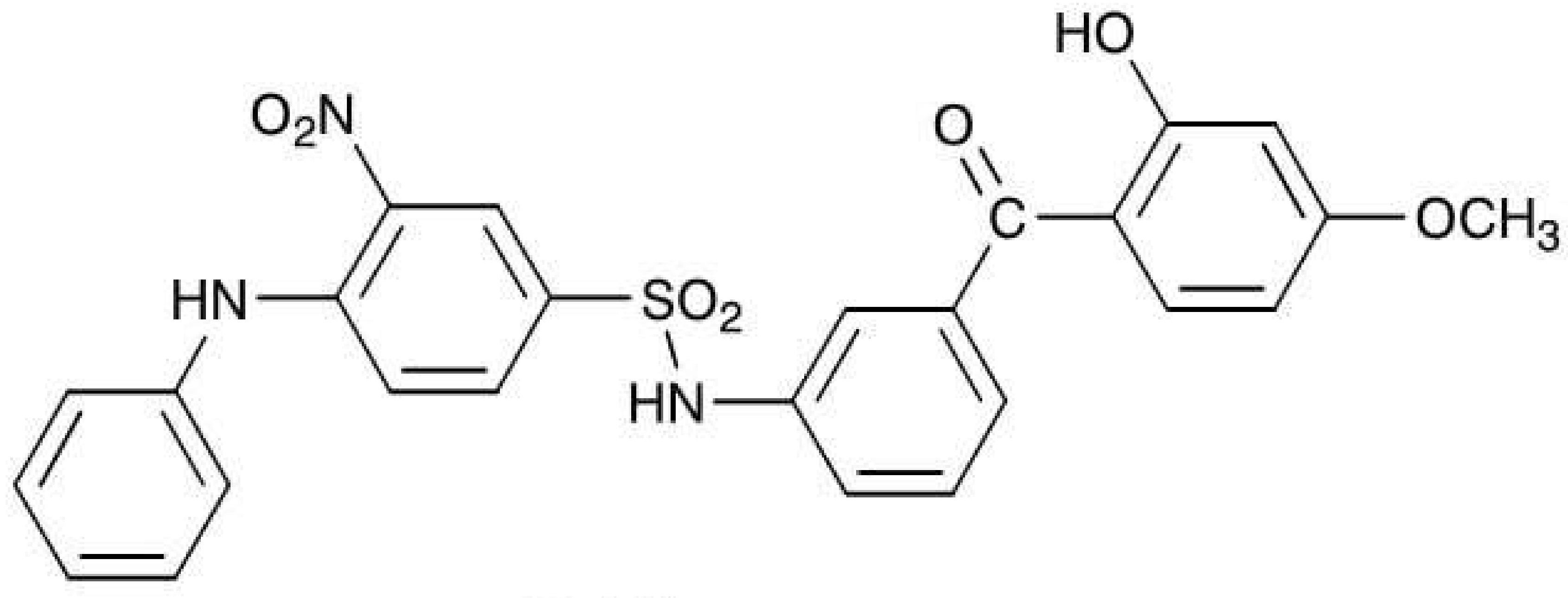


10.150



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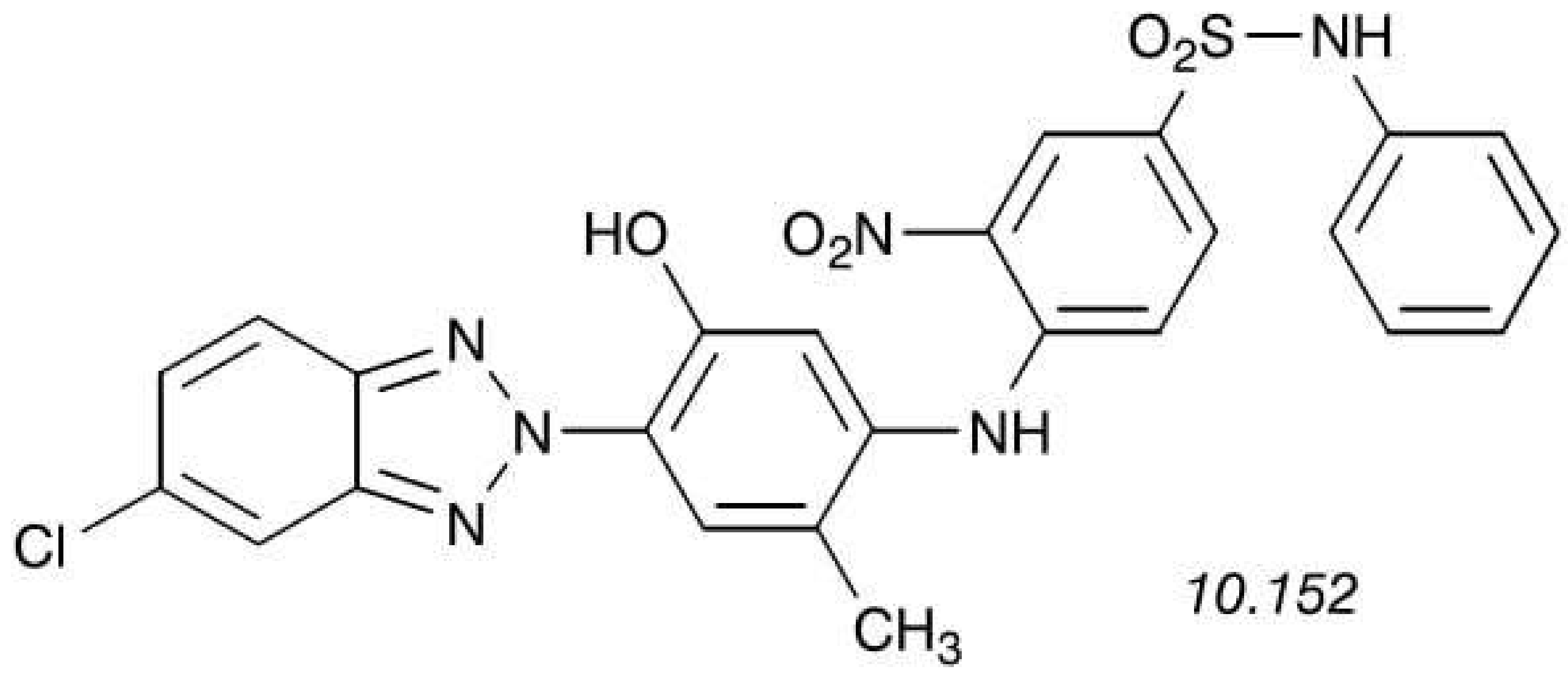
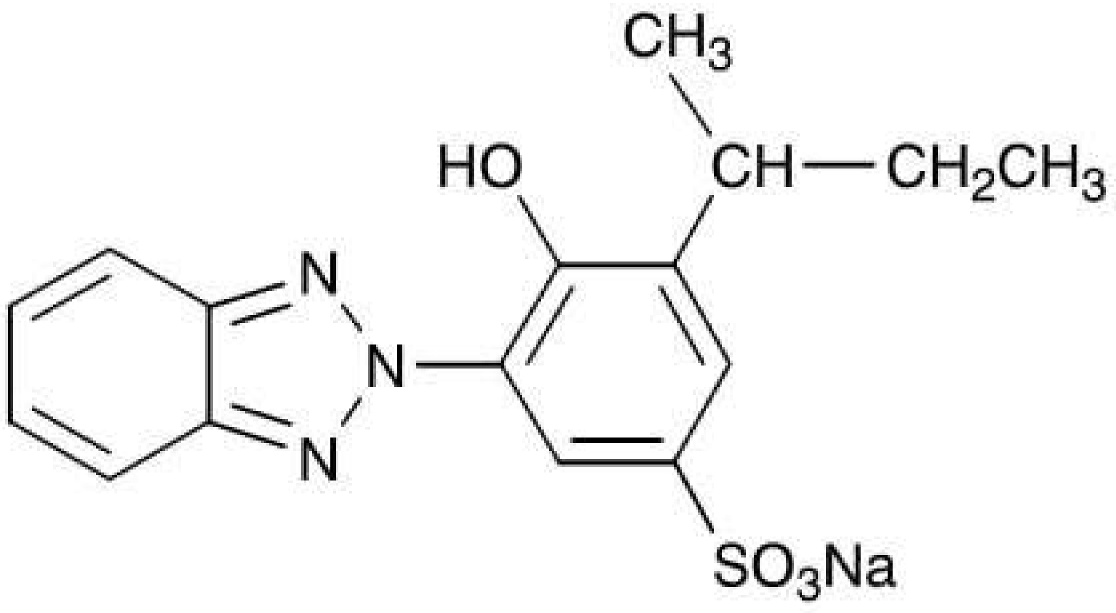


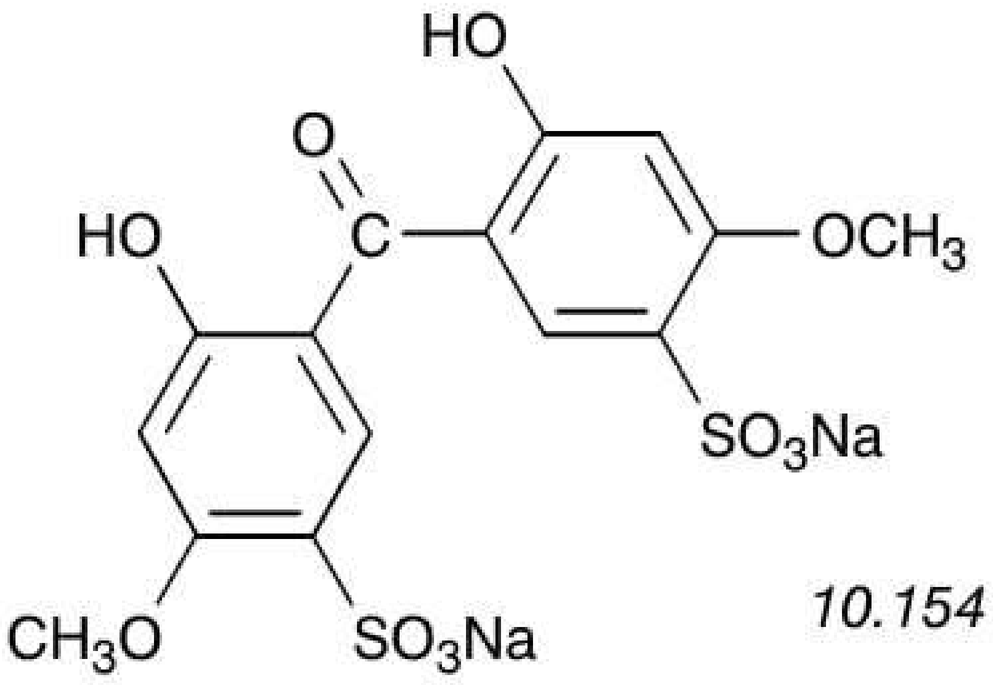
10.152

Polyamides are characteristically prone to photochemical and thermal degradation, although much depends on the structure and purity of the polymer and the types and concentrations of additives present. Although the titanium dioxide delustrant is an effective UV absorber, it is also a sensitiser of the photodegradation of nylon. The decomposition is initiated mainly by free radicals from sensitising impurities. Although most polyamides are resistant to photochemical attack below 40–50 °C, they can degrade fairly rapidly at higher temperatures, particularly with higher concentrations of titanium dioxide present and when dyed in pale or medium depths. Certain metal-complex dyes, however, can act as photostabilisers, especially in full depths. UV absorbers afford protection to nylon only at black-panel temperatures below 40–50 °C. Since degradation is largely the result of oxidative free-radical attack, protective effects are shown by antioxidant addition, either alone or in conjunction with a UV absorber. Both agents may be incorporated during fibre manufacture or can be applied during dyeing or finishing. Some commercial formulations contain both types of agent.

Water-soluble UV absorbers are preferred for nylon, particularly sulphonated benzotriazoles of the general type represented by 10.148, with halo, sulpho or sulphonated arylalkyl substituents in the benzotriazole nucleus and alkyl, alkoxy or sulpho groups in the phenolic nucleus. A specific example is provided by structure 10.153. Sulphonated derivatives of the dihydroxybenzophenone structure 10.147 are also suitable. One study of the influence of UV absorbers on light fastness involved a selection of nine acid dyes typical of those used in the dyeing of nylon carpets. The efficacy of four water-soluble agents applied by exhaust dyeing (10.154–10.156 and an undisclosed structure of the anionic *o*-hydroxyphenylbenzotriazole type) and three water-insoluble types applied from solution in tetrachloroethylene (10.157–10.159) was evaluated [412]. Some of the UV absorbers significantly improved light fastness, but others gave significantly lower ratings. Overall, the behaviour of the UV absorbers was dye- and hue-specific [412]. Conversely, in another investigation it was claimed that stabilisers applied to nylon during dyeing can markedly improve fibre stability and light fastness, independently of hue and depth of shade [413].



10.153



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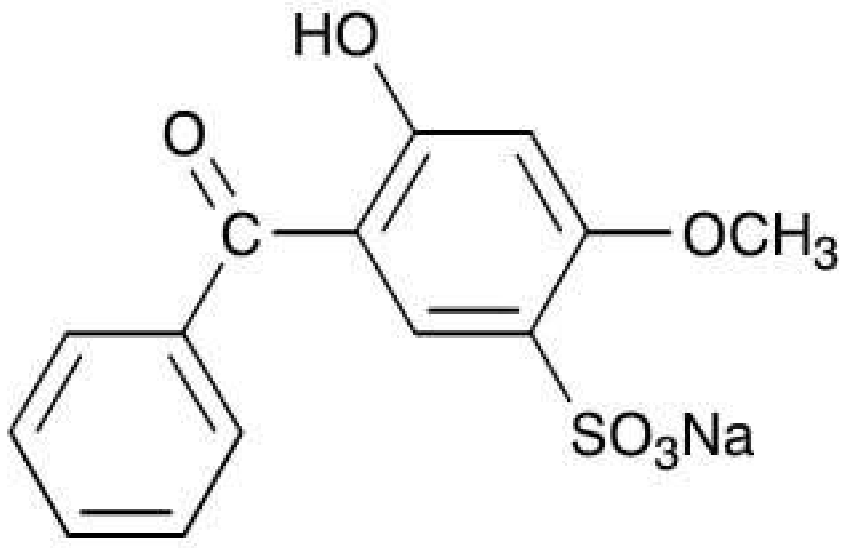

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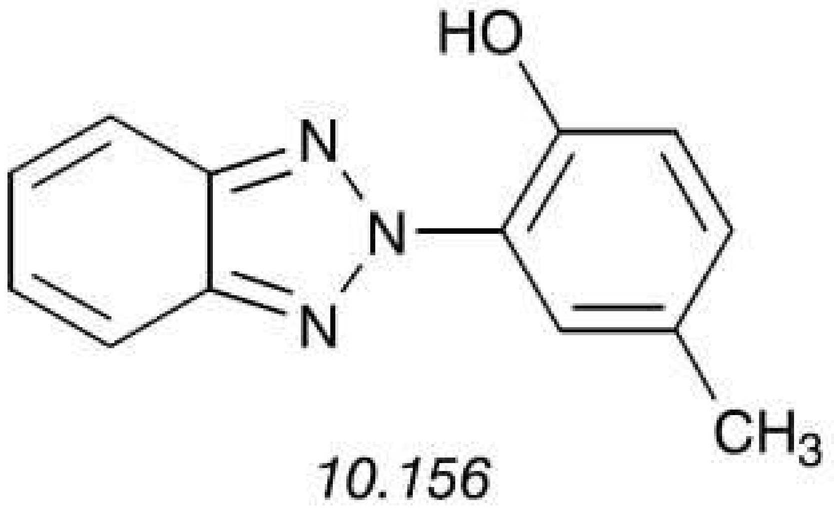

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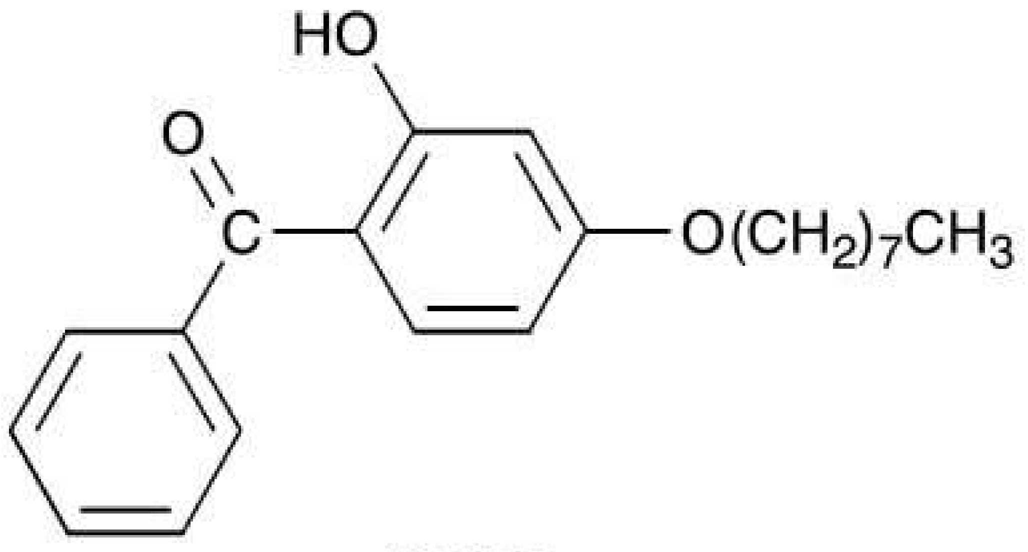

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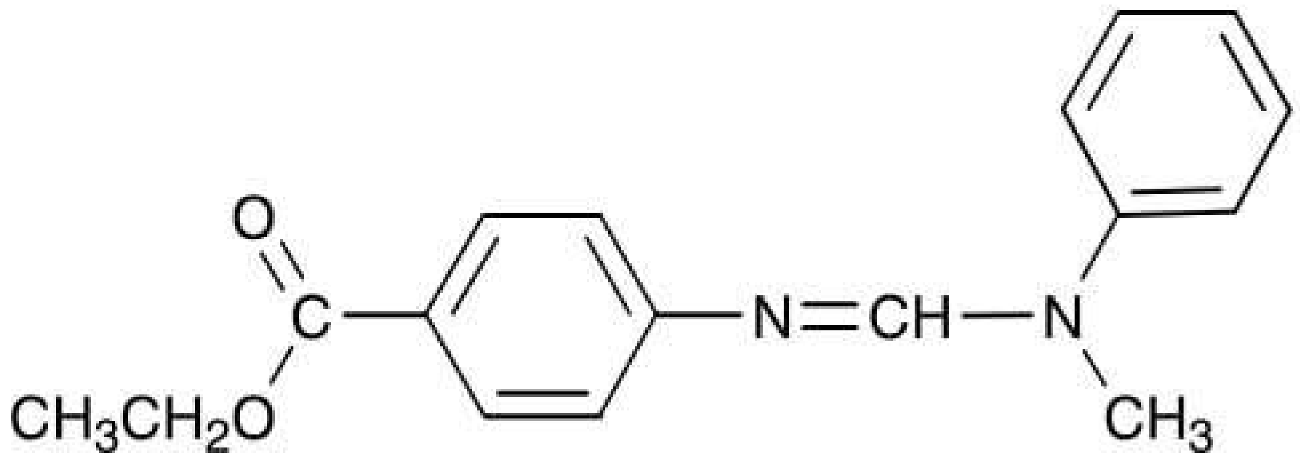

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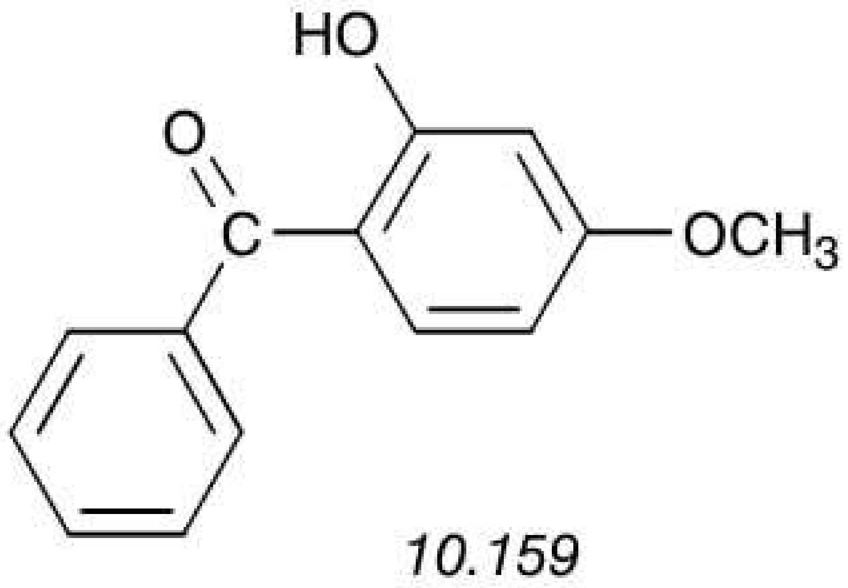
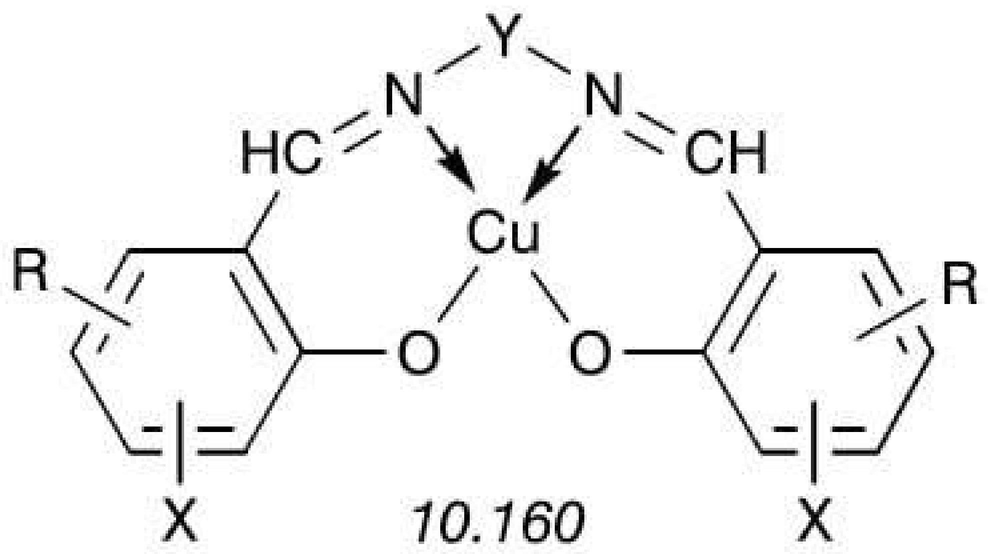


10.159

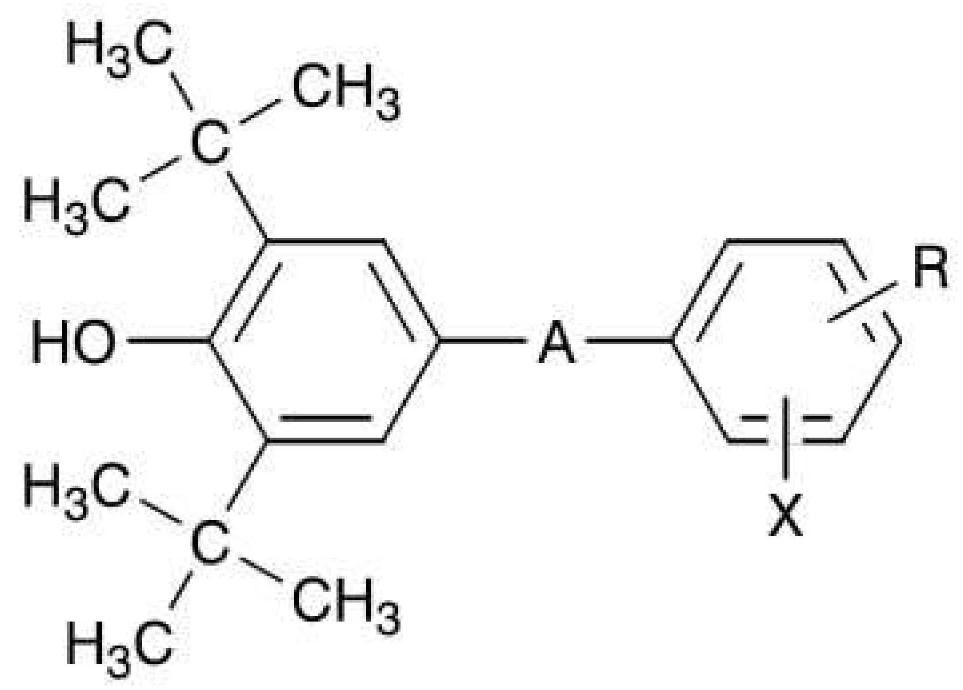
The additional protection given to nylon by antioxidants has already been mentioned. Since the need is to protect against oxidation by free radicals, antioxidants are essentially of two types: peroxide decomposers and radical scavengers. Reviews of these products are available [409,410,413]; these should be consulted for details of the mechanisms involved. Peroxide decomposer types include compounds of manganese(II) or copper(I) and copper(II) complexes, such as azomethine bridge derivatives of the type represented by 10.160, of which numerous water-soluble or water-insoluble variants are possible [409]. These products have a catalytic action and are therefore used in very small amounts.



10.160

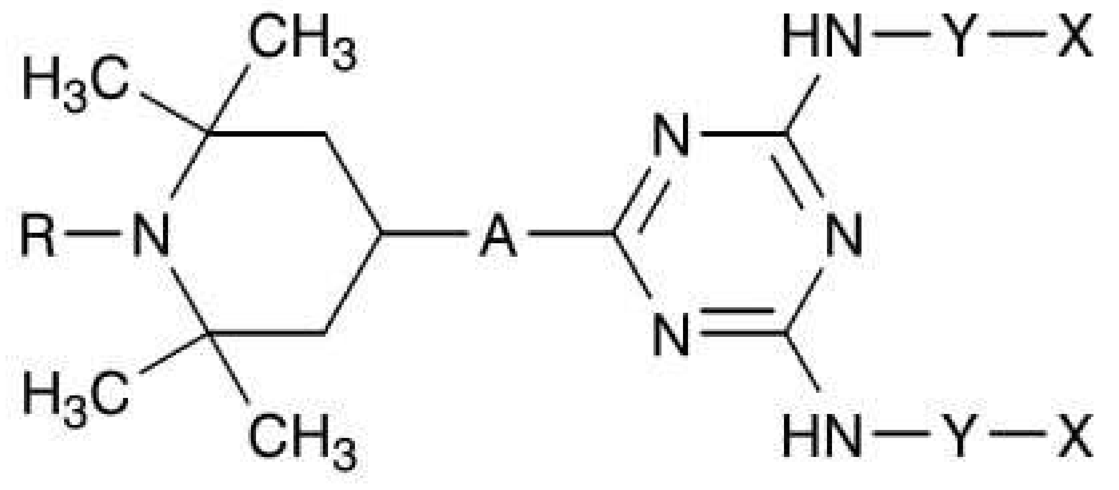
R = H, halo, hydroxy, alkyl, alkoxy
X = H, sulpho, carboxyl, sulphonamide
Y = alkylene, cycloalkylene linkages

Conversely, radical scavengers have to be used in larger amounts because they lack the regeneration capability of catalytic types. The principal product types [409] are sterically hindered phenols (10.161) and sterically hindered amines (10.162). The latter are important because they act not only as scavengers but also as peroxide decomposers [410]. Further compounds include the semicarbazides 10.163 and 10.164, applicable by continuous and exhaust methods respectively. The product 10.165 is suitable only for continuous application. Most radical scavengers are suitable only for thermal stabilisation [410], photostabilising scavengers being restricted to transition-metal chelates, especially nickel(II) dithiocarbamates (10.166), and hindered amines such as 2,2,6,6-tetramethylpiperidine (10.167). Water-soluble triazine derivatives of hindered amines (10.168) have also been used [410].



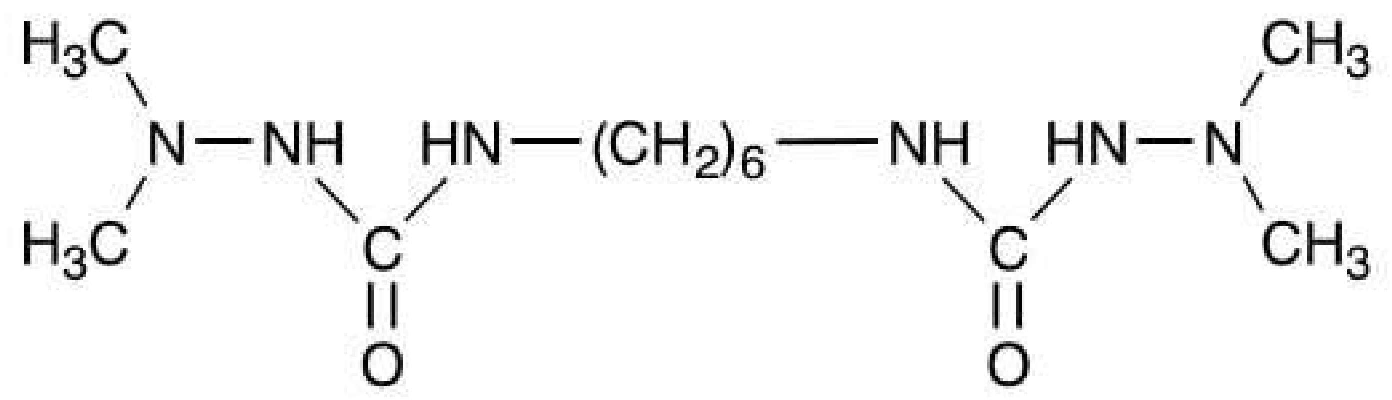
10.161

R = H, halo, alkyl, alkoxy
X = H, sulpho, carboxyl, sulphonamide
A = triazine or $(CH_2)_nCONH$ linkages

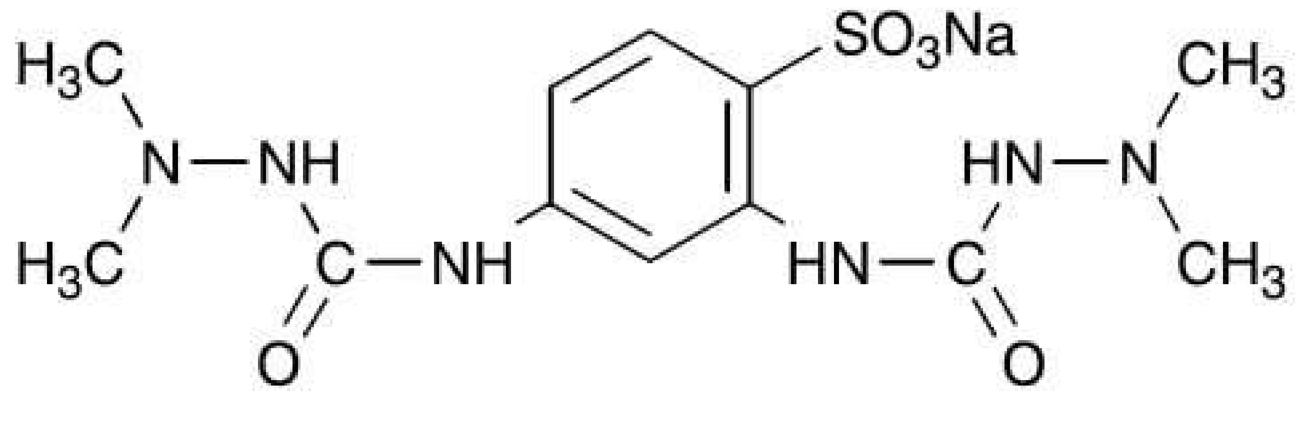


10.162

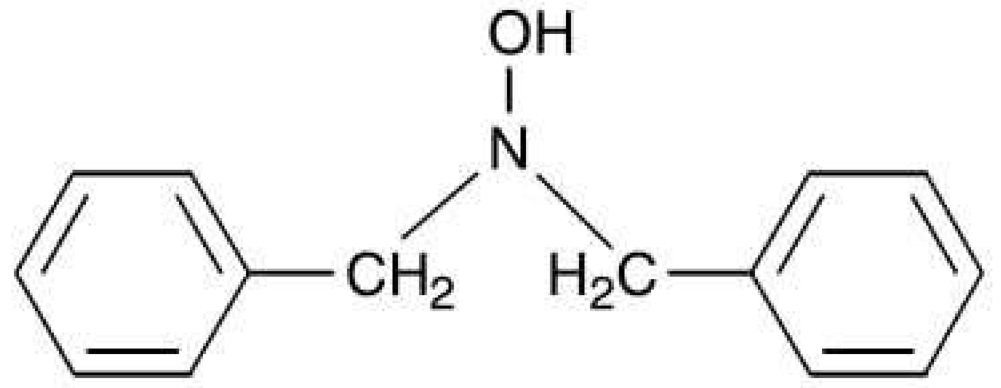
R = H, oxy, hydroxy, acyl, alkyl, alkoxy
A = O or NH
X = H, sulpho, carboxyl
Y = alkylene, arylene, substituted arylene (identical or different)



10.163



10.164



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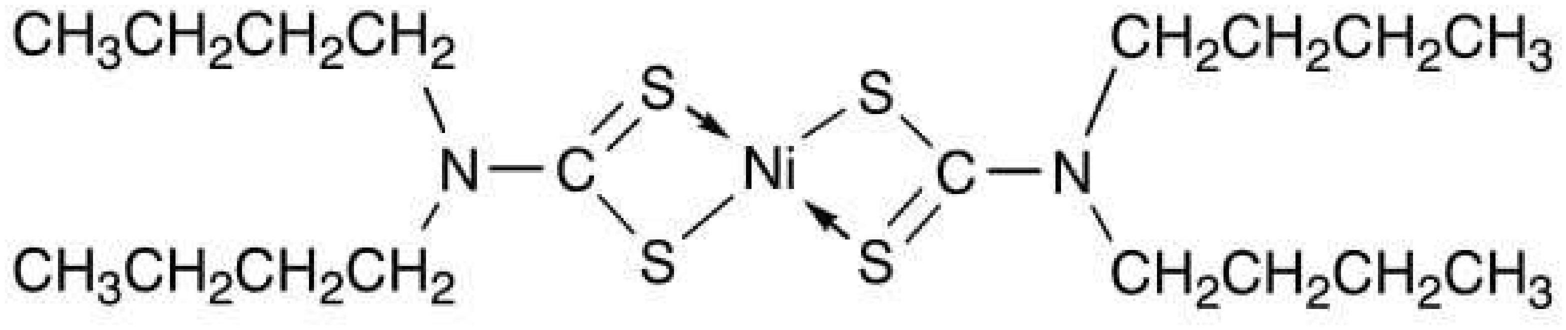

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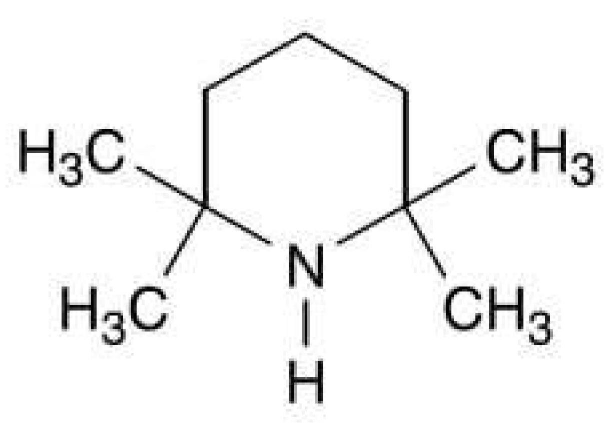
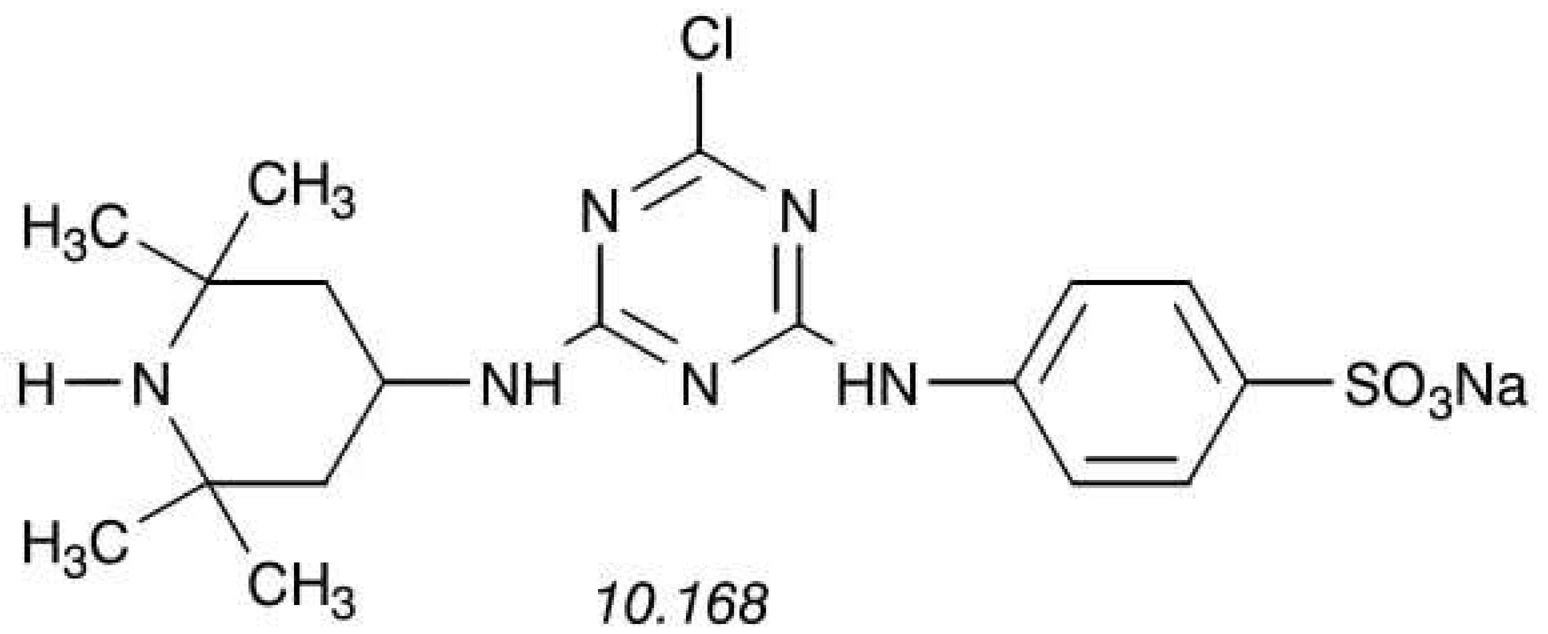
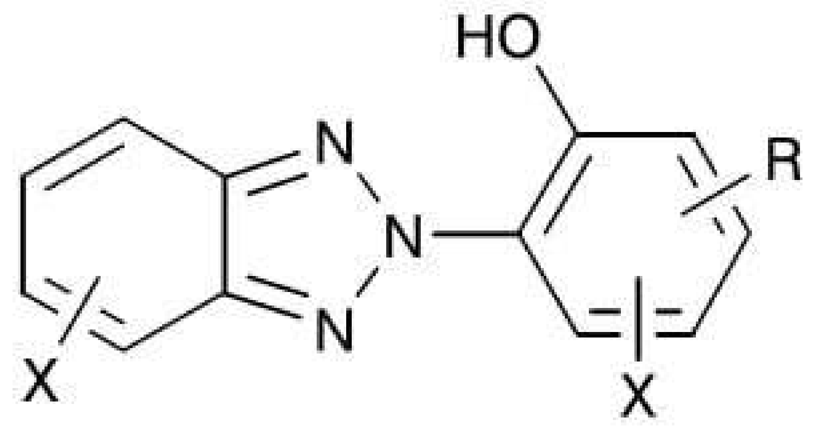


10.167



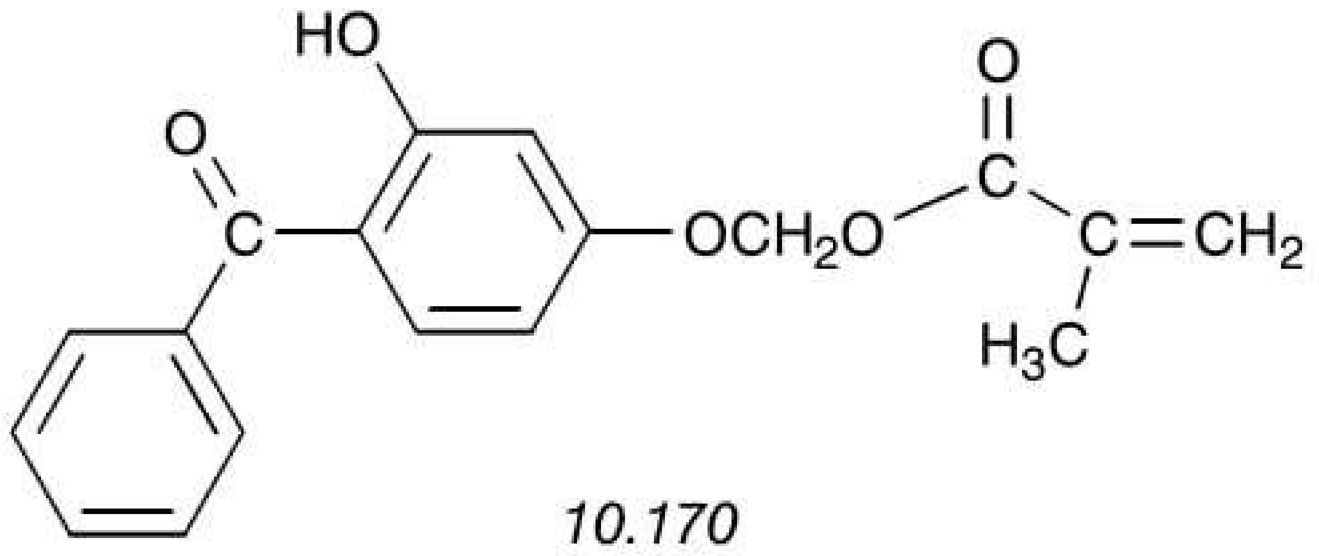
10.168

Water-soluble UV absorbers are preferred on bleached wool, mainly to retard the photoyellowing process. The sulphonated *o*-hydroxybenzotriazole type (10.169) is particularly effective [414]. When applying such products by the exhaust process it is best to avoid the use of sulphates as these lower the exhaustion, as does a pH higher than 5.5 [415,416]. These products are claimed to be fast to hand washing, shampooing and dry cleaning [416]. Nevertheless, polymeric UV absorbers have been developed with the intention of improving on the limited fastness of conventional types [417]. These have typical UV absorber moieties attached to an acrylate, methacrylate or methacrylamide polymer, examples of relevant monomers being 10.170–10.172.

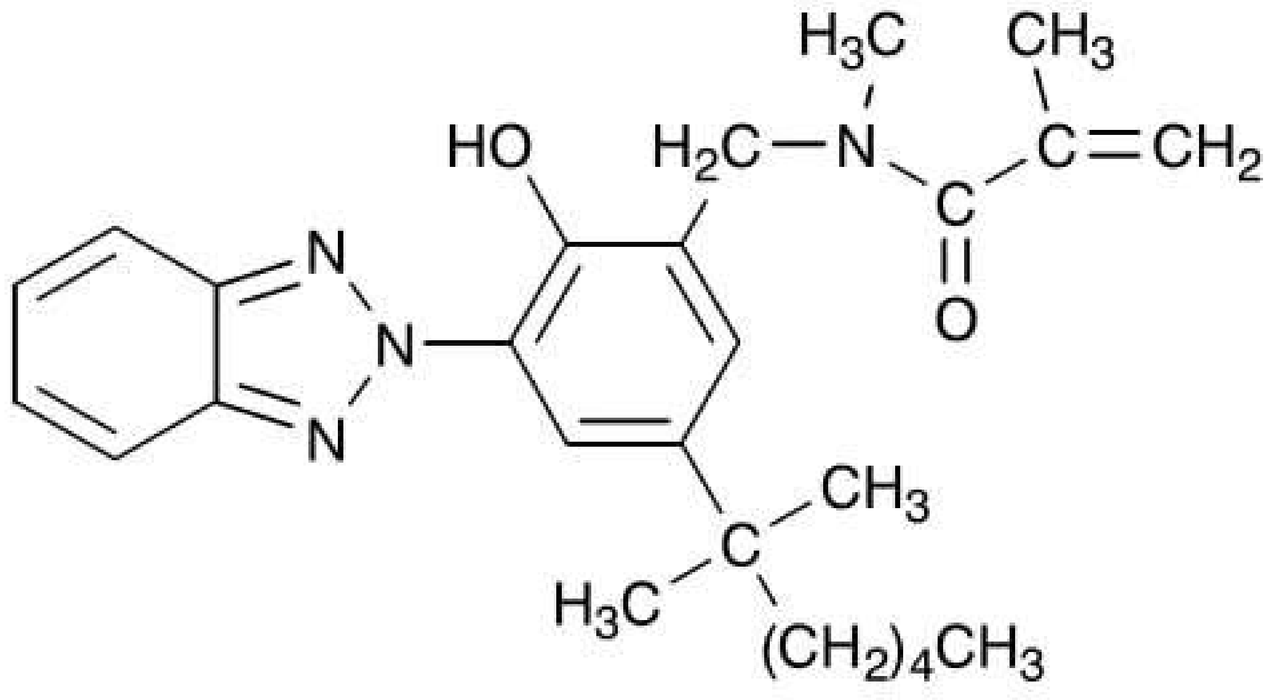


10.169

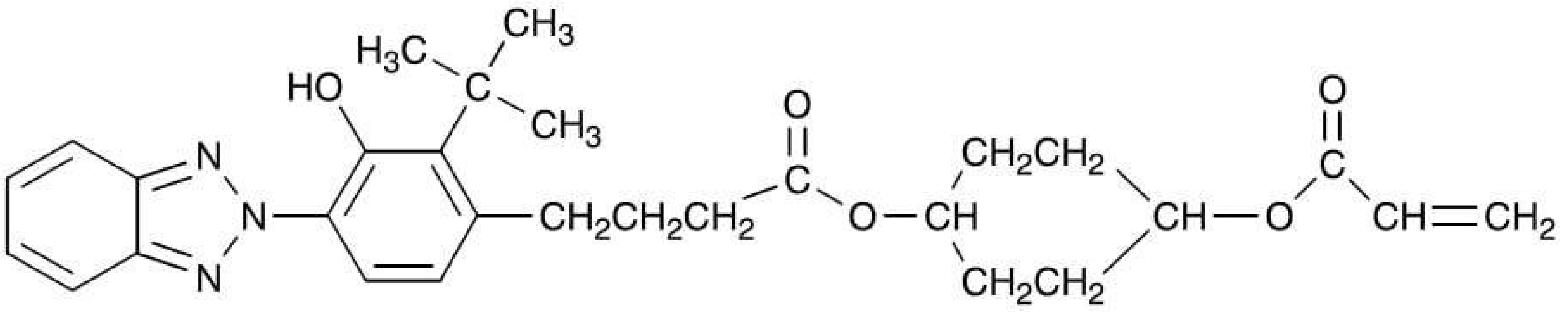
R = alkyl, alkoxy, sulpho
X = H, halo, sulpho, sulphonated arylalkyl



10.170

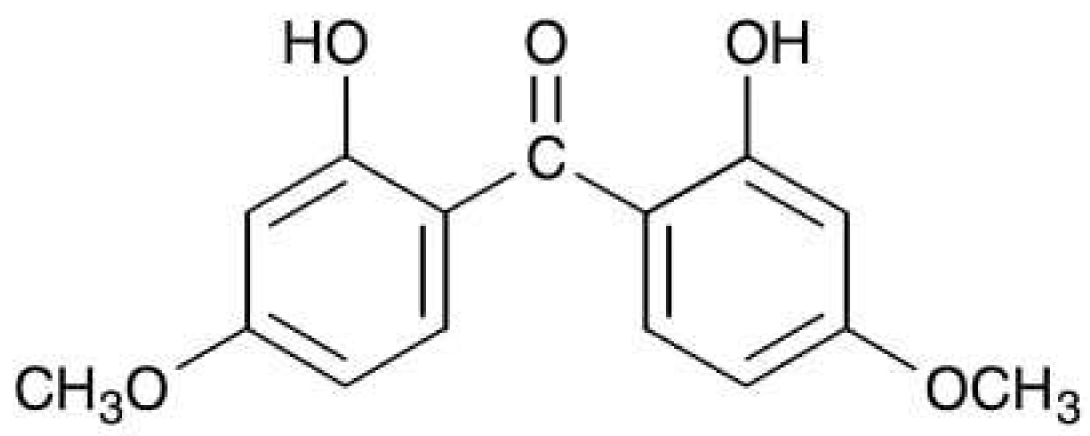


10.171

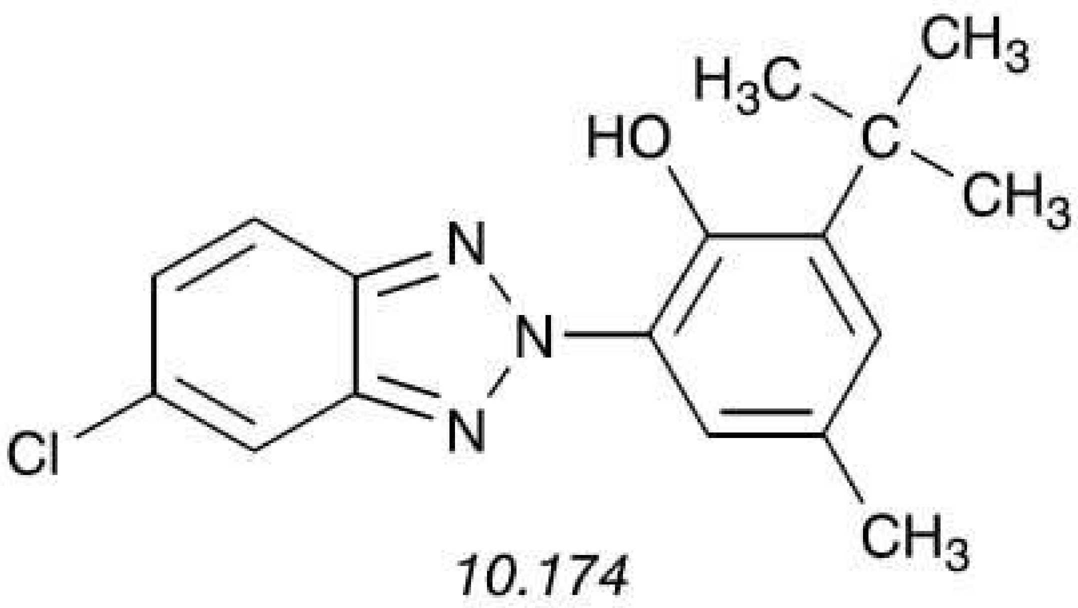


10.172

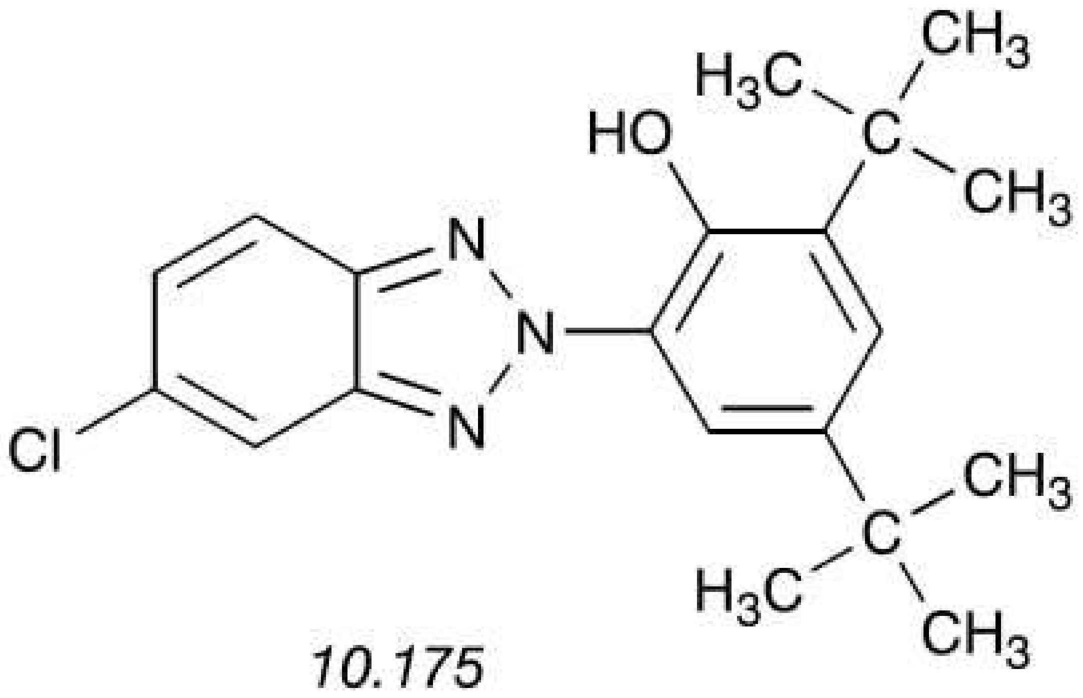
Polyester fibres generally show high resistance to photodegradation providing exposure in the 280–320 nm range is avoided, so the main reason for using UV absorbers on this fibre is to enhance light fastness, particularly to the standards required for automobile furnishings. Indeed, marked improvements generally only become evident with prolonged exposure at high ambient temperatures [409]. Water-insoluble benzophenones and benzotriazoles, such as 10.173 and 10.174 respectively, are widely used. These products, however, have only moderate fastness to sublimation. Where a high setting temperature or pad–thermosol application is involved, *o*-hydroxyphenylbenzotriazoles of greater molecular mass offer higher fastness to sublimation [409]. Water-insoluble mono- (10.149) or bis(*o*-hydroxyphenyl)triazines are also of interest. Derivatives of *o*-hydroxyphenylpyrimidine and benzoxazin-4-one have also been patented [409]. In a recent series of papers [418,419], the effectiveness of the following UV absorbers on polyester was demonstrated: 10.147, 10.156, 10.175 and a benzotriazole of undisclosed structure.



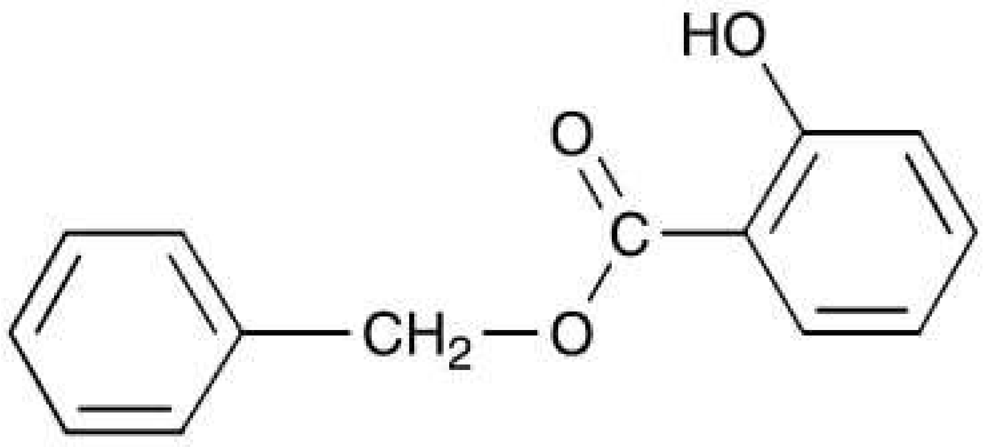
10.173



10.174



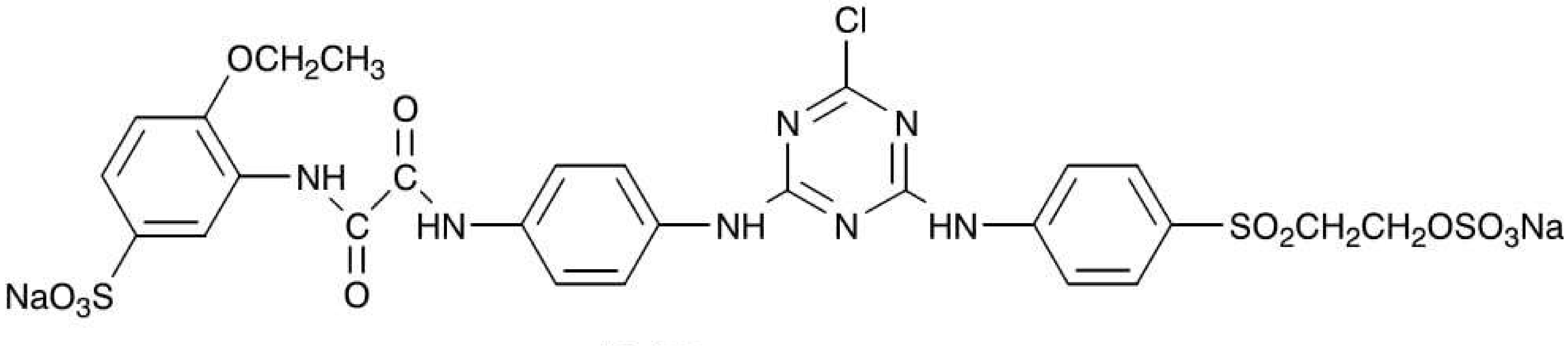
10.175



10.176

Benzyl salicylate (10.176) at an applied concentration of 2% o.w.f. is reported [420] to have given good protection from fading to two anthraquinone acid dyes on silk.

Water-soluble UV absorbers can be used on cotton to improve the photochemical stability of the fibre or to protect the skin from UV radiation but this does not generally improve the light fastness of dyeings. From a chemical viewpoint, bifunctional reactive UV absorbers (10.177) for cotton are of particular interest [421]. The vat dye 10.178 containing two imidazole rings is patented [422] for use by dyeing or printing on cellulosic fibres to improve solar protection both to the wearer and to the fibre. The use of 10.177 in combination with 10.178 is also patented [421]. Normal untreated cotton with a sun protection factor of 5 can be improved to factor 28 after applying 10.178 and to factor 187 when this dye is used in combination with the reactive UV absorber 10.177.



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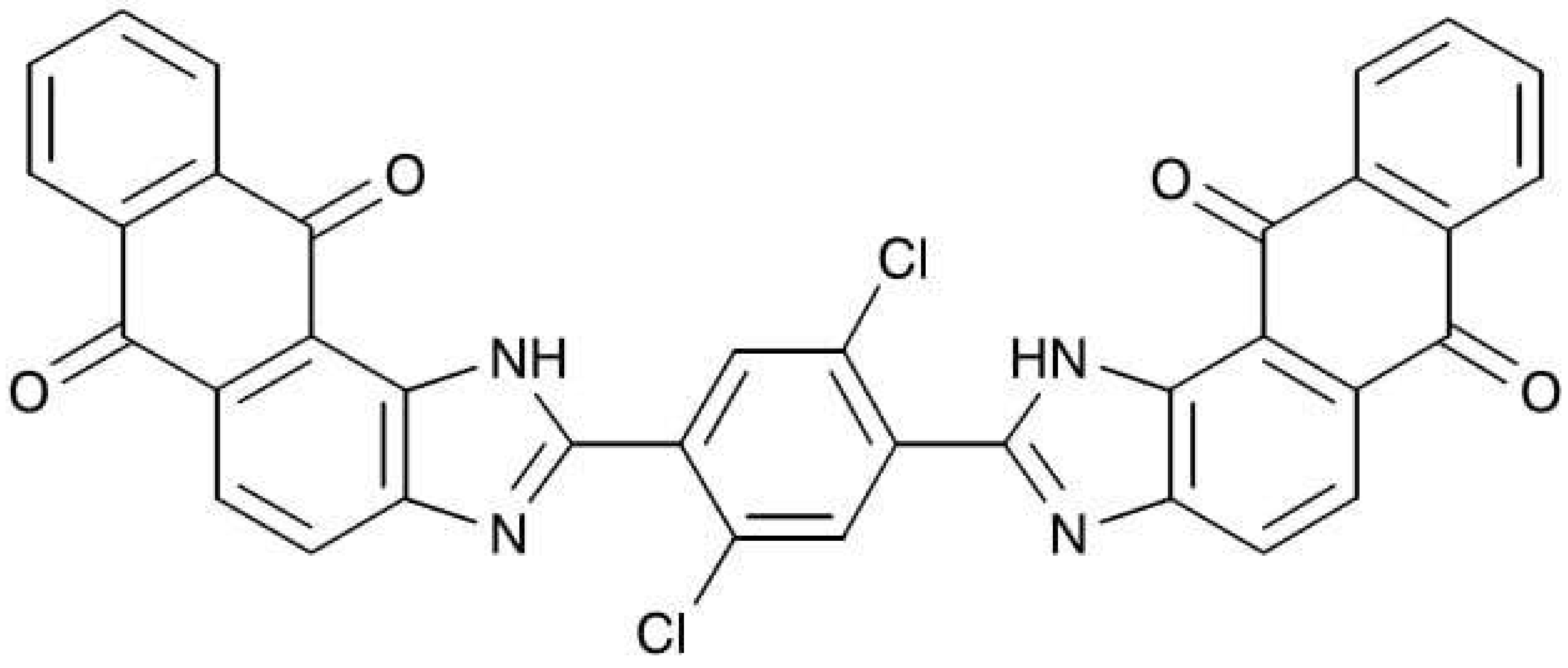
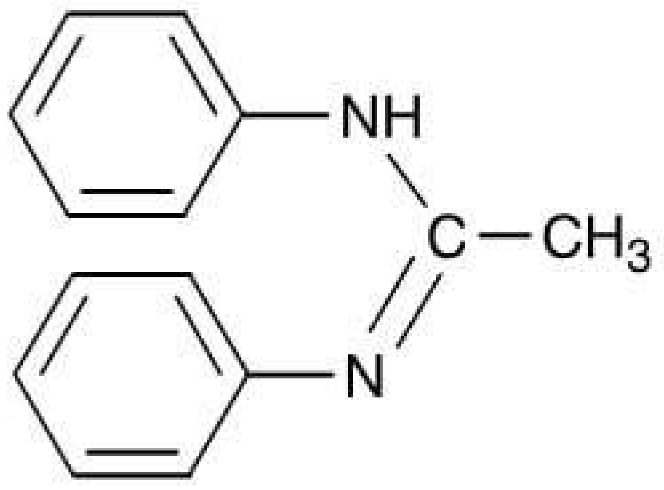


10.178

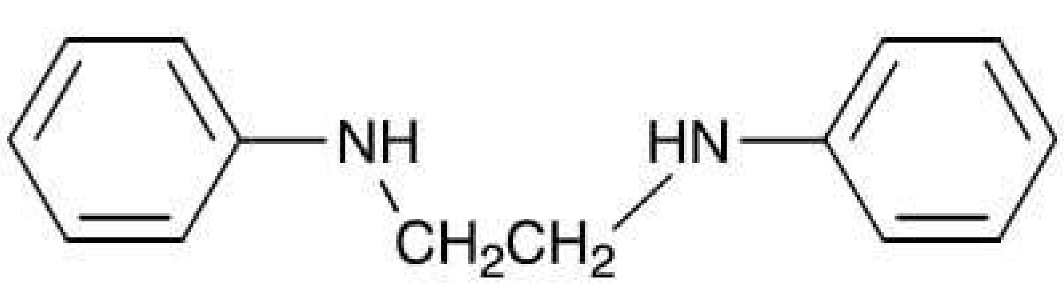
10.9.3 Gas-fume fading inhibitors

Not all disperse dyes on cellulose acetate fibres are resistant to oxides of nitrogen that may be present in the atmosphere. Susceptible dyes, usually those containing primary amino or secondary amino groups, can undergo quite profound changes in hue depending on the reactivity or basicity of the susceptible group(s). The primary general mechanism of fading is believed to be the formation of *N*-nitrosamines [423]. The problem is best avoided by using dyes that do not fade, but this may not always be possible as these tend to be more costly and less easy to apply. Some protection can be obtained by treatment of susceptible dyeings, either during or after dyeing, with colourless agents that react preferentially with oxides of nitrogen. Such agents are known as gas-fume inhibitors. Since they act as scavengers of the acidic oxides of nitrogen, they need to be more basic in character than the dyes they protect. Many such basic compounds, generally applied from aqueous solution or dispersion, have been proposed [424].

The most popular and efficient are substantive to the fibre; typical examples are N,N′-diphenylacetamidine (10.179), which tends to yellow on exposure to oxides of nitrogen, and particularly the diphenylated diamines such as N,N′-diphenylethylenediamine (10.180), which does not yellow. Non-substantive inhibitors applied by padding and drying, such as triethanolamine (10.126) and melamine (10.181), have also been used despite the fact that they are removed on washing. The demand for and commercial availability of gas-fume inhibitors have declined.



10.179



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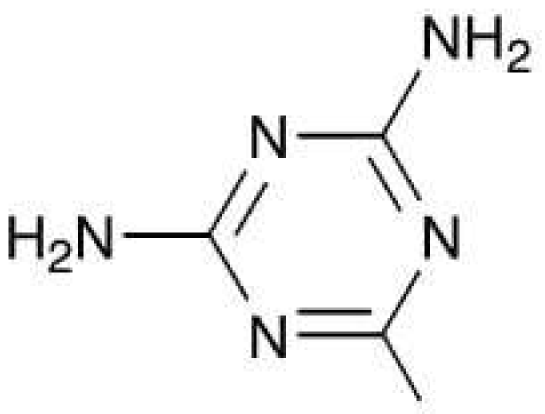
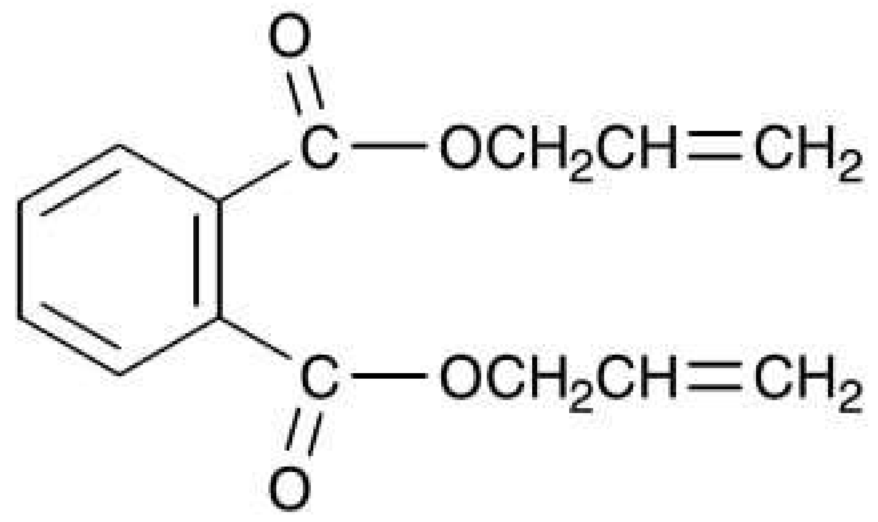


10.181

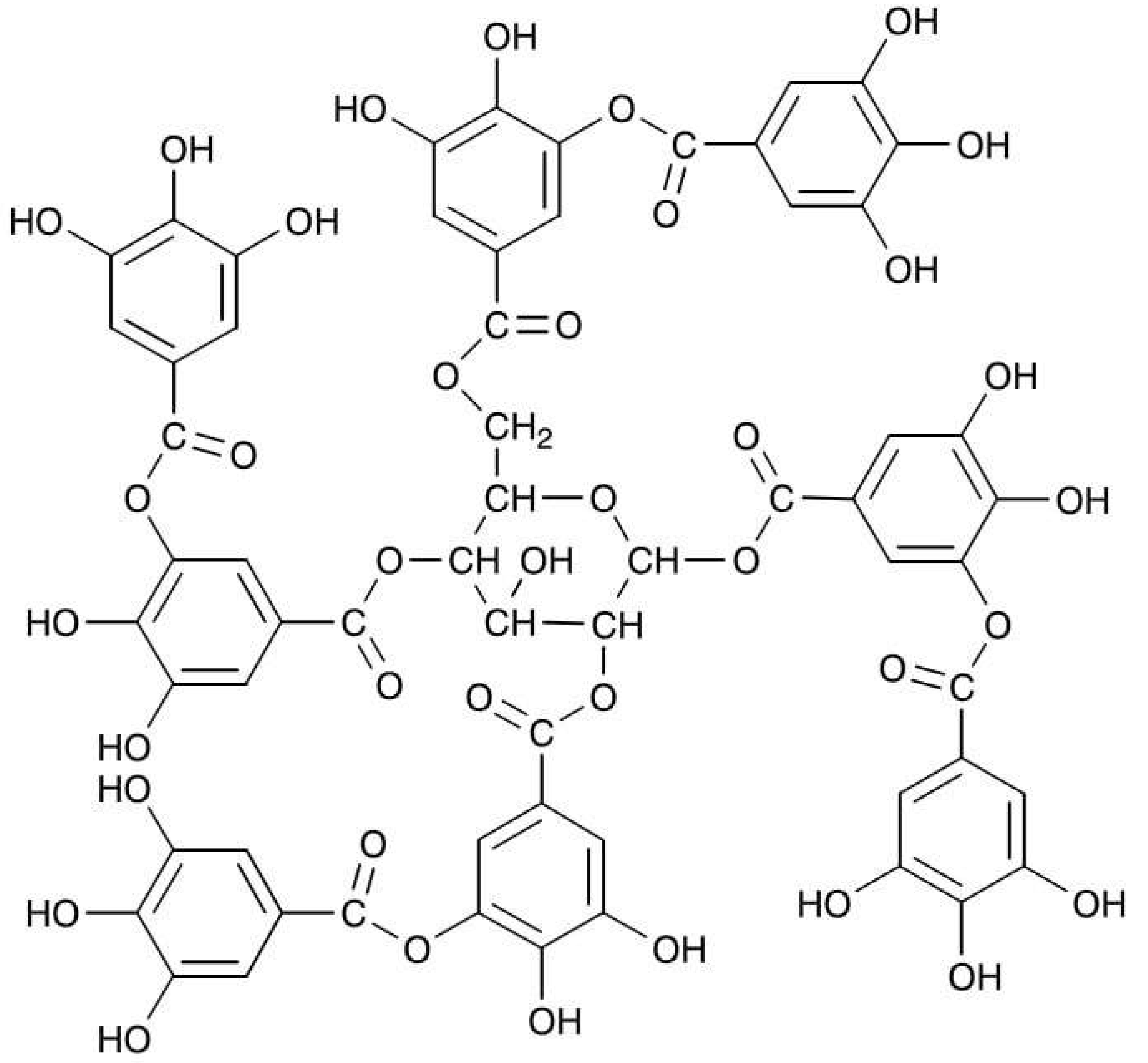
Atmospheric ozone has also been reported as causing fading of certain dyes in some countries [425,426]; diallyl phthalate (10.182) used as a carrier in the dyeing of cellulose triacetate fibres, is said to be an effective ozone inhibitor [427]. Nylon, especially when dyed with certain amino-substituted anthraquinone blue acid dyes, can also be susceptible to ozone fading [428,429]. Selection of ozone-resistant dyes is obviously the best counteractive measure, although hindered phenols (10.161) and hindered amines (10.162) are said to provide some protection.



10.182

10.9.4 Aftertreatments and resist treatments for acid dyes

By far the most important aftertreatment for acid dyeings is the so-called syntan process widely used on nylon, which has superseded the classic full back-tan process. This involved treatment of the dyed nylon first with 'tannic acid' (a highly complex gallotannin or polygalloylated glucose, such as structure 10.183), which hydrolyses to give digallic acid (10.184) or gallic acid (10.185) [391,430], followed by further treatment with potassium antimonyl tartrate (tartar emetic; 10.186). It has been replaced on grounds of its high cost, instability to hot alkali, undesirable effects on fabric handle and light fastness, changes in colour (usually dulling) during treatment, and diffusion and degradation of the antimonyl tannate complex during subsequent steaming or dry heat setting, as well as for health and environmental reasons. Its presumed mechanism of action is complex [391,430].



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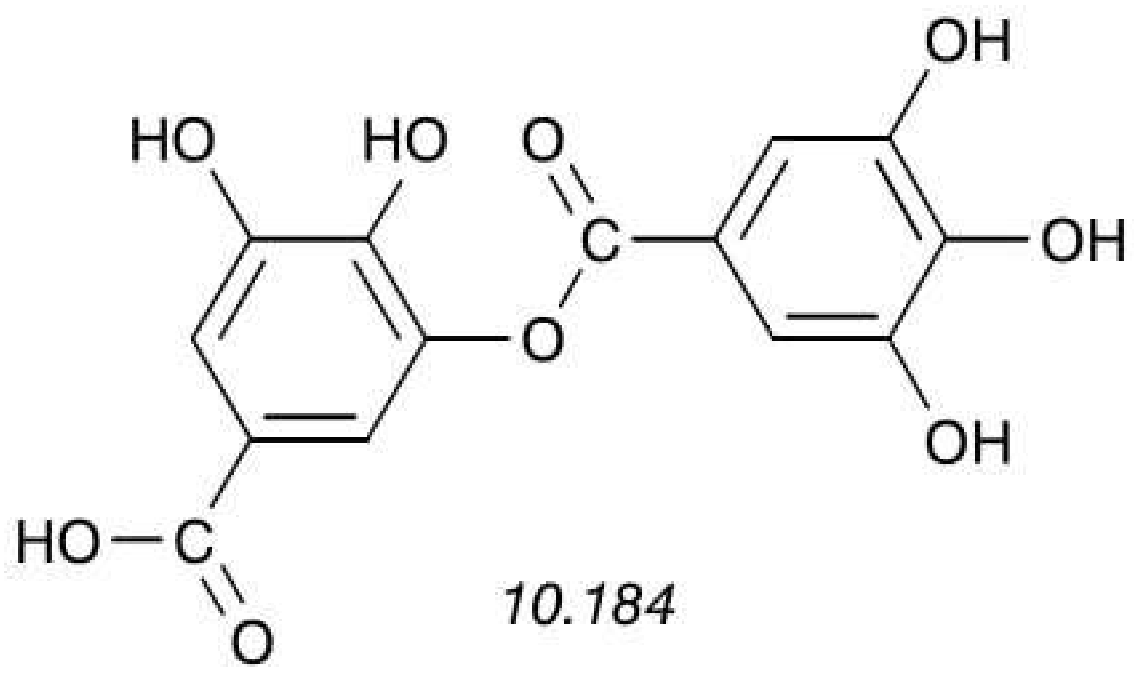

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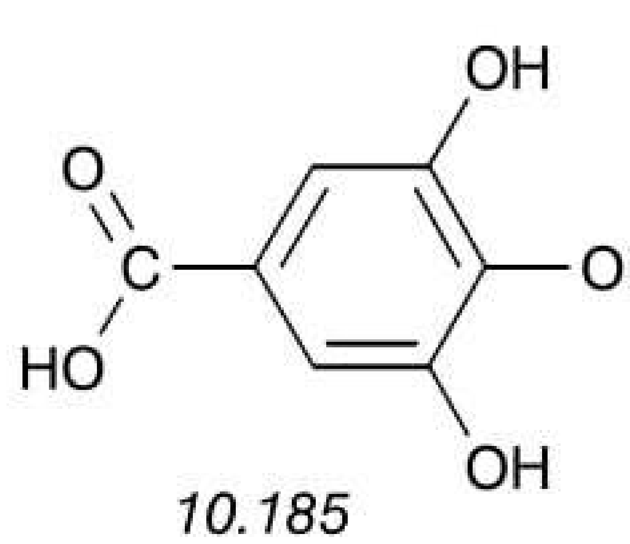

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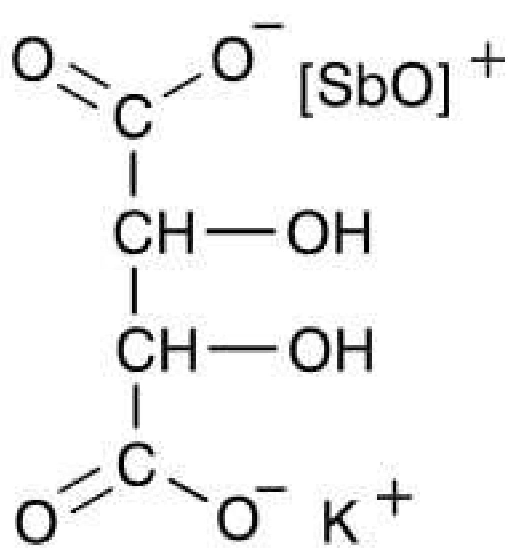


10.186

The synthetic tanning agents (syntans) that have superseded the back-tan have the advantage of being applied in a single process but they tend to be polyphenolic compounds like the naturally derived gallotannins. In fact, compounds of this class have been described in section 10.6.1 as condensation products of formaldehyde with sulphonated phenols, naphthols or naphthylamines. Structures 10.100–10.103 are typical of these compounds although, as mentioned earlier, they form a large and varied group. The precise structural details of typical commercial syntans for nylon are hidden within a plethora of patent literature, much of which pertains to their use as tanning agents for leather [391]. In addition to the products mentioned in section 10.6.1 analogous sulphur-containing products, such as those derived from thiophenols, and heavy-metal phenolates were formerly used.

A brief simplified mechanism whereby syntans are thought to operate can be described, at the risk of incompleteness. Their rapid sorption by the fibre under the (usually acidic) conditions of application is largely the result of electrostatic attraction between negatively charged sulphonate groups and protonated amino groups in the fibre. Hydrogen bonding between uncharged polar groups, and hydrophobic bonding between the nonpolar moieties in the syntan and the fibre, create conditions for the formation of complexes. Maximum improvement in wet fastness results when the complexes are formed at the fibre surface, since any treatment leading to diffusion of the syntan complex into the fibre tends to yield lower fastness. Hence a 'barrier effect' seems to be involved. Possibly multilayers can be formed via a Brunauer, Emmett and Teller (BET) mechanism. Some syntans will give a modest improvement in the wet fastness of disperse dyes on nylon but even with acid dyes the response to the syntan treatment in terms of improved wet fastness varies markedly from dye to dye.

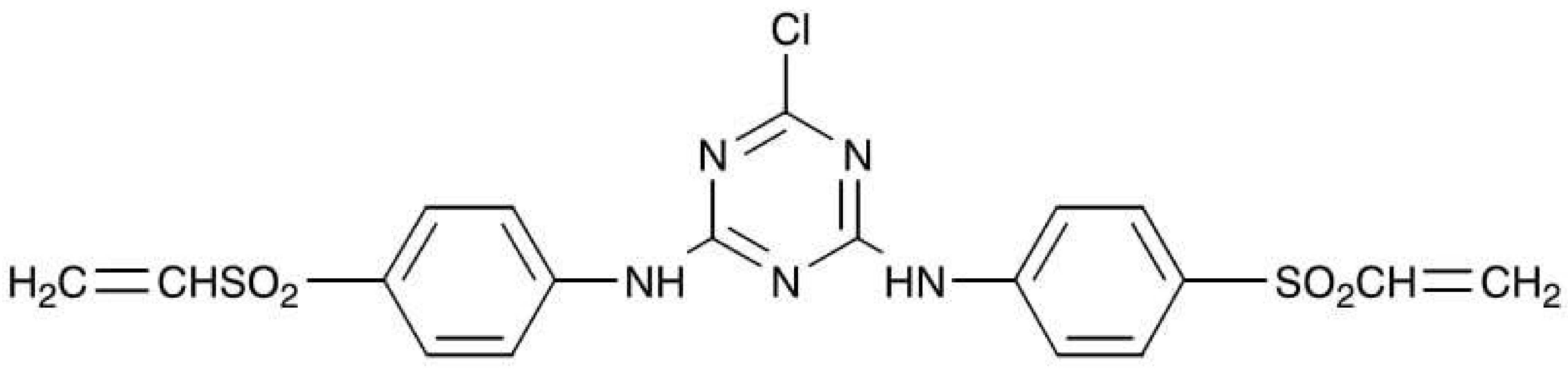
Empiricism has guided the screening of syntans for nylon. Both the affinity of the syntan for the fibre and its diffusion rate are important, and the required values are obtained by balancing the degree of sulphonation and range of molecular sizes present. Moreover, many of these products are used not only as aftertreating agents for the improvement of wet fastness, but also as blocking agents to inhibit absorption of dye either partially or completely – for example, in the dyeing of nylon/wool blends to restrain the usually preferential uptake of dye by the nylon, or to produce resist effects, particularly in printing. The balance of properties required in the syntan may therefore vary somewhat and is influenced by the characteristics of the dye–fibre system for which it is intended.

Studies on nylon, using commercial syntans of undisclosed structure [431–433] showed that the absorption of syntan increased with decreasing pH, providing further evidence for electrostatic interaction. Evidence was also found for the BET mechanism, indicating that other forces are also operating, such as hydrophobic interaction. Uptake of syntan increased with applied concentration and increasing temperature, this being attributable to the higher kinetic energy of the syntan molecules and the greater extent of fibre swelling. Syntan uptake was greater on nylon microfibres (greater surface area) than on conventional nylon staple fibres, but the fastness to washing was inferior on microfibres. Application of a cationic agent subsequent to the syntan treatment gave an additional significant improvement in fastness, particularly where multiple washes were involved [433]. Unsulphonated 1:2 metal-complex dyes showed less desorption of dye than disulphonated types after 1–3 washes but greater loss after 5–10 washes. The cost and inconvenience of these two aftertreatments, however, would not be justifiable under commercial conditions.

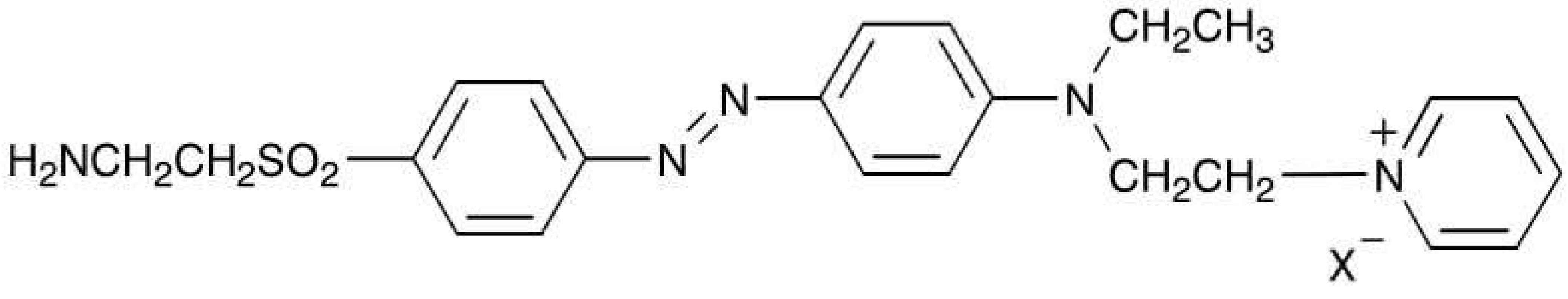
Similar commercial syntans have been evaluated in dye–resist pretreatments on wool [434]. Evidence for both kinds of agent–fibre interaction was again found. The resist effect imparted to the wool was specific to the type of anionic dye applied, giving high resistance to four hydrophilic dyes and low resistance towards two hydrophobic dyes. Syntan desorption occurred during dyeing, indicating that these agents are relatively weakly attached to the fibre. The desorbed syntan had a restraining effect on the uptake of all six dyes examined.

Section 10.9.1 includes an account of nylon pretreatments based on chemistry normally associated with reactive dyes for cellulosic fibres. Similar chemistry has been used to develop alternatives to syntans, both as aftertreatments to improve fastness and as pretreatments to give dye-resist effects. The trifunctional reactive compound XLC (10.95), already discussed as a shrink-resist reactant for wool (section 10.5.5), is hydrolysed under alkaline conditions to the active vinylsulphone form (10.187). This trifunctional crosslinking agent has been evaluated to improve the fastness of nylon dyed under mildly acidic conditions with specially prepared anionic aminoalkylated triazine dyes [435]. Such dyes do not bond covalently with nylon, but aftertreatment with this trifunctional reactive agent results in a significant degree of covalent bonding with a consequent improvement in wet fastness. A cationic aminoethyisulphonyl dye (10.188) was prepared and applied to nylon at the optimum pH 10, followed by treatment with the parent sulphatoethylsulphone crosslinker (10.95). In this way, the dye became fixed covalently via the agent to terminal amino groups in nylon, resulting in improved fastness to washing [435].

Traditional syntan treatments are rather ineffective for improving the wet fastness of anionic dyes on wool, mainly because of weakness of the interaction between syntan and fibre. It is therefore not surprising that covalent reactive systems have been explored to find more effective aftertreatments and dye-resist treatments for this fibre. In an initial study

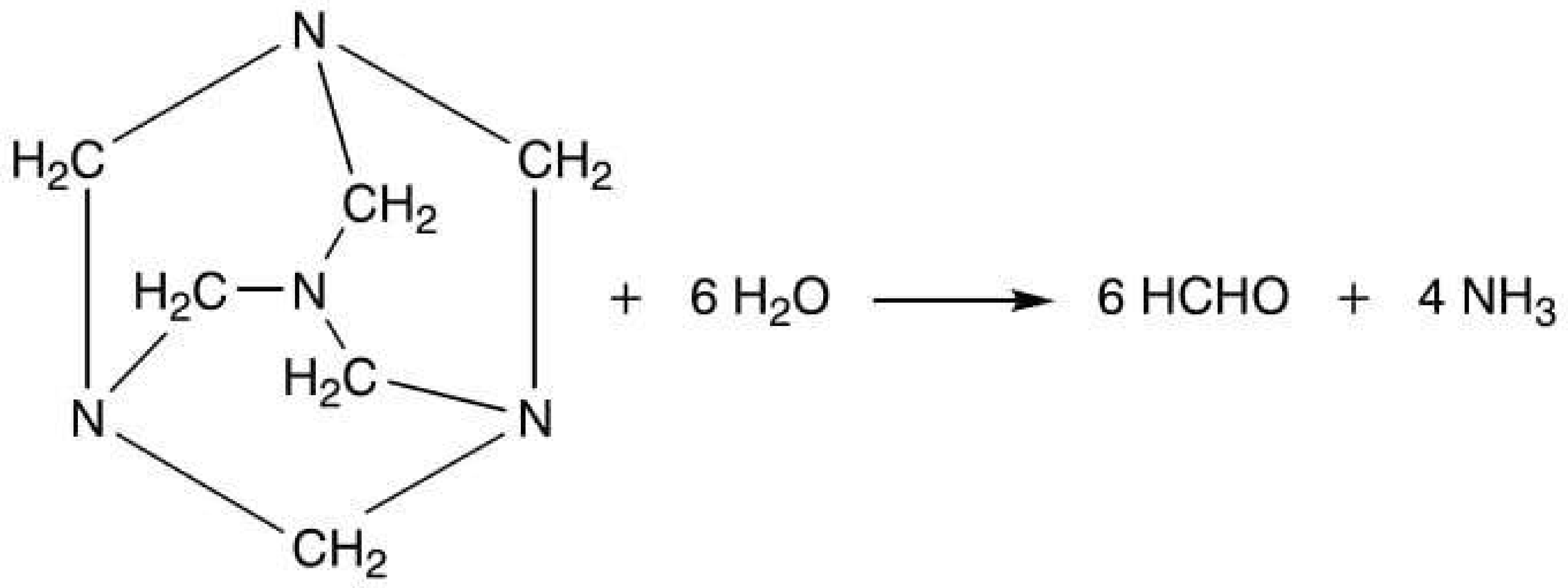


10.187

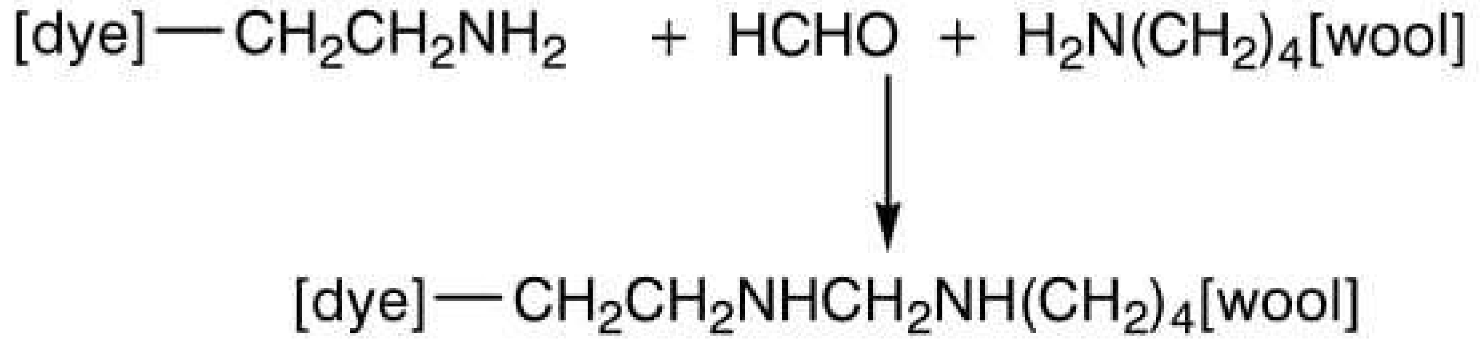


10.188

aimed at producing a system that would overcome the level dyeing problems associated with reactive dyes on wool [436], a specially prepared aminoalkylated dye (not fibre-reactive) was applied together with hexamethylenetetramine, from which formaldehyde was released (Scheme 10.75) to give covalent bonding between the amino groupings in the dye and in the fibre (Scheme 10.76). This process was successful up to a point but gave lower fixation when dyeing in full depths. Certain chromogens also showed marked changes of hue.



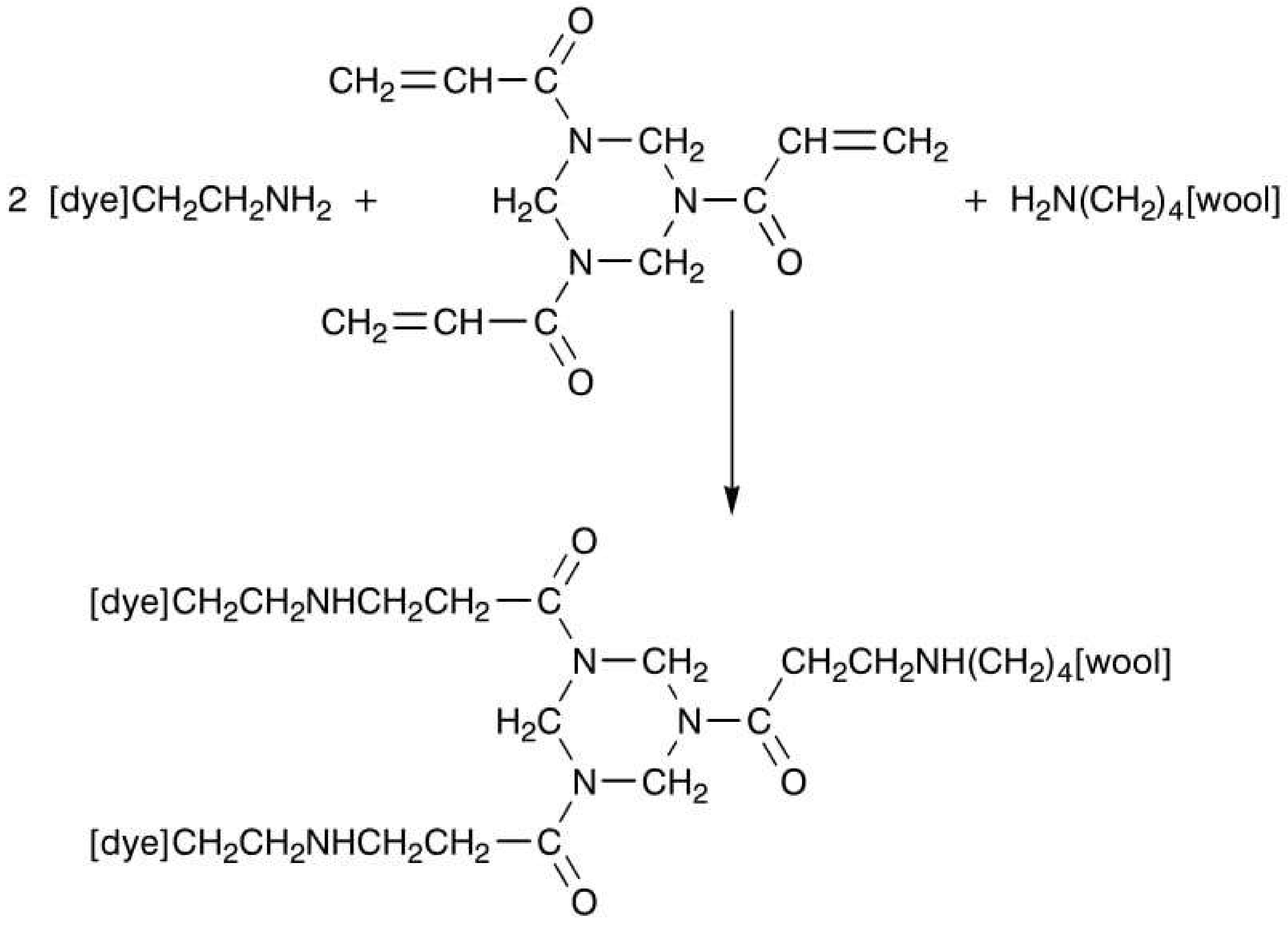
Scheme 10.75



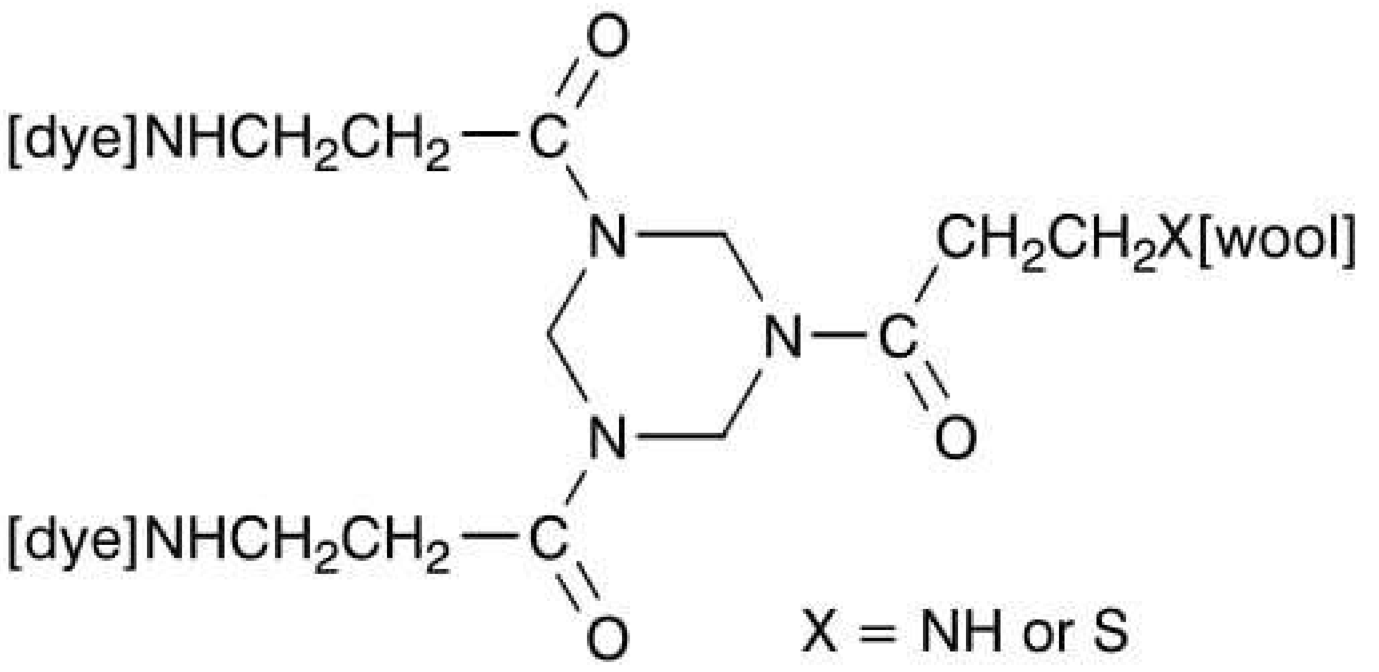
$$[dye]{-}CH_2CH_2NH_2 + HCHO + H_2N(CH_2)_4[wool] \longrightarrow [dye]{-}CH_2CH_2NHCH_2NH(CH_2)_4[wool]$$

Scheme 10.76

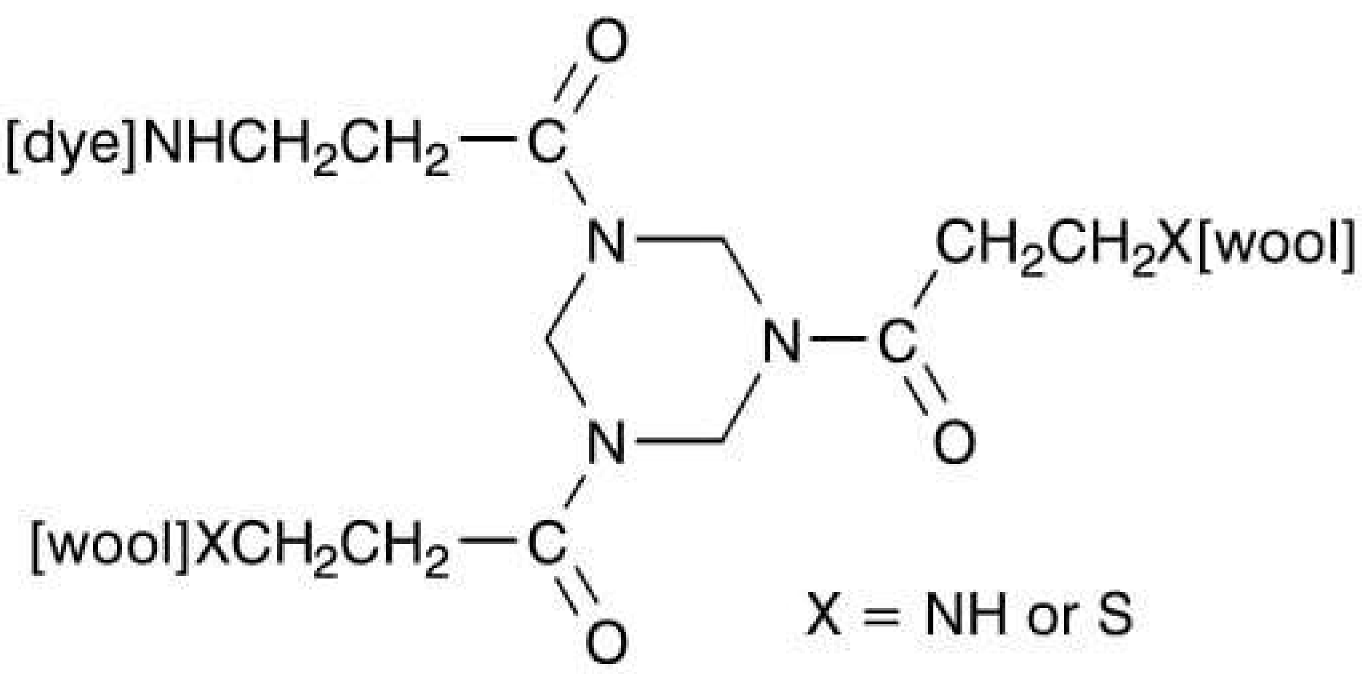
This approach was subsequently improved [437] by dispensing with the formaldehyde precursor and adding a trifunctional crosslinking agent to the dyebath after dye absorption was complete. The crosslinking agent was 1,3,5-tris(acryloyl)hexahydro-*s*-triazine (10.146). Scheme 10.77 represents an idealised reaction for the formation of dye–agent–wool linkages. Since reaction takes place in a random manner, however, the derivatives 10.189–10.192 could equally well be produced. Products 10.191 and 10.192 need to be minimised, because respectively they are linked only to the dye or to the fibre [437].



Scheme 10.77



10.189



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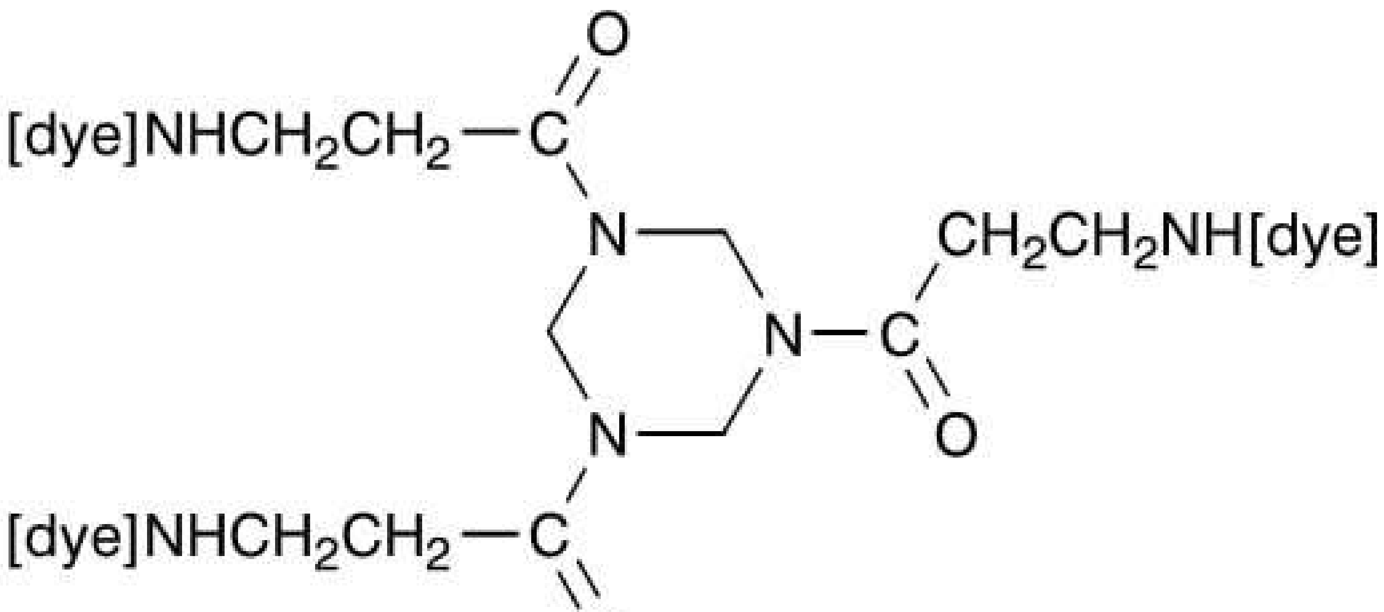

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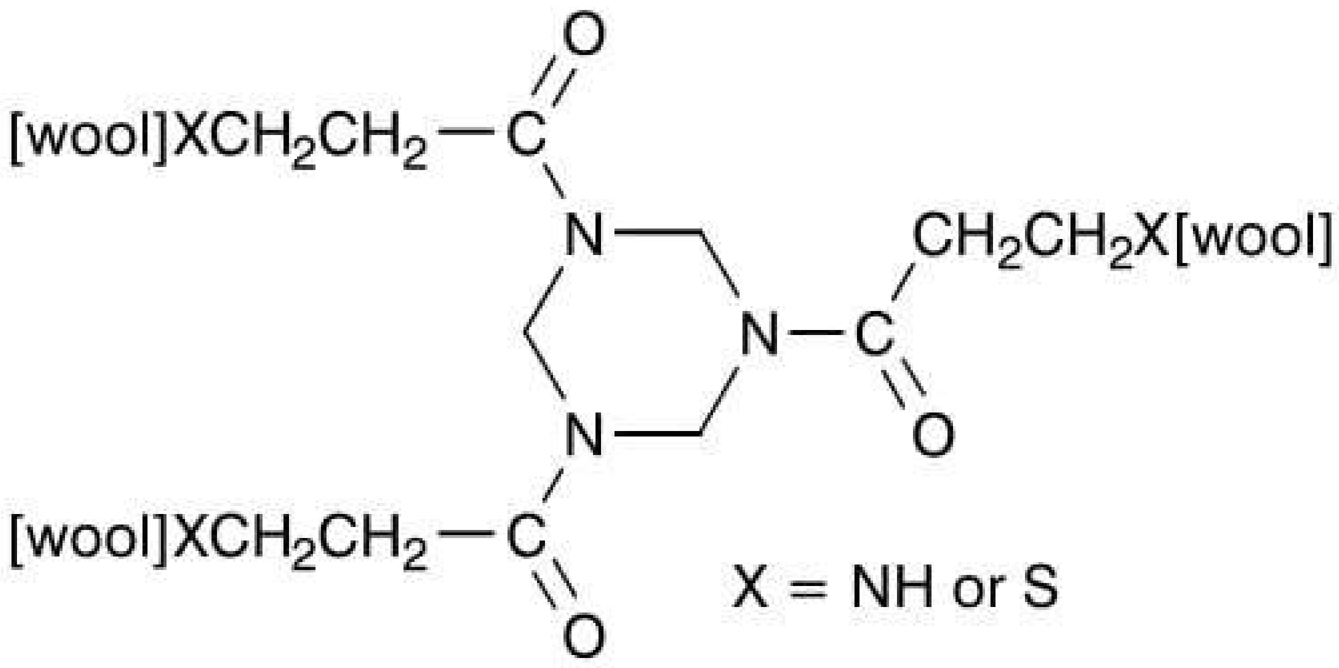
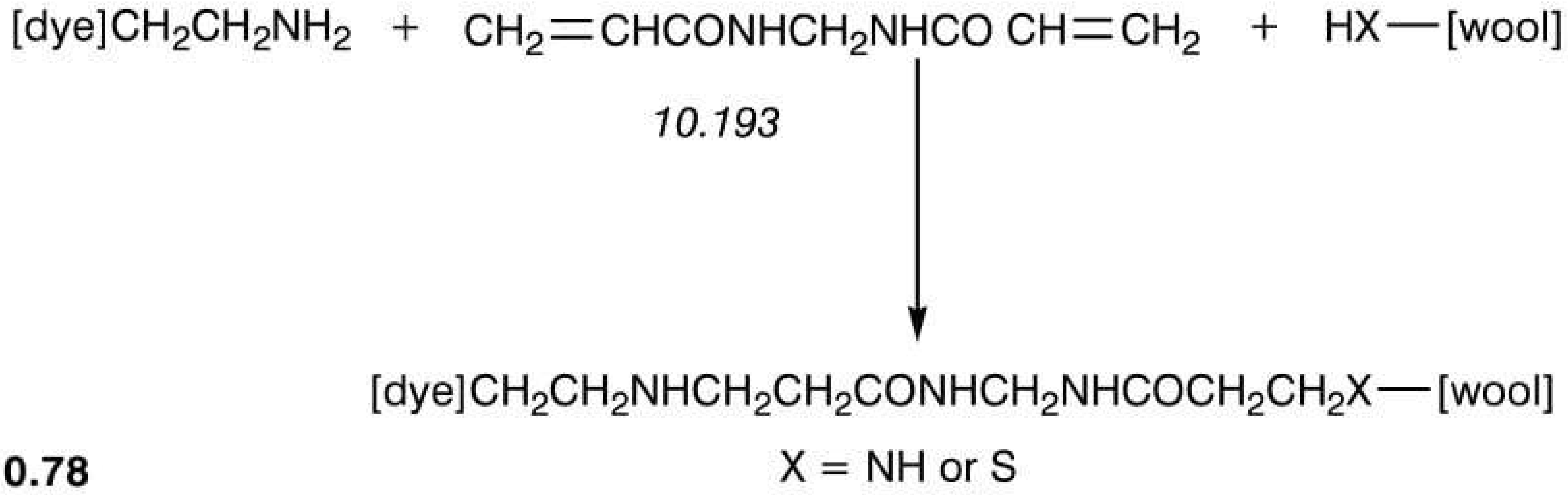


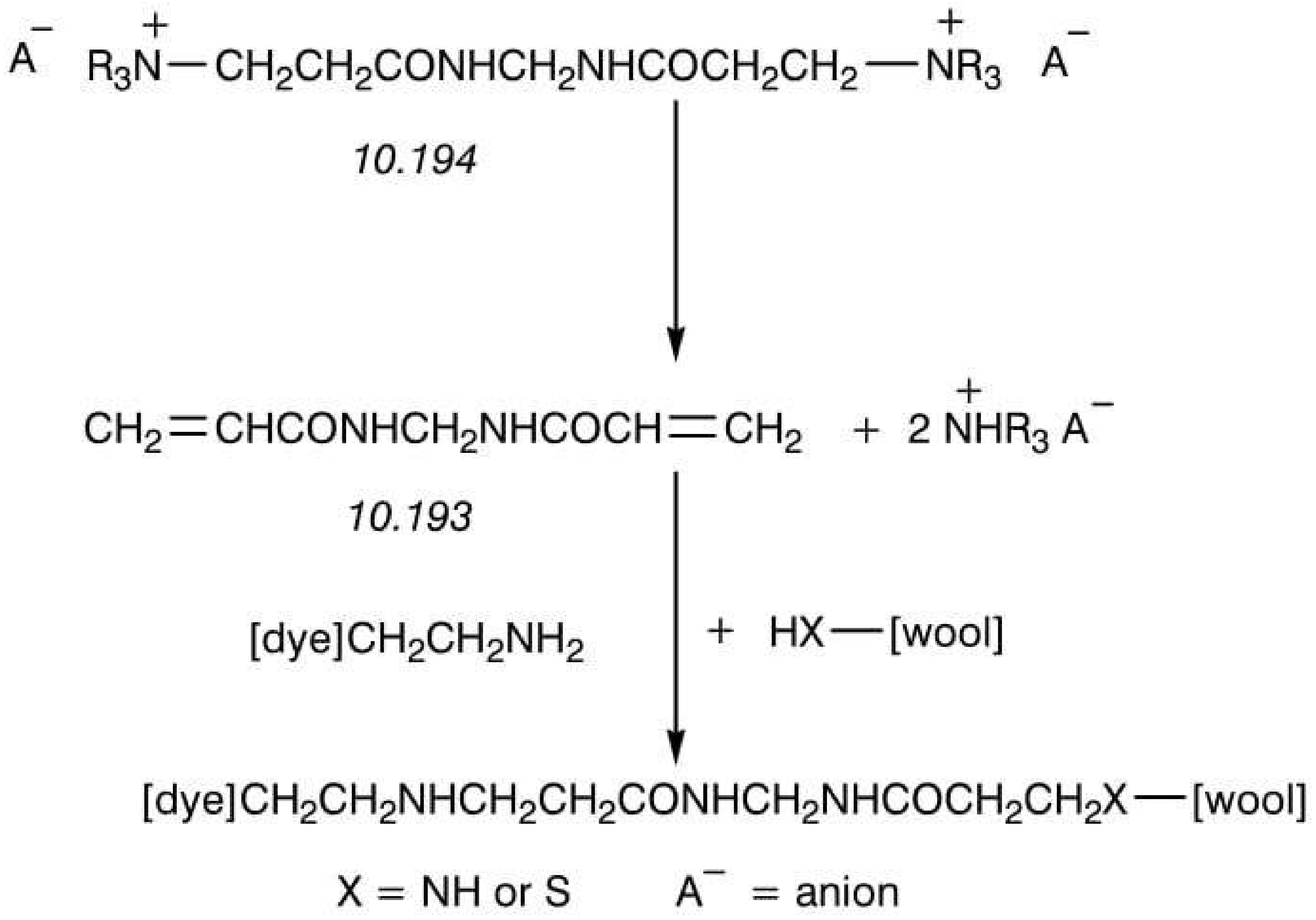
10.192

Subsequently, two more cost-effective bifunctional crosslinking agents, both commercially available, were used to give the same quality of dyeings [438], these being *N*,*N*′-methylene-bis-acrylamide (10.193) and a quaternised precursor (10.194). Idealised reactions with functional groups in the dye and in wool are given in Schemes 10.78 and 10.79. Although these bifunctional reagents are cheaper than the trifunctional product, dyeing has to be carried out at pH 8 as their reactivities are lower than that of tris(acryloyl)hexahydro-*s*-triazine. However, this lower reactivity allows the bis-acrylamide to be added at the beginning of the dyeing process. The quaternised derivative is a more effective crosslinking agent, possibly because of its greater substantivity for wool under slightly alkaline dyeing conditions, but it cannot be added at the beginning of dyeing because of its cationic character.

There has been active interest in exploring the potential of reactive triazines as dye-resist agents for wool. A model structure for reactive dye-resist agents (10.195) has been proposed [439], where Z is a suitable high-reactivity group, NH is a bridging group, Ar is an aryl group and $[SO_3]^-$ is a solubilising and anionic dye-repelling group. Four dichlorotriazine compounds (10.196–10.199) based on this model structure were found to be effective as



Scheme 10.78

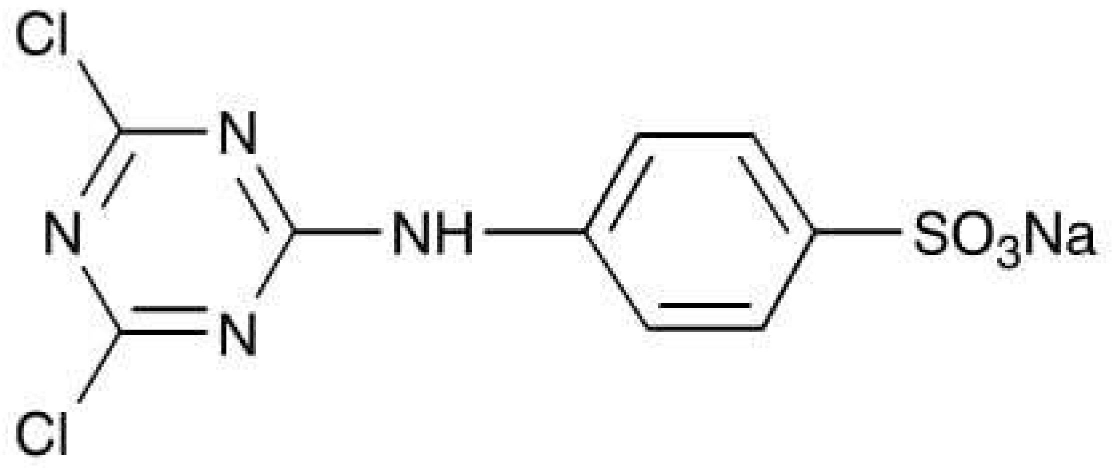


Scheme 10.79

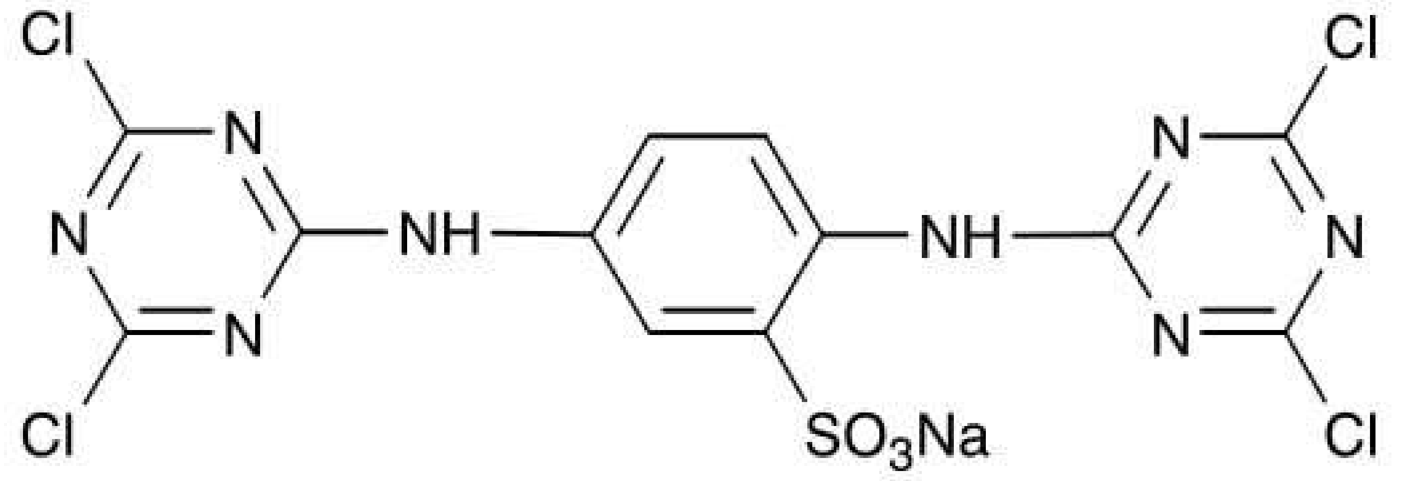
dye-resist agents, although full white resist effects were difficult to achieve [439]. Pursuing this line of research further, several more complex naphthylamine-based dichlorotriazine dye-resist agents (10.200–10.206) were evaluated [440]. These agents each contained at least one dichlorotriazine reactive moiety as well as a sulphonated naphthylamine system that enabled the anionicity of the product to be varied. Using the trisulphonated dye CI Acid Red 27 (10.207), the resist efficiency improved significantly with increasing degree of sulphonation of the agent and with increasing relative molecular mass, enabling lower concentrations of the more effective agents to be used. The upper limit of resist achieved was 98.6%.

$Z{-}NH{-}Ar{-}[SO_3^-]_n$

10.195



10.196



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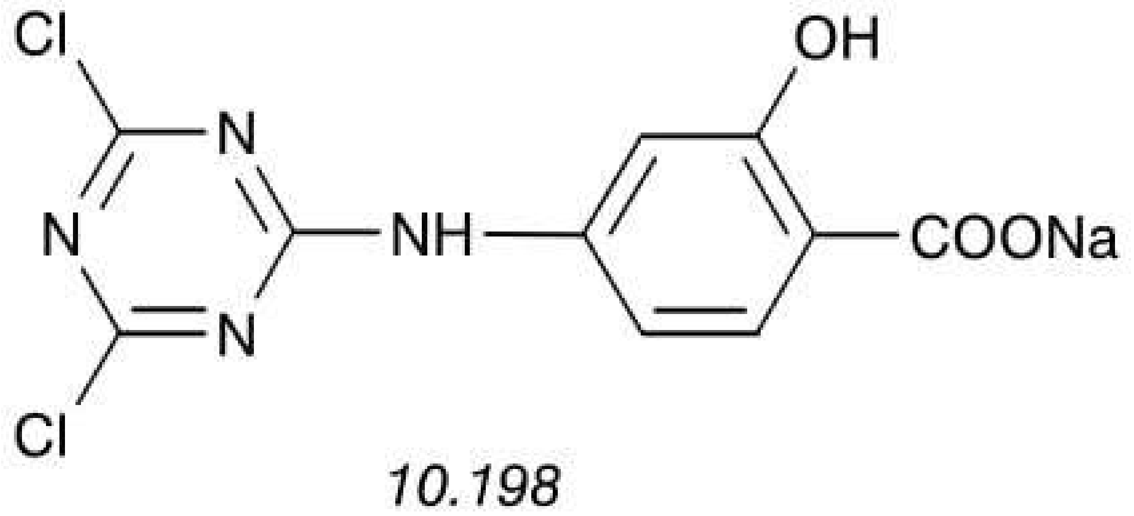

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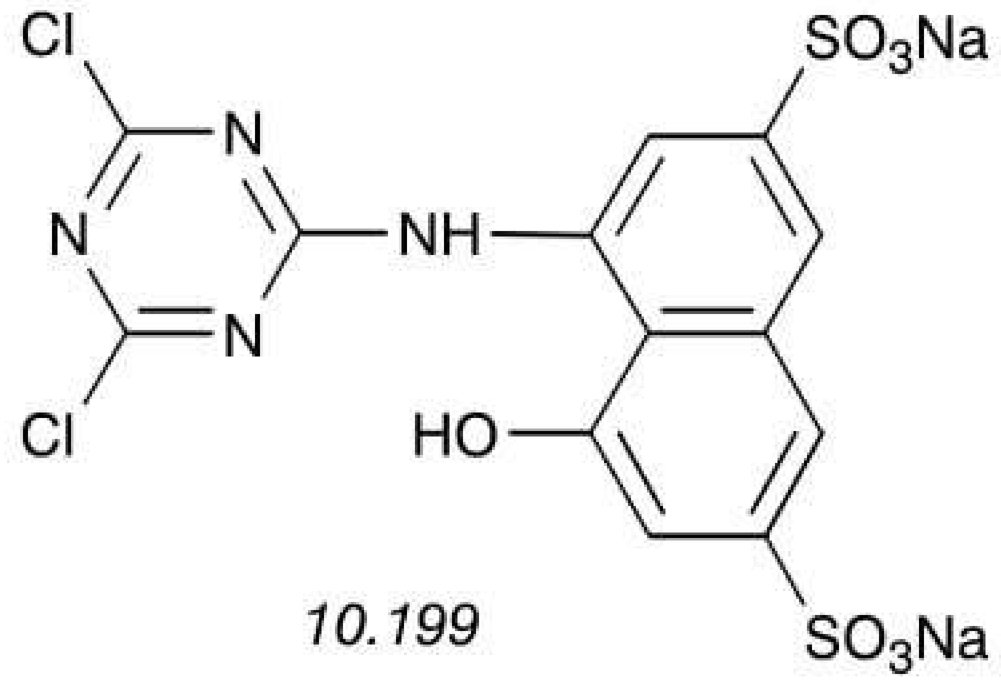

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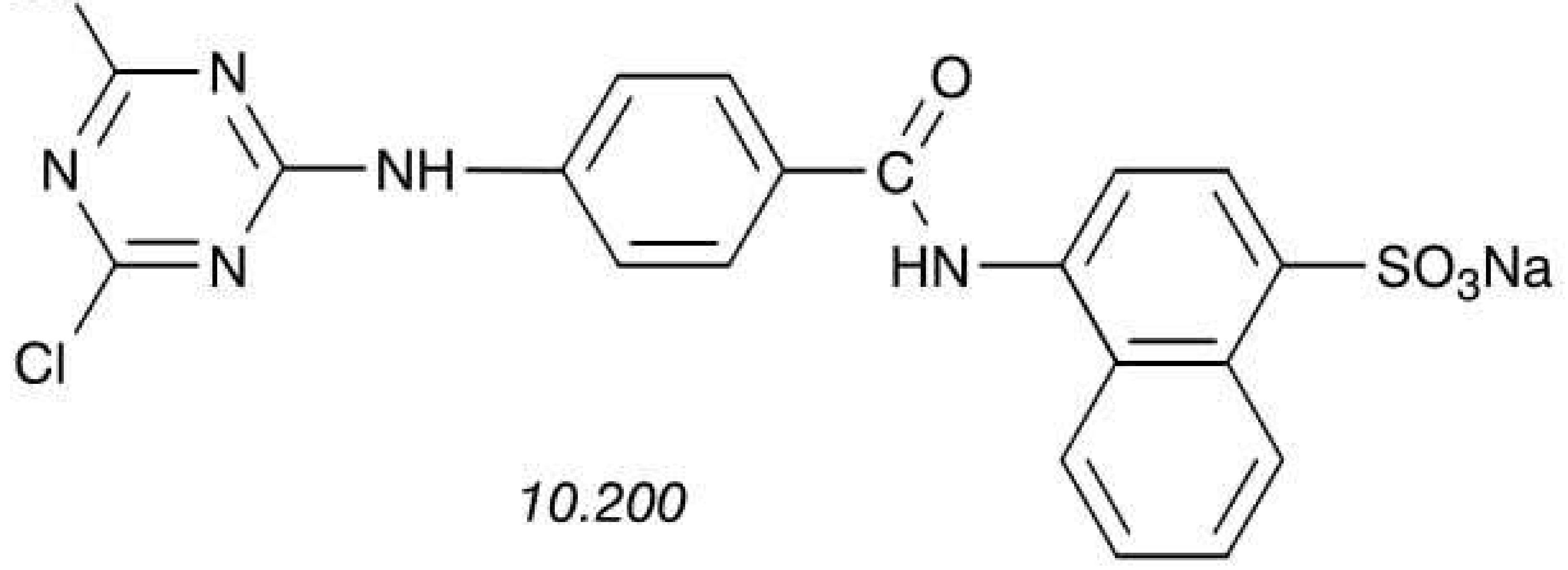
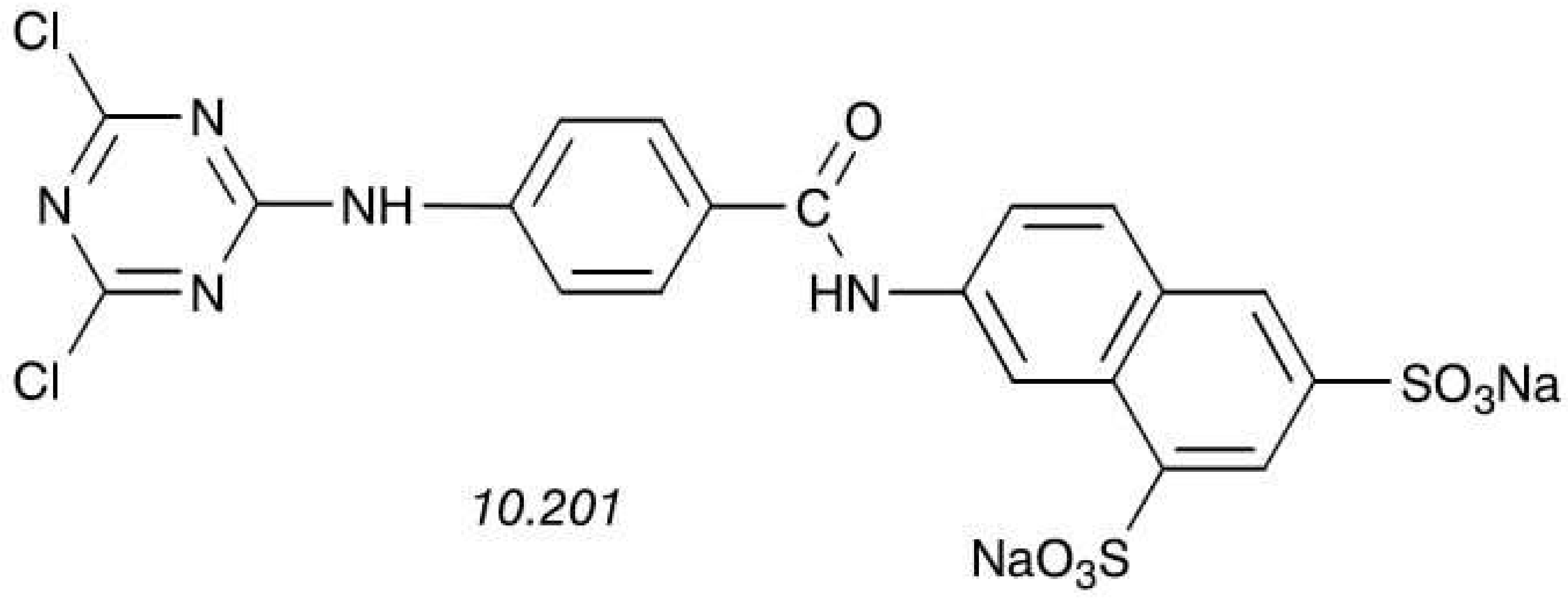


10.200



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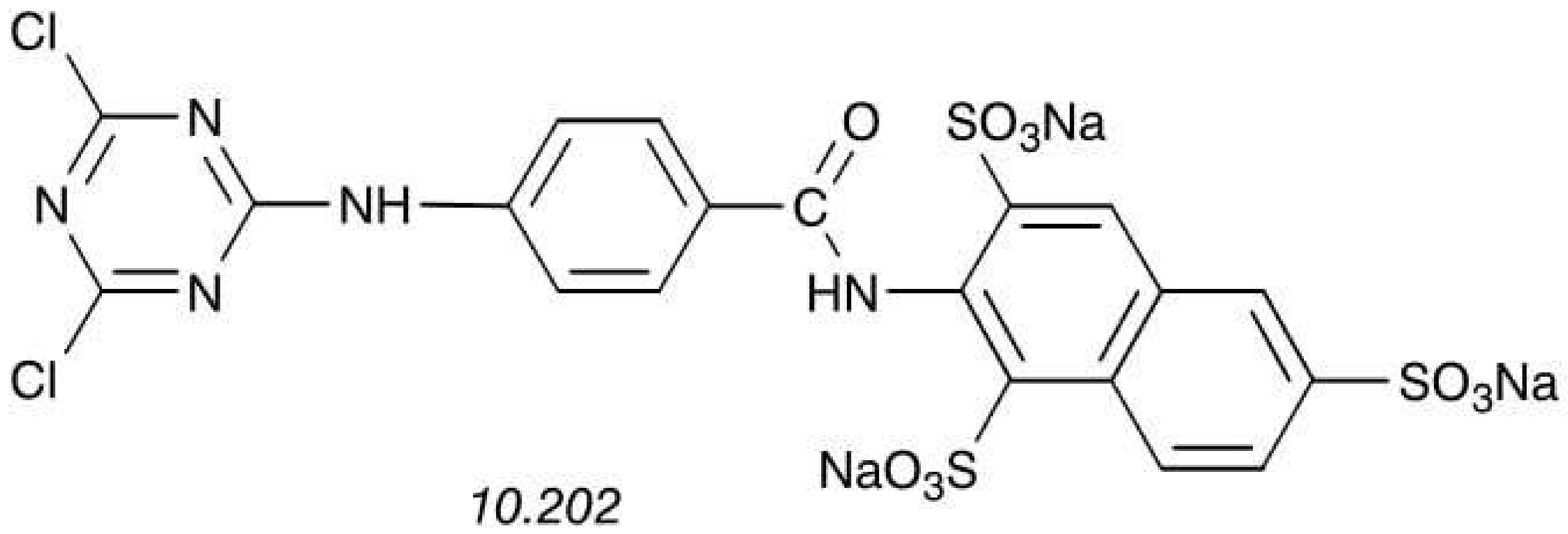

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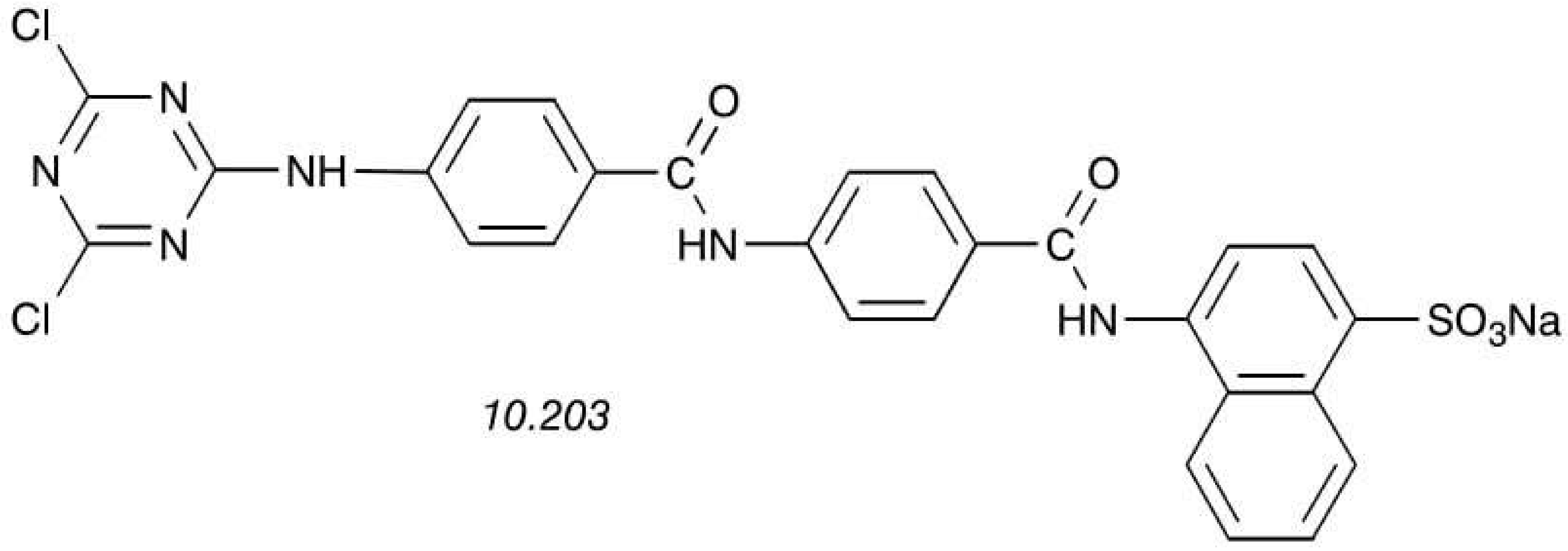

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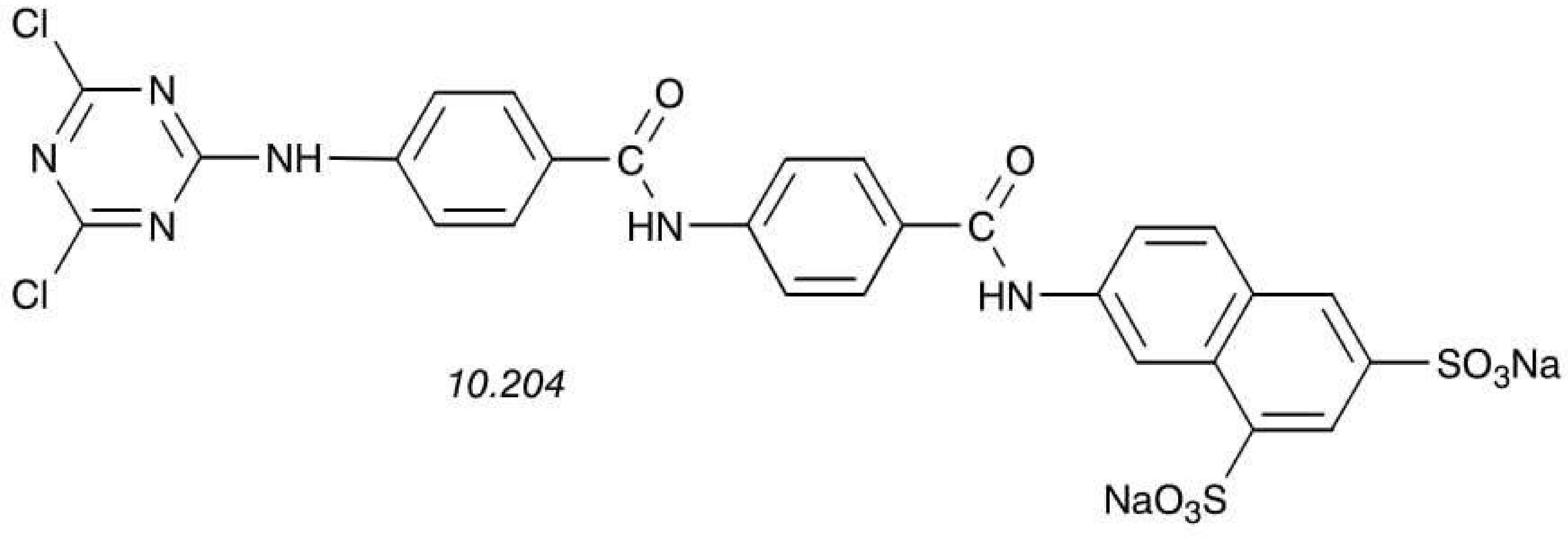

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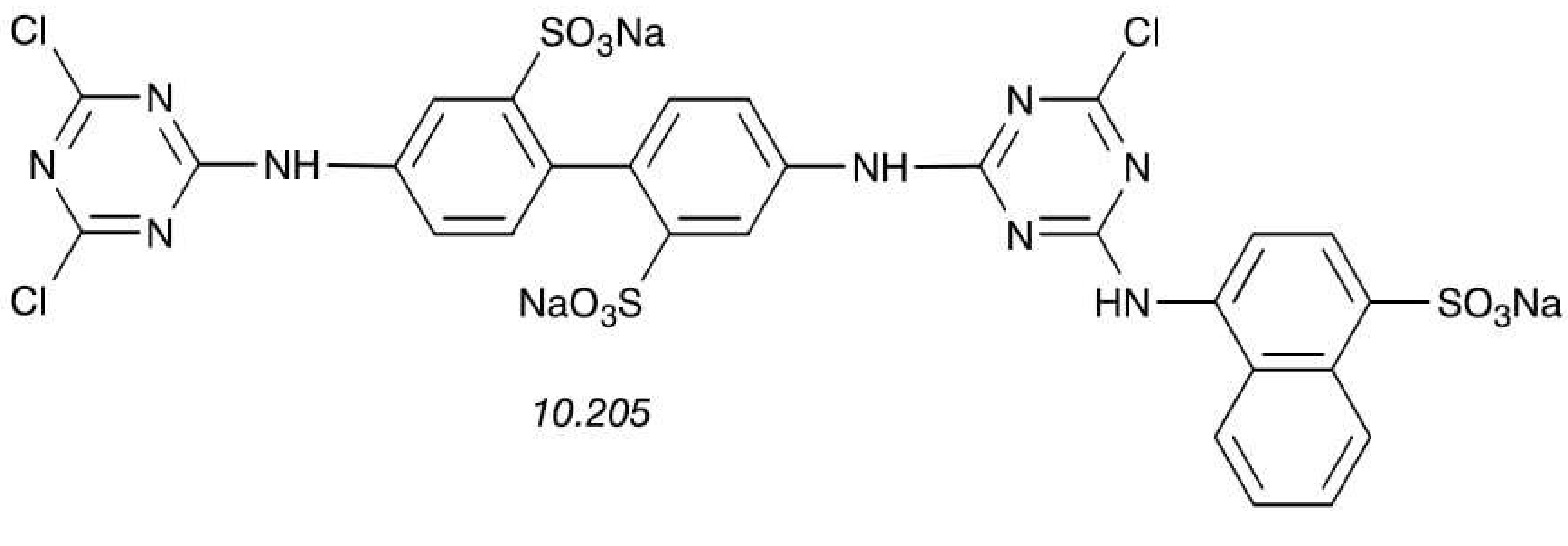

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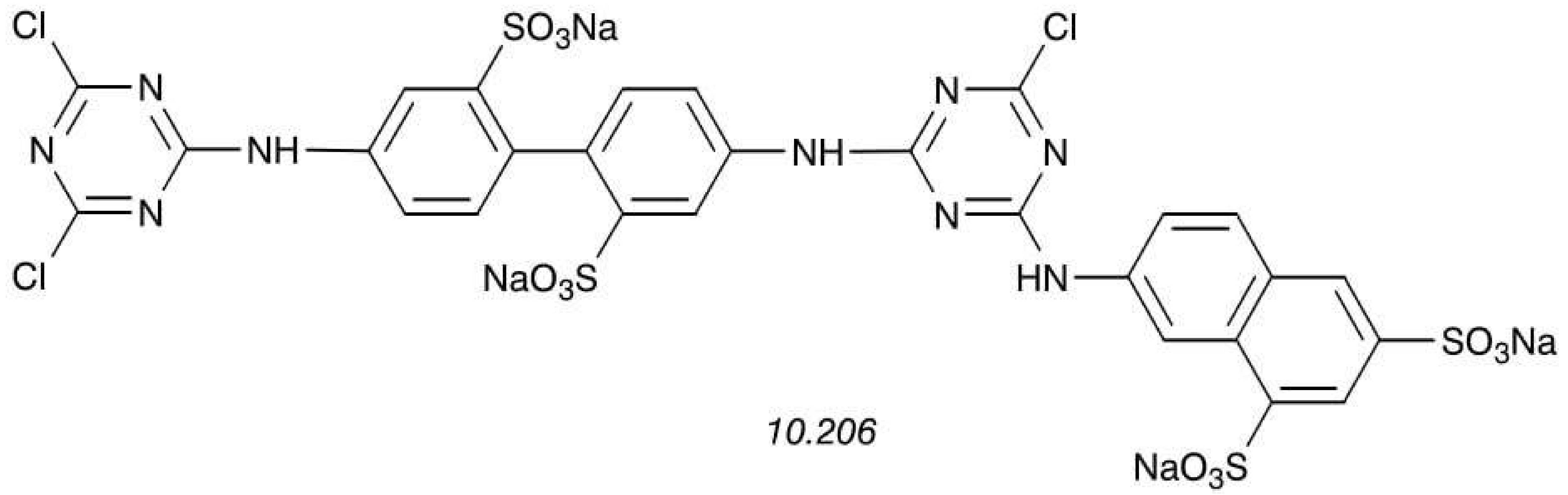

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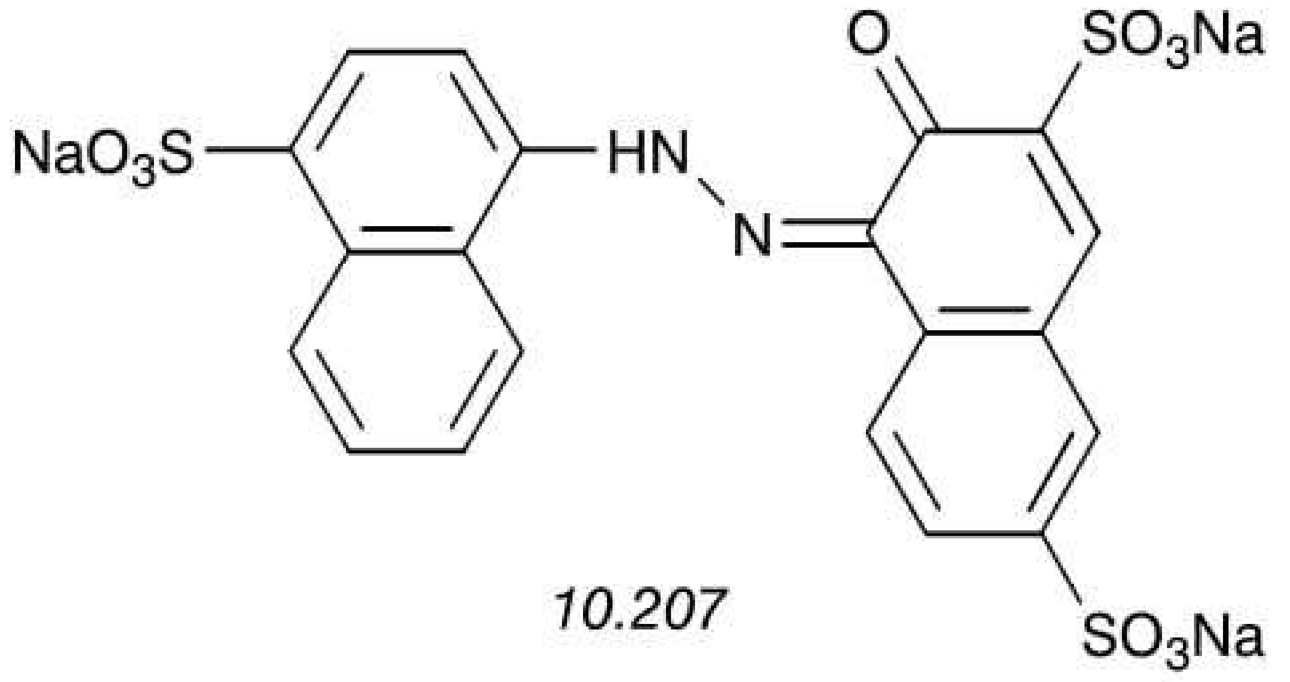


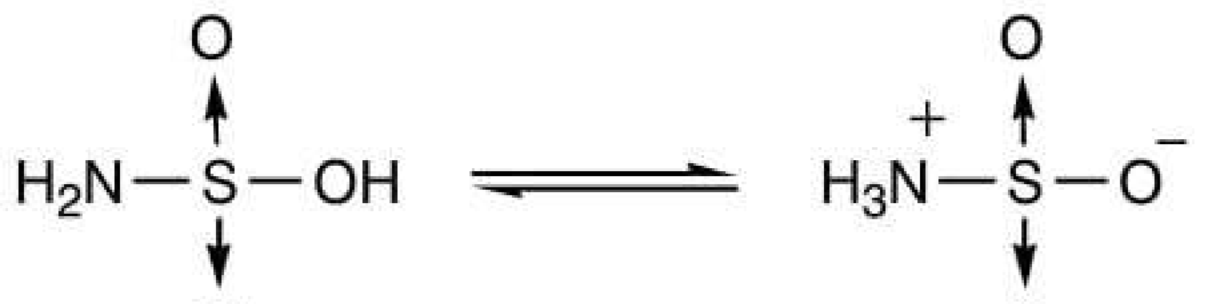
10.207

CI Acid Red 27

A rather different approach [441] to obtaining resist effects on wool involved evaluation of the relatively simple compound sulphamic acid (10.208). From a comparison of curing temperatures over the range 100–150 °C, it was found that only by curing at 140 °C or higher was the sulphamic acid bound sufficiently to resist desorption during dyeing. There are several possible routes of decomposition of sulphamic acid [441], leading to the formation of various sulphonic acids and sulphonamides, as well as the possibility of scission to form sulphur trioxide and ammonia (Scheme 10.80). The reactions of sulphamic acid with wool are mainly through hydroxy groups and to a much lesser extent amino groups in the fibre (Scheme 10.81). Thus the dye-resist effect is provided by the presence on the modified fibre of anionic sulphate and sulphamate groups [442]. This approach was also examined on silk [443]. Compared with wool, silk has a much smaller proportion of nucleophilic amino groups but a substantial content of hydroxy groups with which sulphamic acid reacts preferentially. Excellent dye-resist effects were obtained with acid, 1:2 metal-complex and reactive dyes, better than when a commercial dichlorotriazine reactant (similar to 10.196) was used.

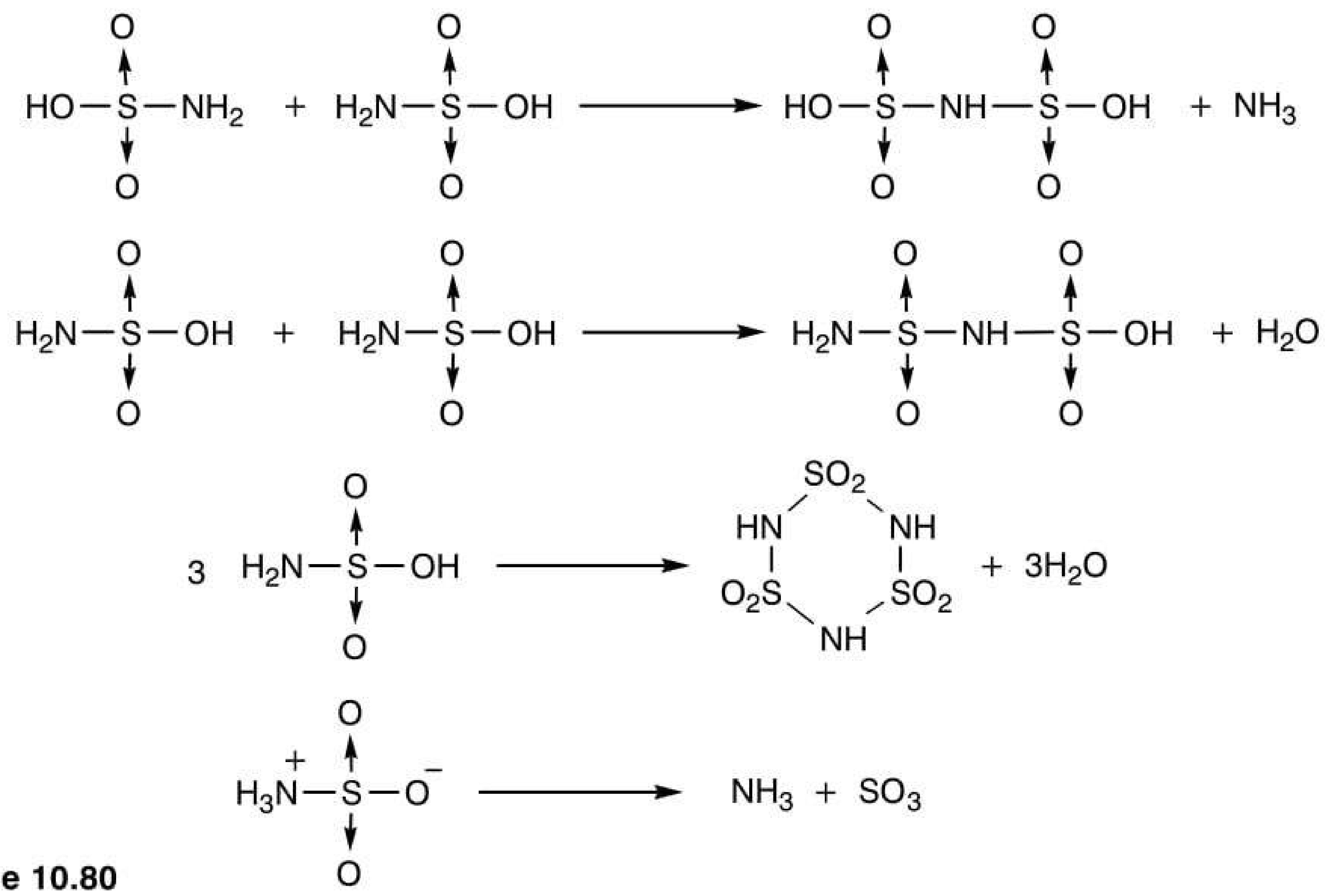
10.9.5 Aftertreatments for direct and reactive dyes on cellulosic fibres

The fact that the aftertreatment of direct dyes has a long history is not surprising since wet fastness within this class is not particularly good. Their prime advantages are ease of application and economy compared with dyes of higher fastness (reactive, sulphur or vat) – hence the continued search for highly effective aftertreatments that improve wet fastness

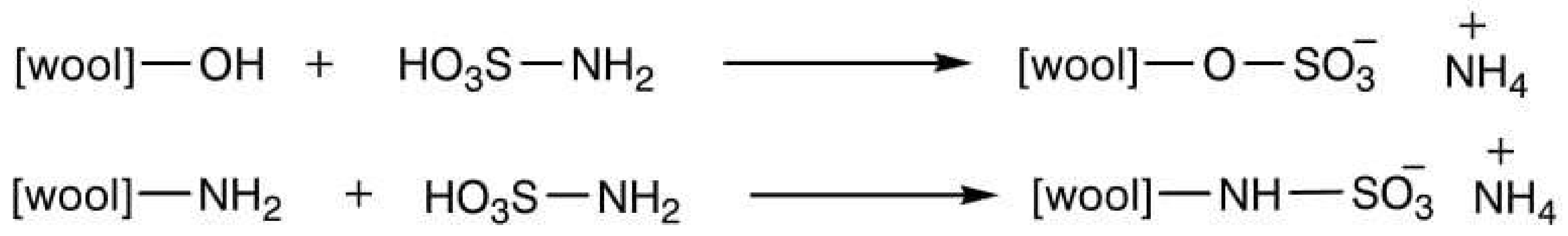


$$\mathrm{H_2N{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}{-}OH \rightleftharpoons \overset{+}{H_3N}{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}{-}O^{-}}$$

10.208



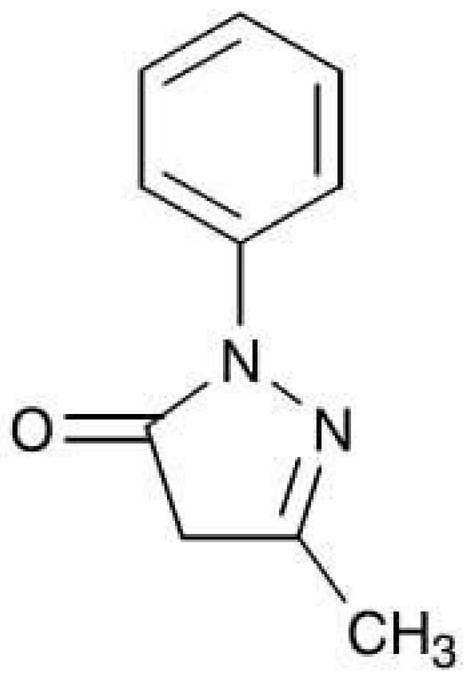
Scheme 10.80



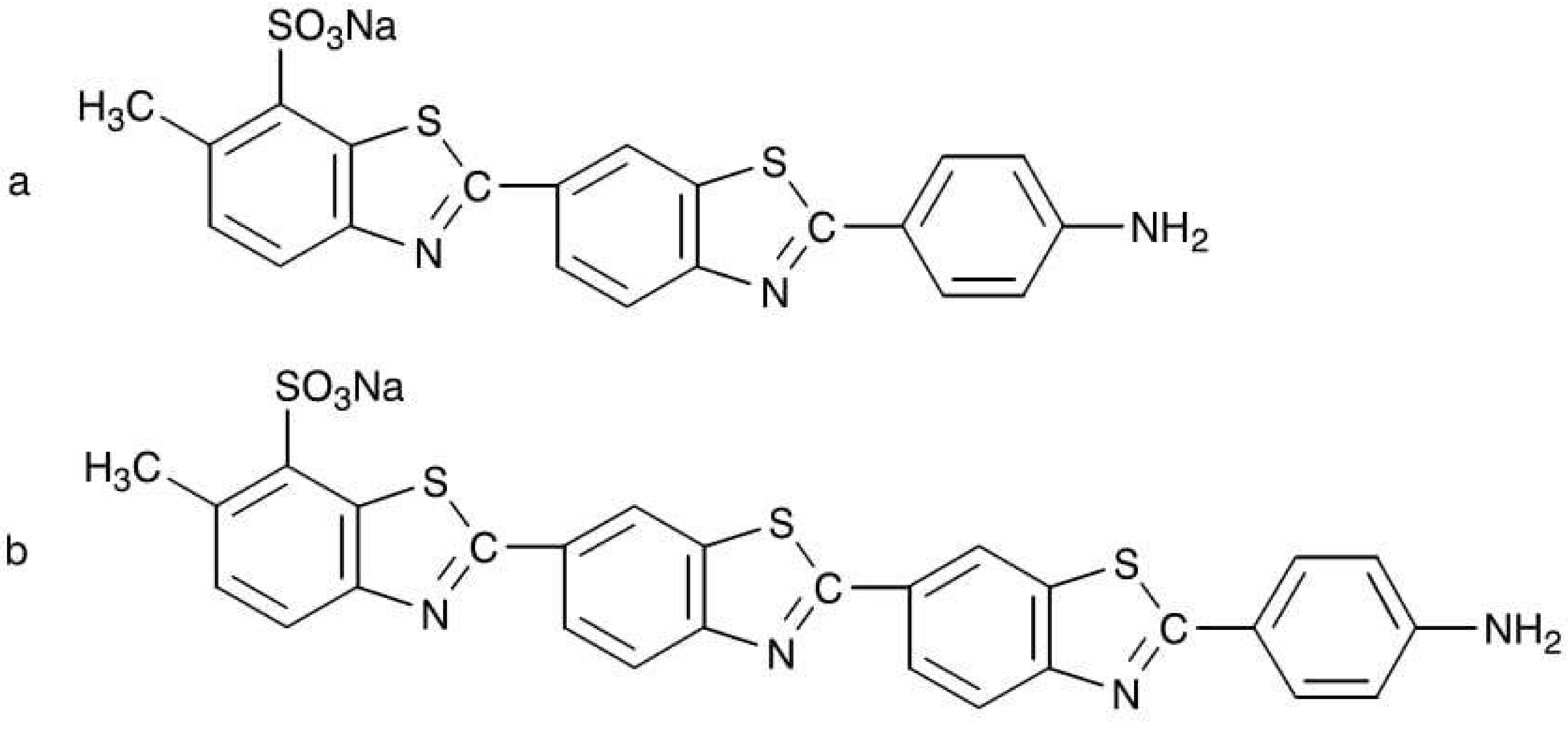
Scheme 10.81

without excessive additional cost. Some of the aftertreatments used for this purpose have also been applied to reactive dyes, as will be described later.

One of the earliest aftertreatment processes employed diazotisation of free amino groups in the adsorbed dye, followed by coupling (development) with a suitable component such as a phenol, naphthol or amine; 2-naphthol, *m*-phenylenediamine, resorcinol and 1-phenyl-3-methylpyrazol-5-one (10.209) were particularly popular. Obviously, this was only possible with dyes containing a diazotisable amino group, an example being CI Direct Yellow 59, the classic primuline (a mixture of structures 10.210a and b), which was converted on the fibre from a greenish yellow to a bluish red by diazotisation and development with 2-naphthol. The reverse approach, application of a dye containing a phenolic group and aftertreatment with a solution of a diazotised amine, such as *p*-nitrobenzenediazonium chloride, was also used.

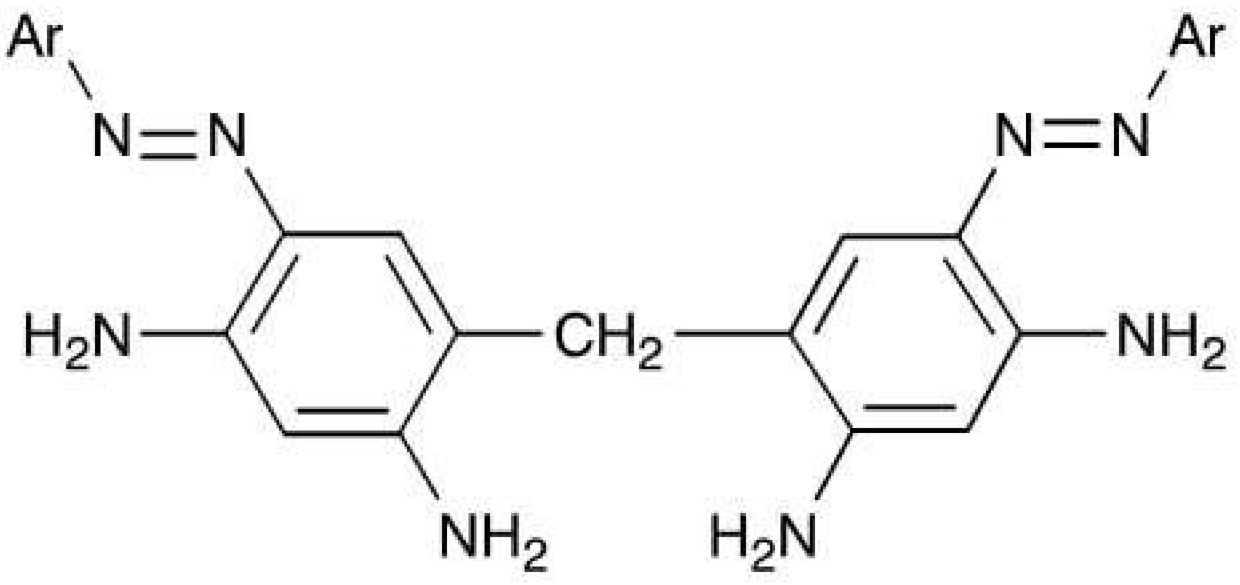


10.209



10.210

Formaldehyde aftertreatment was employed to link together pairs of amino-substituted dye molecules by a methylene bridge (10.211). The required reactivity of the sites in the dye towards formaldehyde was ensured by pairs of *o*- and *p*-directing electron-donating groups provided by resorcinol, *m*-phenylenediamine or 3-aminophenol.



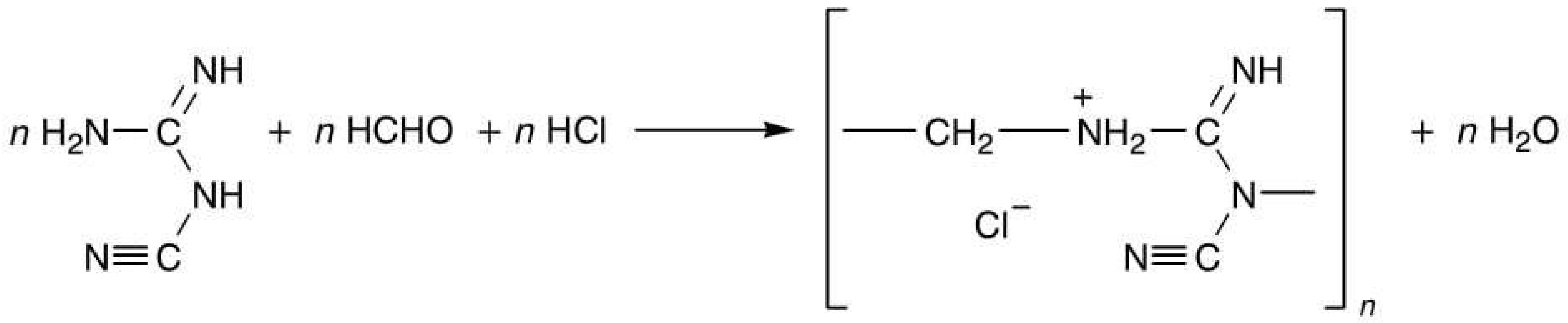
10.211

A third approach utilised copper salts, especially copper(II) sulphate, in conjunction with dyes containing chelatable groupings such as salicylic acid or o,o′-dihydroxyazo moieties. Indeed, special ranges of ‘copperable’ direct dyes, for which the treatment with copper(II) sulphate was really part of the dyeing process rather than an optional aftertreatment, were introduced. In the past the main use of this chelation treatment was to enhance light fastness, but it is little used for this purpose nowadays.

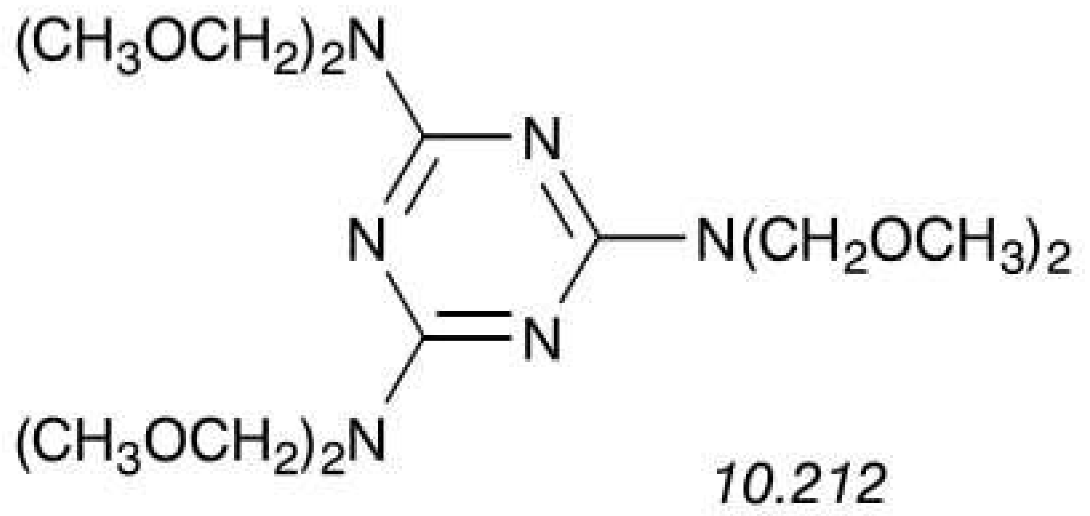
Since direct dyes have anionic structures, many cationic surfactants such as quaternary ammonium compounds were used as aftertreatments to form surfactant–dye complexes of reduced aqueous solubility and therefore higher wet fastness. The improved fastness related only to non-detergent agencies such as perspiration and water, however. In soap-based washing processes the stronger interaction between the anionic soap and the cationic agent tended to cleave the dye–cation complex, thus effectively negating the aftertreatment even after a single mild wash. The aftertreatment often brought about changes in hue and reduced light fastness, although the latter could sometimes be countered by a combined or subsequent treatment with a metal salt such as copper(II) sulphate, as described in the preceding paragraph.

All the aftertreatment processes so far described have declined considerably in commercial significance and are now rarely carried out. Nevertheless, their common principle of creating on the fibre a dye–agent complex of larger size, reduced solubility and a correspondingly lower rate of desorption has survived in today's use of resin-type fixing agents. The principle of cationic aftertreatment, in particular, has seen noteworthy development.

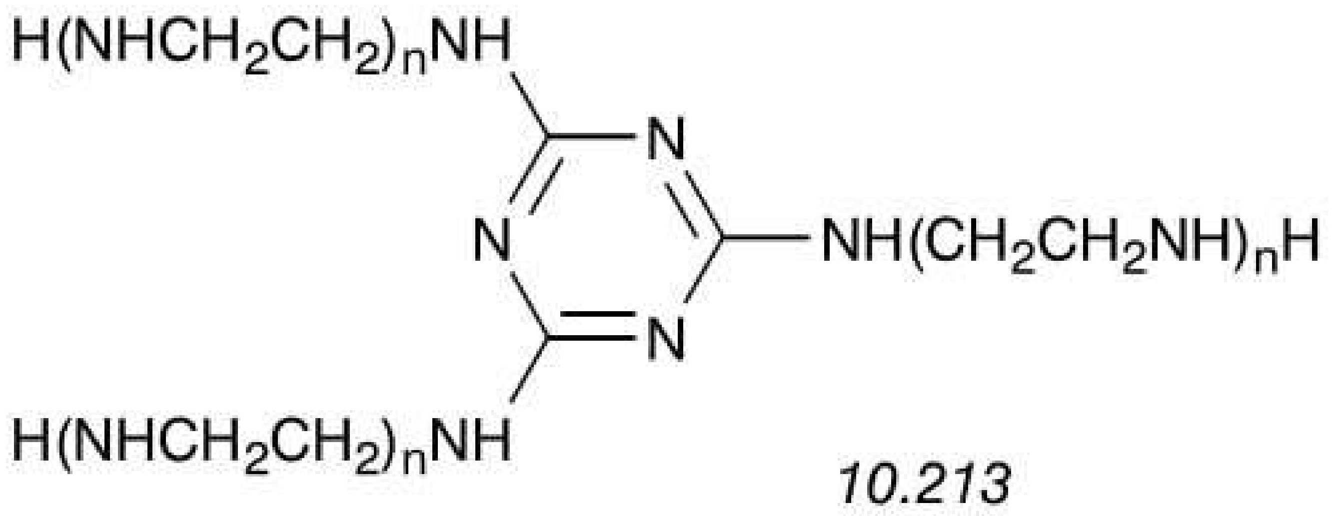
The earliest polymeric cationic aftertreatments stemmed from the development of crease-resist finishes for cellulosic fibres. One such, promoted specifically for its colour fastness improvements when applied as an aftertreatment to direct dyeings, was a condensation product of formaldehyde with dicyandiamide (Scheme 10.82). Many similar compounds followed, such as condensation products of formaldehyde with melamine (10.212), poly(ethylene imine) with cyanuric chloride (10.213) and alkyl chlorides with poly(ethylene imine) (10.214; R = alkyl).



Scheme 10.82



10.212



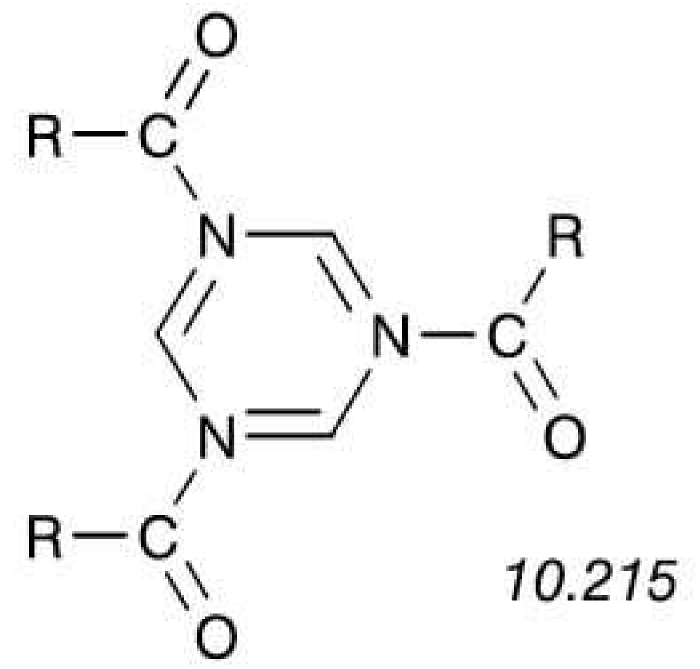
10.213

$RNH(CH_2CH_2NH)_nCH_2CH_2\overset{+}{N}H_3\ Cl^-$

10.214

These condensates were an improvement on the simpler cationic surfactants mentioned earlier. Their interaction still relies on electrostatic bonding between agent cation and dye anion; hence the major weakness remains fastness to washing with anionic detergents. This limitation of conventional cationic agents has been overcome by the development of bi-, tri- and tetra-functional agents which carry reactive groups capable of forming covalent bonds by reaction with other suitable groups in the dye and/or the hydroxy groups in the cellulosic fibre. Studies on the functionality and reactivity of various multifunctional crosslinking agents [442] led to the selection of 1,3,5-tris(acyl)hexahydro-*s*-triazines (10.215) as being particularly effective, their efficiency arising from the lability of the chloro substituents and the strongly polarising effect of the carbonyl groups.

The tris(acryloyl) derivative (R is $CH{=}CH_2$) was subsequently developed as a fixing agent for use with the Basazol(BASF) dyes in the printing of cellulosic fibres, in conjunction with urea as hydrotrope [444]. It has also been shown [445] that aftertreatment with 1,3,5-tris(acryloyl)hexahydro-*s*-triazine or the tris (β-chloropropionyl) derivative improves the wet



10.215

R = —CH=CH$_2$ —C(Cl)=CH$_2$ —CH(Cl)—CH$_2$Cl or —CH$_2$CH$_2$Cl

fastness of direct dyes, providing the dyes contain suitable nucleophilic groups. The same compounds have useful properties with reactive dyes (other than the Basazols) in giving increased colour yield through fixation of hydrolysed dye, an aspect discussed in more detail below.

The basic mechanism of action of multifunctional fixing agents has been well described [446] (Figures 10.54 and 10.55). However, the multifunctional products are no better than monofunctional types when used with conventional direct dyes that do not contain suitable nucleophilic groups through which to link the fixing agent. Direct dyes suitable for forming additional bonds have been termed reactant-fixable dyes and are mostly of the copper-complex type. Thus brightness of shade is limited.

A range of bifunctional, trifunctional and tetrafunctional fixing agents was developed [446,447] for use with a selected range of copper-complex (Indosol) dyes. The bifunctional type, which reacts only with the dye, was applied in a fresh bath at about 60 °C and gave fastness to washing at 50 °C through the formation of an extensive dye–agent complex within the fibre. The trifunctional type additionally forms covalent bonds with cellulose and is applied at 40 °C for about 15 minutes, followed by addition of alkali to bring about reaction; this confers a higher degree of fastness to washing at 60 °C even with deep shades.

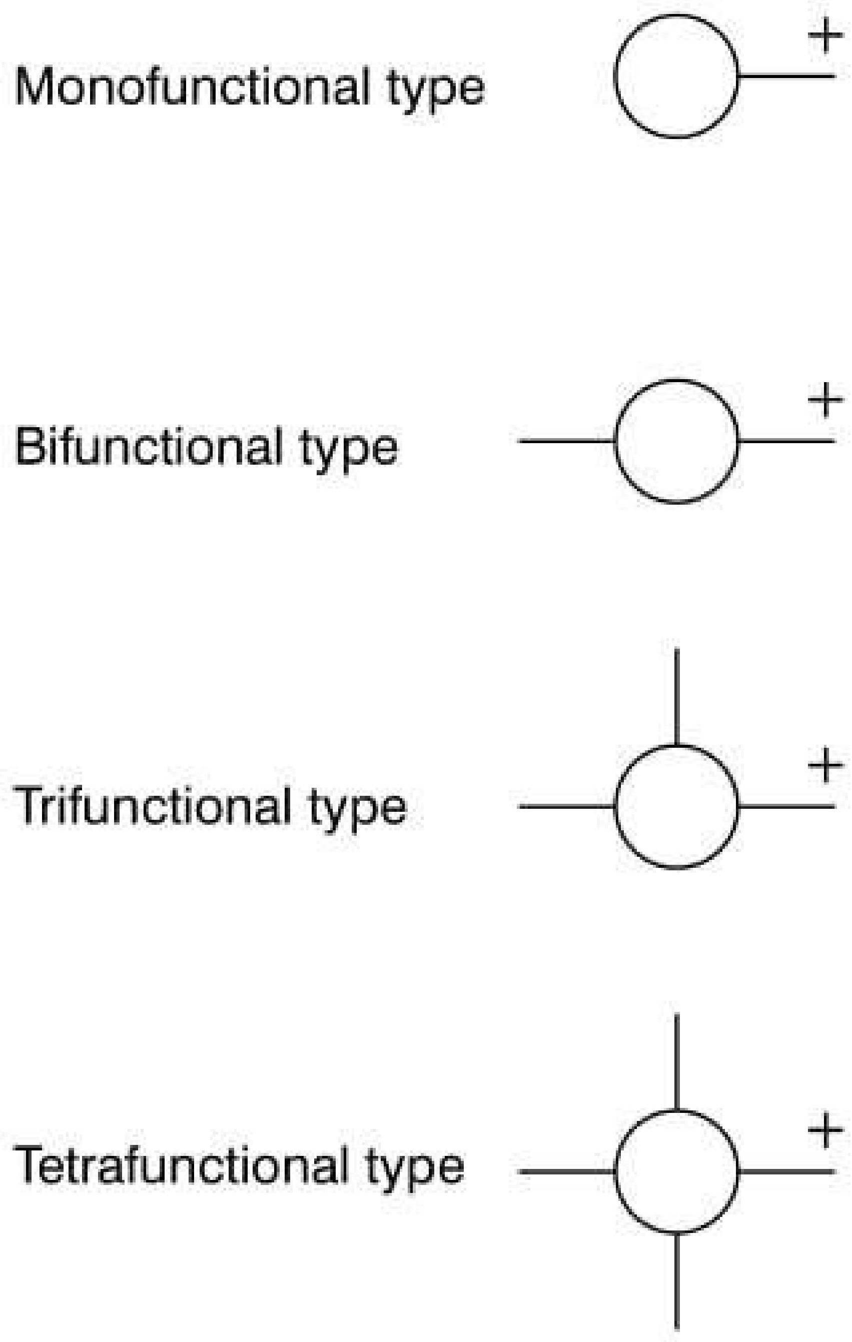


Figure 10.54 Fixing agents showing various degress of functionality [446]

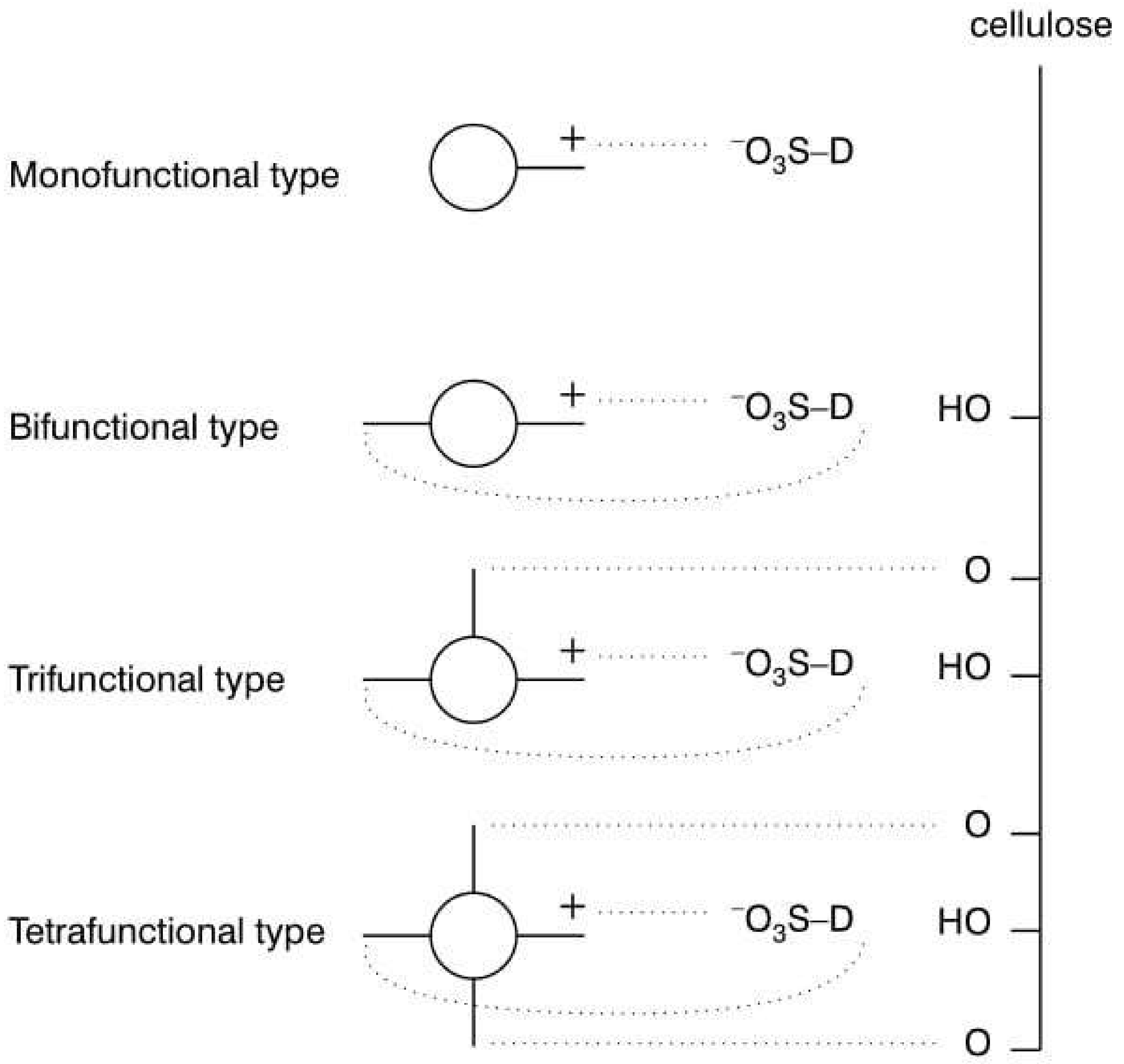


Figure 10.55 Modes of reaction of the various fixing agents [446]

Tetrafunctional reactant resins confer the highest fastness, even to washing at the boil. Typical polymers are made by the reaction of an amine such as diethylenetriamine with cyanamide, dicyandiamide (especially), guanidine or biguanide. A cationic polymer of this type is applied with an *N*-methylol reactant such as dimethyloldihydroxyethyleneurea and an acid-liberating catalyst such as magnesium chloride to give a commercial product sold as a cationic reactant resin. This formulation is applied to the dyeing by padding, at which stage a dye–agent complex is believed to be formed. The fabric is then treated at 175–180 °C, resulting in covalent reaction between the cationic agent and the *N*-methylol groups as well as crosslinking of cellulose chains by the *N*-methylol reactant, conferring not only excellent wet fastness but also improved crease resistance and good dimensional stability.

The multifunctional agents offer an alternative aftertreatment for reactive dyeings [446], if problems arise from the presence on the fibre of unfixed hydrolysed dye, normally removed by 'soaping'. This process is invariably lengthy, expensive and not always fully effective. Multifunctional cationic reactants will react with unfixed (still reactive) dye and with hydrolysed (hydroxy-containing) dye. Tri- and tetra-functional reactants will further fix them by covalent bonding to the fibre. Improved wet fastness can also ensue when tetrafunctional products are used, including considerably improved resistance to hydrolysis of the dye–fibre bond and better fastness to treatments involving chlorine or perborates. Deleterious effects on hue and light fastness still have to be carefully considered in the selection of dyes for aftertreatment, however.

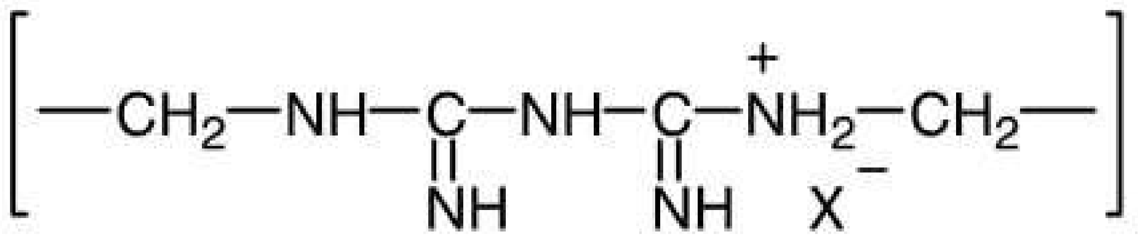
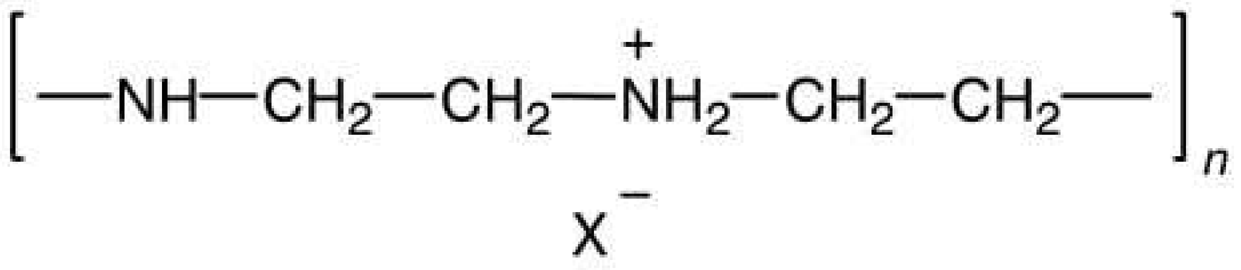
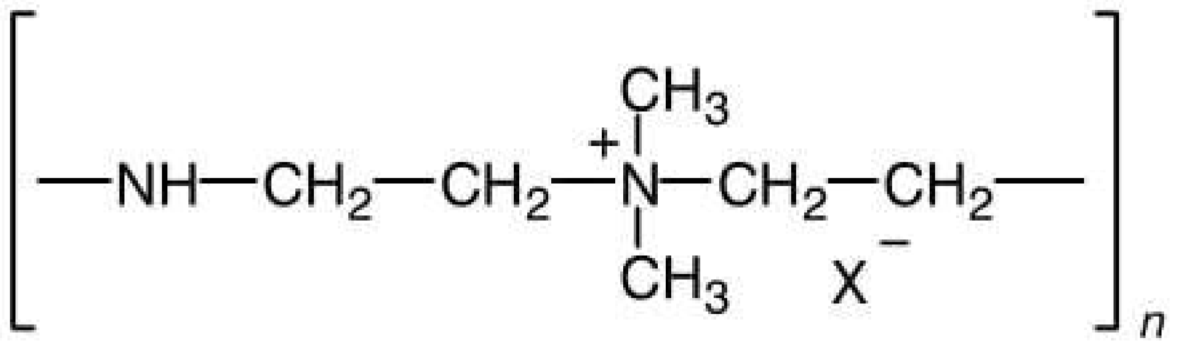
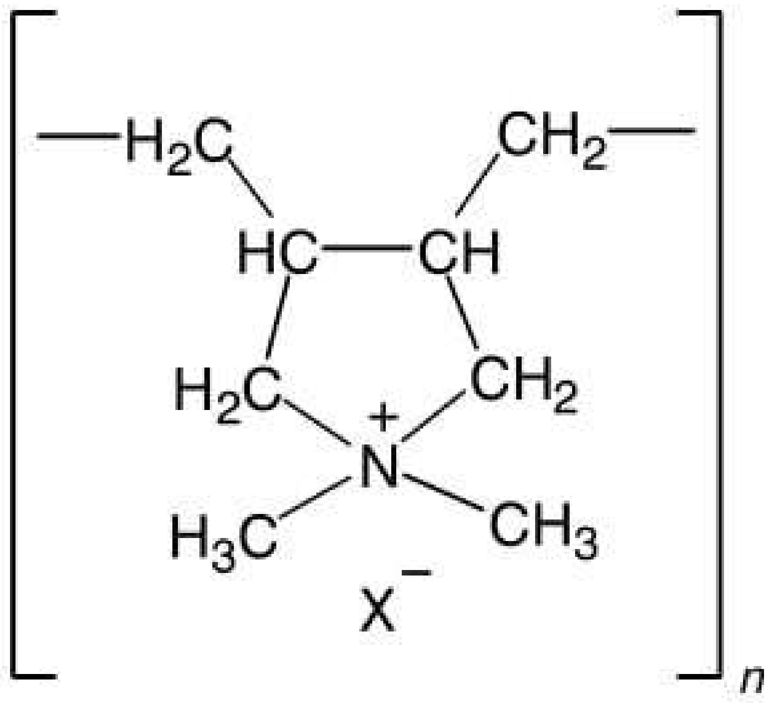
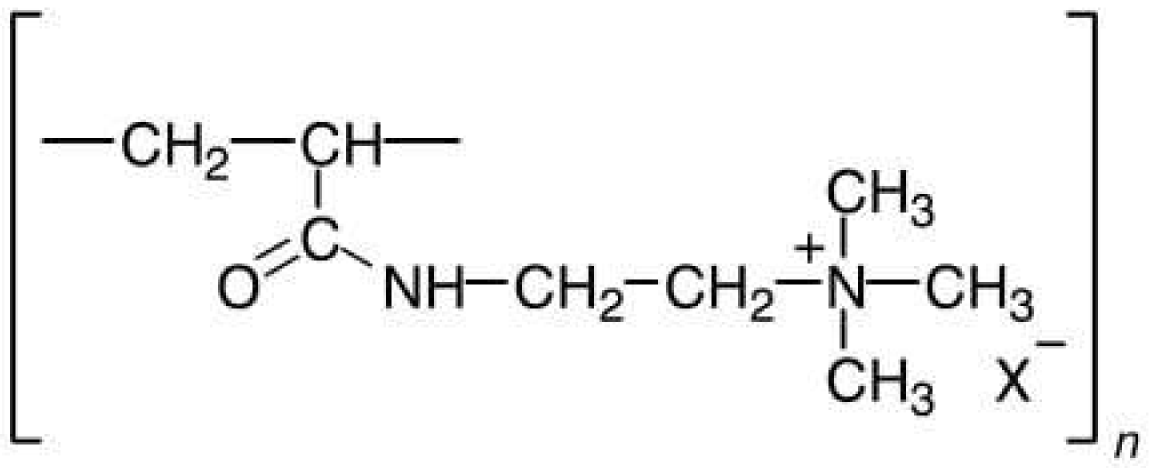
Most of the polymeric cationic products available [448] are based on the types described in Table 10.44. The ideal aftertreating agent must fulfil many requirements [448]. There is a high demand for:

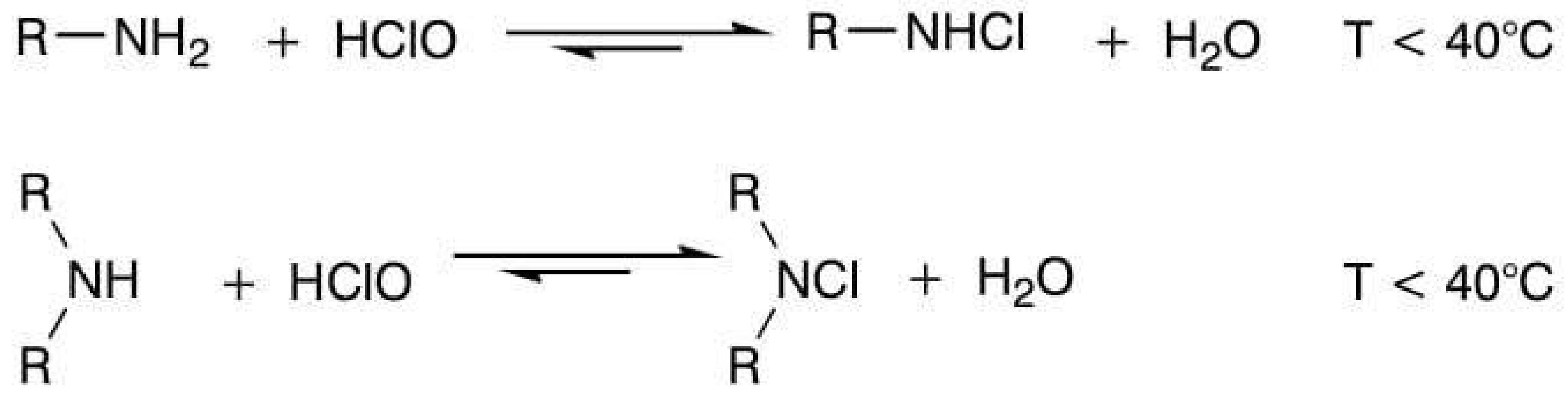
- improved fastness to washing and other wet treatments
- low price

- applicability by exhaustion
- applicability with various dye classes and on various fibres and blends
- stability to electrolytes
- capability to minimise migration of hydrolysed reactive dyes
- stripping and overdyeing performance
- ease of cleaning of stained machinery
- biological elimination.

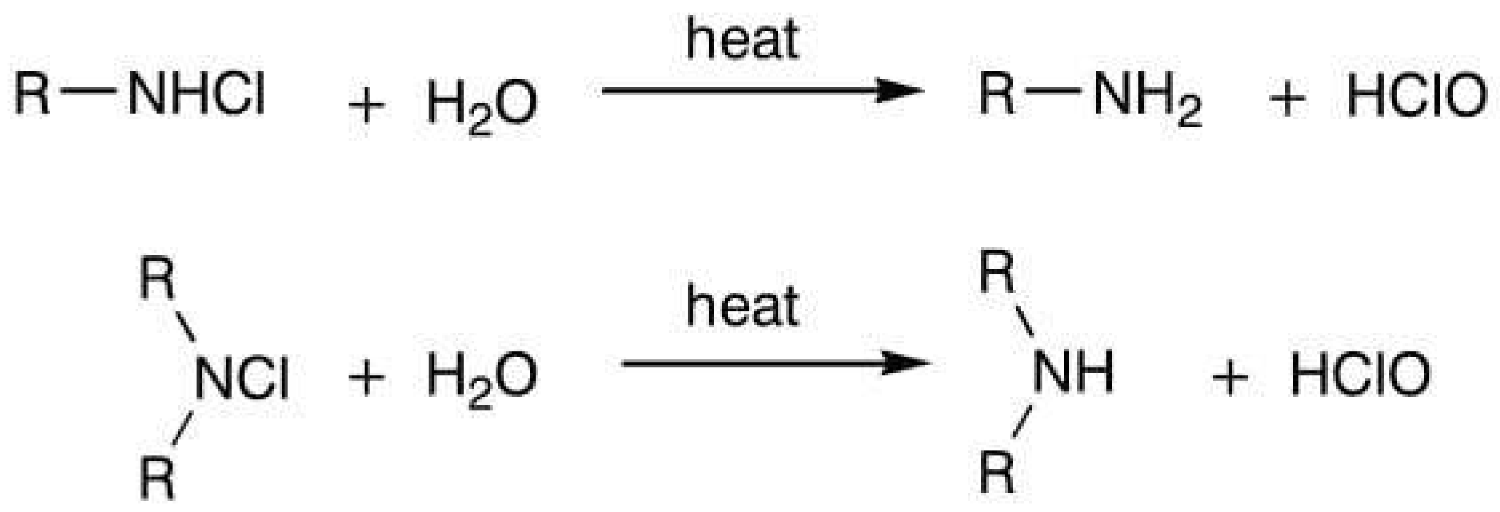
In addition, the ideal agent must not:
- cause significant changes of shade of dyeings
- increase chlorine retention or free formaldehyde content
- impair the handle, hydrophilicity, light fastness, gas-fume fastness or sewability of the fabric
- be toxic to humans or irritate the skin.

Table 10.44 Classes of polymeric cationic agents for aftertreatment of dyed cellulosic fibres [448]

Amide–formaldehyde condensates	No defined structure
Polybiguanides	 $\left[-CH_2-NH-\underset{NH}{\underset{\|}{C}}-NH-\underset{NH}{\underset{\|}{C}}-\underset{X^-}{\overset{+}{N}H_2}-CH_2-\right]_n$
Poly(ethylene imine)	 $\left[-NH-CH_2-CH_2-\underset{X^-}{\overset{+}{N}H_2}-CH_2-CH_2-\right]_n$
Quaternised poly(ethylene imine)	 $\left[-NH-CH_2-CH_2-\overset{+}{\underset{CH_3}{\overset{CH_3}{N}}}-CH_2-CH_2-\right]_n\ X^-$
Quaternised polyheterocycles	
Quaternised polyacrylamides	 $\left[-CH_2-\underset{\underset{O=C-NH-CH_2-CH_2-\overset{+}{\underset{CH_3}{\overset{CH_3}{N}}}-CH_3\ X^-}{\|}}{CH}-\right]_n$



Scheme 10.83



Scheme 10.84

Amines can give rise to chloramines during hypochlorite bleaching (Scheme 10.83). In addition to increasing AOX values, this can result in cellulose oxidative degradation by hypochlorite on subsequent hydrolysis of the chloramines (Scheme 10.84) [448].

Cationic fixing agents remain associated with the dyes on the fibre and are only partially removed by subsequent washing. Skin irritation is therefore an important consideration and in this respect they appear to have negligible influence. In common with cationic surfactants, however, they are readily absorbed by protein material and show moderately high toxicity to aquatic organisms, although interaction with excess anionic surfactant can considerably reduce this problem. *In vitro* they can show poor biodegradability, BOD values being typically not more than 10–20% of COD values, which are usually in the region of 40–400 mg/g oxygen. However, they are highly absorbed by activated sludge, resulting in about 95–98% bioelimination accompanied by about 80% actual biodegradation.

Studies of the effectiveness of cationic polymers for aftertreatment of dyeings continue to appear, although not all researchers disclose the detailed structures of the polymers evaluated. One comparison involved three types of commercial fixing agents for improving the fastness of six direct dyes on cotton, the agents being described as a dicyandiamide–formaldehyde condensate, a cationic nitrogenous polymer and a long-chain polyamine-type product. The long-chain polyamine imparted higher wet fastness than the dicyandiamide type, but fastness characteristics were found to be influenced by the number and position of solubilising and hydrogen bonding groups in the dye structures [449].

A polyacrylamide with a molecular mass of 1.87×10^5 was prepared by polymerising a 5% w/v aqueous solution of acrylamide monomer in the presence of 0.15% w/w benzyl alcohol and 0.025% w/w potassium persulphate for 45 minutes at 80 °C. This product was effective in preventing the bleeding of direct dyes and hydrolysed reactive dyes from dyed cotton, which was simply dipped in a 1% solution of the polyacrylamide and dried in air [450].

Ecological factors, as well as the improvement of wet fastness, were taken into consideration in a study of viscose dyed with direct dyes (CI Direct Yellow 126, Red 83:1 and Blue 90) and aftertreated with three cationic agents described as monofunctional, bifunctional and trifunctional [451]. For a system to be biodegradable, the BOD_5/COD ratio should be at least 0.5. For the systems examined, this ratio ranged from 0.00 to 0.38. Thus, all of them proved difficult to treat, biodegradation taking at least 20 days. It was difficult to decide which of the three agents was least hazardous in environmental terms. The bifunctional agent gave the best overall performance, since it was not more environmentally hazardous than the others and gave the smallest colour change, together with good fastness to washing at 60 °C.

There has been interest recently in comparing formaldehyde-free, low-formaldehyde and conventional *N*-methylol fixing agents with direct [452] and reactive [453] dyes. Advantages are claimed for formaldehyde-free products in giving less dye bleeding, less change in shade and excellent fastness to light and wet treatments [453].

The effect of conventional cationic aftertreating agents in improving the fastness of direct dyes can be further enhanced, albeit to only a small extent, by subsequent treatment with a syntan [454]. This may result from the formation of a larger electrostatically linked complex between the anionic syntan and the cationic fixing agent at the fibre surface, having low aqueous solubility and slow diffusion behaviour. Traditionally, cationic fixing agents have been applied to direct dyeings at neutral or slightly acidic pH. There is now some evidence [455] that they can be somewhat more effective if applied under alkaline conditions. The reasons for this remain speculative and more than one mechanism may be operating.

10.9.6 Aftertreatments for sulphur dyes on cellulosic fibres

The fastness of sulphur dyes to the increasingly severe conditions of washing currently demanded, especially in the presence of peroxide-containing detergents, can sometimes be improved by an alkylation treatment. The best-known products for this purpose are adducts of epichlorohydrin with either ethylenediamine (especially) or ammonium salts. Typically the procedure involves the application of 2–3% o.w.f. of a proprietary alkylating agent with 1–2% o.w.f. sodium carbonate (pH 10 and 30–40 °C), raising the temperature to 90–95 °C and allowing the reaction to reach completion at this temperature, which it does after 10 minutes. This treatment usually replaces the traditional oxidation treatment, except for dyes having a distinctly yellow leuco form.

There has been interest recently in extending the use of cationic fixing agents normally used with direct dyes to sulphur dyes. Five cationic polymers markedly improved the fastness to washing of solubilised sulphur, leuco sulphur and insoluble sulphur dyes when the cationic treatment was applied by a simple exhaust method typical of their application to direct dyeings [456]. The polymers were similarly effective when applied to leuco sulphur dyeings by pad–dry and pad–flash cure methods [457]. The mechanisms operating were thought to resemble those with direct dyes, i.e. the formation of electrostatically linked dye–agent complexes and/or the formation of a peripheral layer of polycations restricting dye mobility. The use of a reactive cationic agent has also been examined [458], this being of a type used successfully as a pretreatment to enhance dyeability. Washing fastness of reoxidised, solubilised sulphur dyes when aftertreated by an exhaust method was markedly improved. It was shown that the cationic aftertreatment could replace the usual reoxidation procedure, giving enhanced fastness.

10.10 AGENTS FOR FIBRE LUBRICATION, SOFTENING, ANTISTATIC EFFECTS, SOIL RELEASE, SOIL REPELLENCY AND BACTERICIDAL ACTIVITY

Most of the title products are finishing agents rather than dyeing or printing auxiliaries. Although in principle they could be applied before, during or after coloration (with the exception of lubricants applied during textile manufacture), economic reasons firmly put the preference on conjunct application with colorants wherever possible. Whilst not dyeing auxiliaries as such, their inclusion often has a bearing on choice and behaviour of dyes as well as on possible problems encountered during coloration (compatibility or otherwise of the components) and afterwards (fastness properties). Many of these products have useful activity in more than one function. Thus an agent (and especially a composite commercial product) promoted chiefly as a softener may also have antistatic, yarn lubricating and soil release properties, and it is useful to bear this diversity of function in mind.

10.10.1 Fibre lubricants

The main consideration here is lubricants applied during wet processing although some consideration will also be given to those included during textile manufacture. The basic requirement of a lubricant is that it should form a thin uniform protective coating around the fibres to lower their surface friction and flexural rigidity, thus assisting a process such as weaving or minimising the formation of durable creases during rope dyeing, particularly at high temperatures. In general practice a lubricant may, and usually does, contain more than one component, a typical composition comprising base lubricant(s), antistatic agent and surfactant(s). HPLC provides a useful means for the analytical separation and identification of the components of a lubricant formulation [459].

From the point of view of subsequent wet processing, it is usually preferable that fabrics be free from fatty substances such as oils and waxes. From the weaver's viewpoint, however, it is usually contended that such fatty lubricants are essential to minimise wear of machine parts and to prevent yarn abrasion and breakages, more especially where high-speed weaving processes are concerned. Weaving lubricants of this kind are usually applied with the sizing agent (section 10.5.2) and they must operate in conjunction, one of the main functions of the lubricant being to increase the film-forming properties of the size polymer(s). However, such fatty lubricants are difficult to remove and may complicate subsequent desizing, bleaching and coloration processes. This practice of using fatty lubricants has been questioned in recent times, based on evidence that such hydrophobic agents can actually impair the performance of the size as well as creating difficulties in desizing [460–463].

This is the main reason why surfactants are often used with fatty lubricants, to improve compatibility with size polymers and to assist emulsification and removal. However, arguments have been advanced [463] for the use of carefully selected surfactants as lubricating agents. The fatty or hydrophobic moiety of a surfactant produces a low coefficient of friction between surfaces to which it is applied and so acts as a lubricant, whereas the hydrophilic moiety makes for built-in ease of subsequent removal. In addition, the use of inorganic salts such as sodium silicate and sodium carbonate, as routinely used in detergent formulations, enhances the performance of the surfactant as a lubricant, a typical formulation comprising 0.6% surfactant, 0.6–1.0% sodium silicate and 0.5% sodium carbonate. It is claimed that such a composition performs just as well as a fatty lubricant in sizing and yet it is much easier to remove during subsequent scouring or desizing. Anionic and nonionic surfactants were compared but unfortunately no details of structure were disclosed. Clearly a good deal of development work would be required to evaluate a range of surfactants varying in hydrophobicity, in order to obtain optimum performance with a specific size composition and substrate. This is essential in any case, irrespective of whether the surfactant is to replace a traditional lubricant or is in support of one.

Compatibility with other components becomes a critical factor when lubricants are used in the dyebath. The properties of the ideal dyebath lubricant have been summarised as follows [464]:

(1) excellent fibre-to-fibre and fibre-to-metal lubrication;
(2) economical;
(3) no effect on other physical properties such as handle, water-repellency and absorbency;
(4) a foam suppressant or deaerating agent;
(5) no effect on reproducibility of dyeing;
(6) no effect on fastness properties;
(7) non-yellowing;
(8) easily washed out; and
(9) biodegradable.

When formulating a dyebath lubricant, particular attention must be paid to the type of substrate (hydrophilic or hydrophobic) and to substantivity of the lubricant for that substrate. Another important consideration is ionicity of the lubricant in relation to the components of the dyebath, since this has such an important bearing on compatibility (clearly, anionic lubricants should be avoided when basic dyes are used). Solubility and/or dispersibility in relation to dyebath composition and the conditions of dyeing (temperature, pH, liquor ratio) are also important, since the overall hydrophobic/hydrophilic balance has a major influence on compatibility. The behaviour of the lubricant during drying can be just as critical as during dyeing. Many lubricants promote undesirable thermomigration of disperse dyes on polyester during high-temperature drying and heat setting, leading to lower wet fastness.

Natural products such as animal fats and vegetable oils still constitute an important share of the lubricants market although synthetic types are gaining acceptance [464]. Natural fats and oils include saponified fatty acids, fatty esters, fatty alcohols and fatty amides. Various anionic groups are suitable, including carboxylate, phosphate, phosphonate, sulphate or sulphonate, the last-named being the most widely preferred. Esterification of the fatty acids is particularly useful. For example, ethoxylation with ethylene oxide enables products of subtly graded character to be produced, depending on the degree of hydrophobicity of the fatty acid and the degree of ethoxylation. Sulphonates offer greater stability at higher pH and ionic strength but they can generate troublesome foaming.

Synthetic-based lubricants include polyacrylates, acrylamide/acrylic acid copolymers, emulsified paraffin oils and waxes, modified silicones. The acrylates generally combine excellent solubility in the dyebath with fabric lubrication and such polymers can be designed to cover a wide range of solubility, rinsibility and lubricating performance. Ionicity can be varied, whilst acrylic esters offer scope for incorporating other functionalities along the polymer chain. Acrylic esters also allow the degree of anionicity to be varied. Acrylamide groups generally result in increased stability, especially in acidic media where the amido groups are partially protonated and thus mildly cationic, whilst in neutral media they behave substantially as nonionic moieties.

Paraffin hydrocarbons of molecular mass 300 to 700 (i.e. 20–50 carbon atoms) require emulsification with surfactants. They show good resistance to oxidation and yellowing.

However, the stability of these systems is critically dependent on effective emulsification. Viscosity is usually low, a concomitant of this being that the emulsifier constitutes a substantial proportion of the system. Ideally, the emulsifier should contribute to the lubricating power of the product. Related to the paraffins are the even more hydrophobic polyethylenes, primarily used as sewing lubricants or handle modifiers. These polymers may be difficult to wash out, although their ionic character can be varied according to whether anionic, cationic or nonionic emulsifying systems are chosen. Paraffin waxes and polyethylenes have an advantage over paraffin oils in that they are terminated with a mildly ionic functionality that assists their emulsification and, coupled with their high molecular mass, increases substantivity. This tendency, however, can make them difficult to wash out and leads to compatibility problems in dyeing. They are perhaps best regarded as softeners.

Alkoxylated polysiloxanes are a relatively new class of dyebath lubricants. They have practically no substantivity for the substrate, yet combine adequate lubrication with water solubility and easy rinsability. If the silicones contain primary hydroxy groups, these can be modified by esterification, phosphation, phosphonation, sulphation, sulphonation or carboxylation. These anionic substituents confer substantivity for various substrates without losing rinsability. Anionic organic sulphates and sulphonates probably offer the best overall properties for dyebath lubricants, whilst other types can be more suitable for selected applications [464].

Certain problems associated with lubricants

The manufacture of textile fabrics for automotive trims normally requires the application of a spin finish, a considerable percentage of which is still present in the finished fabric [465]. Residual lubricants can give rise to 'fogging' on the interior of car windows, caused by condensation on the glass of volatile components present: other similar products, such as antistats and softeners, may also be implicated. Fogging is measured by reflectance and is expressed as the ratio of the reflectance values of a glass plate before and after exposure to fogging (DIN 75021), a high value representing a low degree of fogging. Low-fogging compounds typically give values of at least 90%; some measured values [465] are shown in Table 10.45. Chemical type is not a direct indicator of propensity to fogging, since volatility varies with hydrophobic/hydrophilic balance as determined by chain length and structural type on the one hand and the degree of polar character, including ionicity, on the other.

Yellowing can occur with certain lubricants during drying or ageing. This phenomenon has been investigated on wool and acrylic fibres and blends of them lubricated with a

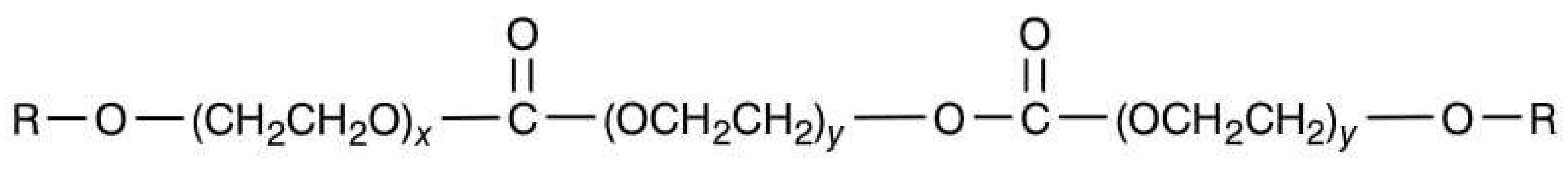
Table 10.45 Fogging values of lubricants [465]

Lubricant chemical type	Fogging value (%)
Alkylbenzene	36
Poly(ethylene glycol)	86
Fatty acid polyglycol ester No. 1	55
Fatty acid polyglycol ester No. 2	95
Poly(ethylene/propylene glycols)	>95
Phosphate monoester/diester	>90

cationic fatty acid condensation product, a cationic nitrogenous condensation product, a quaternary stearylalkylamino ester, a nonionic oxyethylated carbonate/phosphate and a polyglycol carbonate ester formulated with a nonionic surfactant [466]. Yellowing did not occur when the lubricant manufacturer's instructions regarding concentration and drying temperature were followed. In some circumstances, however, such as radio-frequency drying, cationic compounds can induce the formation of sparks that may result in yellowing, indicating a need to reduce the power of the dryer and/or to use a lower concentration of lubricant.

As already mentioned, some lubricants can be difficult to remove by washing and surfactants are often added to overcome this problem [463]. Lubricants can impair fastness properties, particularly those of disperse dyes. They may influence the uptake of dyes either positively or negatively, although seldom seriously except where it results in unlevelness. For example, knitting oils can increase the yield of relatively oleophilic reactive dyes on cotton and yet with highly hydrophilic types they may cause dye-resist effects [467].

When considering the environmental aspects of lubricants, it is necessary to bear in mind that commercial formulations are often more or less complex mixtures and that even small amounts of toxicologically questionable components can lead to restrictions on use, depending on local regulations. Thermally stable, readily biodegradable esterified oil emulsions can offer a compromise solution, being environmentally preferable to unmodified oils, fats and waxes, although problems can still arise in high-temperature processes such as texturising or heat setting, as a result of cracking reactions leading to the formation of harmful residues or condensates [468]. In order to overcome this problem of cracking, attention must be paid to the susceptible rupture points in the molecule. This has been done in the development [468,469] of a range of ecologically friendly lubricants by using carbonate ester bridging groups to combine fatty alcohols or their ethoxylates with poly(ethylene glycol) (10.216). Such products are readily water-soluble, self-emulsifiable, thermally stable compounds with excellent cracking behaviour. Their lubricity is such that they can be used in amounts 50–80% lower than normal. They show excellent biodegradability and skin compatibility properties. Emission values are 10–20 times less than with comparable esters or mineral oils. Environmentally friendly lubricants containing alkylglucoside with emulsifier (1:2) or amine oxide with emulsifier (1:2) have also been claimed [470].



$$R{-}O{-}(CH_2CH_2O)_x{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(OCH_2CH_2)_y{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(OCH_2CH_2)_y{-}O{-}R$$

10.216

10.10.2 Antistatic agents

Antistatic agents are useful to prevent garments accumulating charges of static electricity, particularly those made entirely from hydrophobic fibres. Whilst this is desirable for domestic wear, it takes on added importance in many other sectors, when working in explosion hazard areas, with micro-electronic components, in electronic data processing environments, near textile dust filtering systems, or in certain areas of military and space travel technology. Antistatic treatments may be impermanent (easily removed on washing) or have a degree of durability. They operate through their hydrotropic properties, creating a moist microclimate that discourages the build-up of static, or by having some degree of conductivity, thus dissipating any localised static charge into a wider area of lower potential.

Impermanent antistats

Surfactants may exhibit a degree of hydrotropy and thus function as antistatic agents. They are often used for this and for their emulsifying properties in conjunction with fibre lubricants, or may be used alone in a dual capacity as lubricant and antistat. Suitably active surfactants can be found amongst all four ionic types, some typical examples being [471]:

- quaternary ammonium derivatives of fatty acids
- polyethoxylated quaternary ammonium derivatives
- quaternised alkylenediamines
- alkyl sulphates, chlorides or phosphates
- mixtures of mono- and di-esters of phosphoric acid
- long chain amine oxides
- polyethoxylated and polypropoxylated nonionics.

Nonionic and cationic types are generally preferred, usually on grounds of fibre compatibility, higher hygroscopicity and higher oil solubility. The quaternary ammonium derivatives of fatty acids in particular impart static protection at a low level of application (i.e. 0.25%), whilst the polyoxyethylated versions give higher solubility in water. The nonionic and cationic types dominate particularly in spin finishes [471]. However, the cationic types may create subsequent problems if anionic surfactants are used at the washing stage.

Impermanent antistatic agents that are not surface-active include triethanolamine, glycerol in combination with potassium acetate, as well as inorganic salts such as lithium chloride [471].

The major requirements for impermanent antistats are [471]:

(1) effective at low levels of humidity;
(2) low volatility;
(3) non-corrosive;
(4) low toxicity; and
(5) no yellowing.

In addition, if used in spin finishes they must be thermally stable, oil-soluble and exhibit low migration on the fibre.

Durable antistats

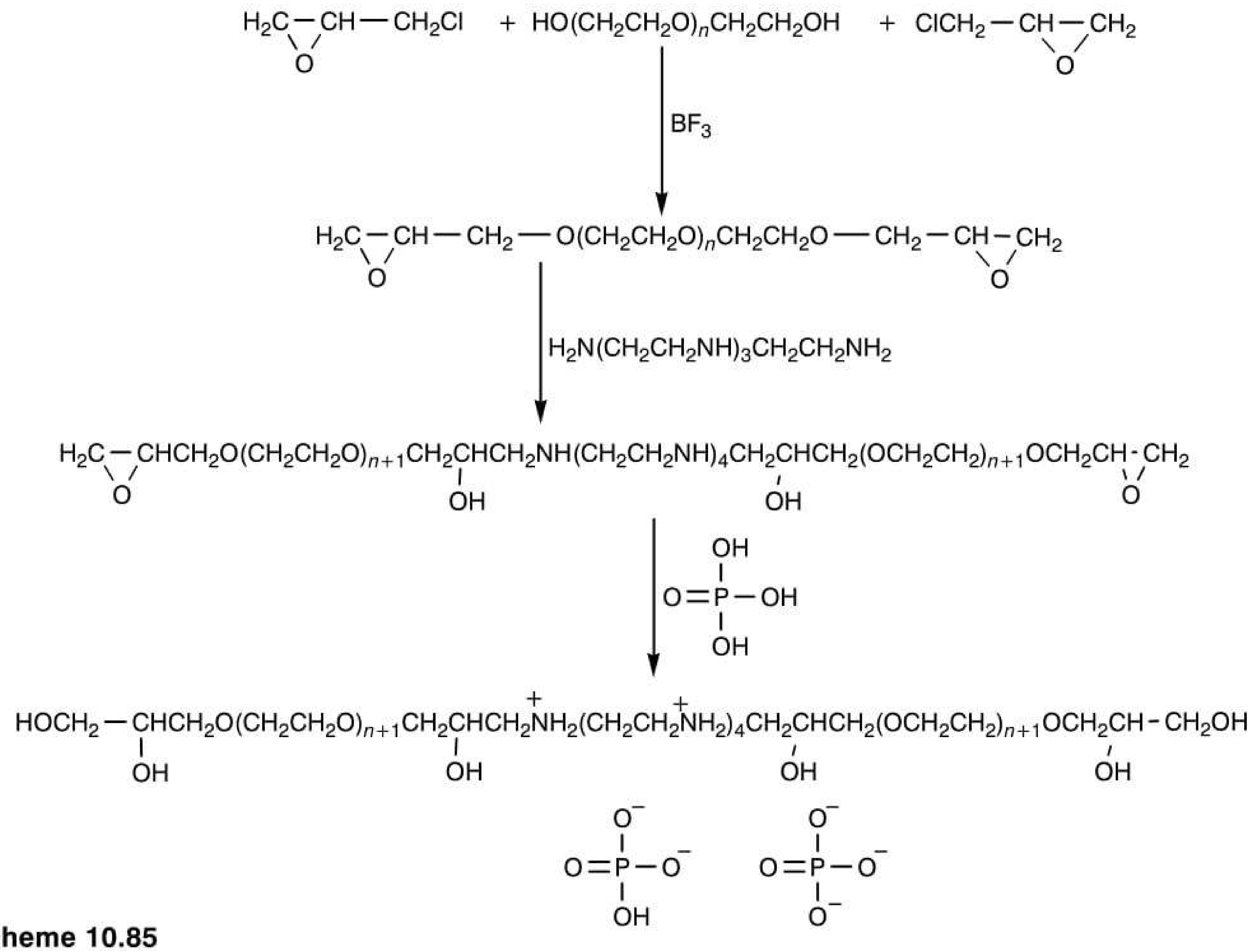
There are two types of durable antistat. The first (so-called external antistatic agent) is applied at some stage after fibre manufacture whilst the second type is incorporated during manufacture. The former type exhibits varying degrees of durability and is not usually as durable as the latter.

External antistatic treatments generally involve the formation of a crosslinked polymer containing ionic and/or hygroscopic groups, cationic polyelectrolytes containing poly(ethylene oxide) units being widely used. Many crosslinking agents are suitable to insolubilise hydrophilic components within a fibre, including poly(ethylene glycol) dihalides, epoxy compounds, cyanuric chloride, derivatives of piperazine, hexahydro-*s*-triazine, polyaziridines, polyacrylamide and polyamines [471].

Casein modified by graft copolymerisation with esters of acrylic acid and methacrylic acid has been traditionally used for the coating of leather. Casein modified in this way by grafting with ethyl acrylate [472] showed good film-forming properties on textile materials, particularly as an antistatic agent in the backing of carpets and as an additive in pigment printing. This polymer satisfied ecological requirements and its antistatic properties were substantially enhanced by incorporating electroconductive materials such as carbon black and powdered metals.

In another evaluation [473], durable antistatic properties were obtained using water-soluble quaternary ammonium polyamines applied to polyester by padding and curing at 160 °C. These products were prepared according to Scheme 10.85. Epichlorohydrin was condensed with poly(ethylene glycol) 600 (known for its hygroscopicity and antistatic effect) using boron trifluoride as catalyst to give the poly(ethylene glycol) diglycidyl ether. This was then reacted with the highly electroconductive tetra-ethylenepentamine to give a water-soluble polyamine. Finally, in order to prevent gelation and to improve the stability in aqueous solution, this polyamine was cationised as the phosphate salt.

An obvious means of increasing conductivity is to incorporate metals into the fabric. Thus fabric can be sprayed with a liquid resembling metallic paint, containing micron-sized metallic particles such as copper incorporated into a binder such as a polyester, epoxy or acrylic resin. During curing the metallic particles come into contact with one another, thus



Scheme 10.85

providing excellent conductivity throughout the material [474]. The presence of copper, however, may present environmental problems when waste material of this kind requires disposal.

An unusual method of imparting antistatic properties to acrylic fibres involves saponification of some of the nitrile groups to give amide and carboxyl groups, using sodium hydroxide under exhaust (80 °C), pad–batch (varying within 15–120 minutes at 160–60 °C) or pad–steam conditions. The pad–steam method in particular provides convenient surface modification of acrylic fibres, giving antistatic properties together with improved soil-release and improved dyeing properties with basic dyes [475]. This method may be substrate-specific since acrylic fibres vary widely in their sensitivity to alkali, some being quite easily discoloured.

Methods of incorporating durable antistats during fibre manufacture include:

- incorporation of a hydrophilic component, such as a surfactant
- formation of a lattice of highly conductive components within the fibre.

This approach is outside the scope of the present chapter but details may be found elsewhere [471,476,477].

10.10.3 Softeners

It is difficult to define unequivocally the quality of fabric handle or softness/firmness differences, since this involves many factors. It is often linked with lubrication, especially as similar products are often used for softening and lubrication. Whilst experienced assessors can be quite remarkable in the extent to which they can grade and assess softeners simply by means of a highly developed tactile sense, more objective methods are clearly desirable for scientific investigations. Since many factors combine in producing an overall sense of softness, it is not surprising that objective determination of softness involves more than one parameter of measurement. The details of assessment are outside the scope of this chapter, but descriptions and discussions are available elsewhere [478–481]. Suffice it to say here that the Kawabata system has acquired considerable importance in quantifying various aspects of fabric handle.

The oils and waxes described as lubricants in section 10.10.1, as well as talc, can be used as softeners but have now been superseded by more effective products. These may be non-reactive or reactive and may be cationic, anionic, nonionic or amphoteric. Although many compounds have been patented, by far the most important are cationic quaternary ammonium compounds and various silicones. Until quite recently the field was led by the cationic types but there is now evidence that aminofunctional polysiloxanes have become the most important product group [482].

Before dealing with the detailed chemistry of softening agents, it is useful to consider some general factors. The desirable properties of an ideal softener can be summarised as follows [482]:

- easy to handle (suitable for pumping, stable on dilution)
- low foaming, stable to shearing, free from deposits on rollers
- compatible with other chemicals
- good exhaustion properties
- applicable by spraying

- stable to high temperatures, non-volatile especially in steam
- no effect on shade or fastness
- no yellowing
- easily biodegradable
- non-toxic, dermatologically harmless, non-corrosive
- no restrictions for transport or storage.

No single product satisfies all the above requirements. Commercial softeners are usually more or less complex mixtures, available as aqueous emulsions with a solids content of 15–25%. As well as the softener component(s) other additives are also present, including the emulsifying and/or dispersing agents necessary. It cannot be over-emphasised that emulsion stability is just as important as softener effectiveness, since it is crucial to the performance of the product. Nonionic emulsifying agents are especially useful, showing all-round compatibility with other substances even if they are different in ionicity. Consideration needs to be given to cloud point phenomena and stability to electrolytes when using nonionic surfactants. In such cases the emulsifying system itself may be a mixture.

Softener emulsions are available in different commercial grades. Semimicro-emulsions have an average particle size of <0.1 μm, allowing for penetration to the fibre core and giving excellent distribution of the softener. Micro-emulsions have an average particle size of <0.01 μm, giving the substrate an excellent inner softness and a distinctive surface smoothness without looking greasy [482]. Micro-emulsions have good stability and a decreased tendency for deposition on rollers. Critically optimised products are particularly necessary when using micro-emulsions on high-speed equipment where high shearing forces are developed [482]. Irrespective of the basic chemical type, the fabric handle can be modified by varying the hydrophilic–hydrophobic balance of the softener. Thus increasing hydrophobicity by incorporating a longer alkyl chain imparts an increasingly greasy handle to the fabric.

The ionicity of the softener influences its substantivity for different fibres. Whilst this can be significant in padding applications, it is of primary importance for application by exhaust methods. Cationic softeners are highly substantive to acrylic fibres, whilst anionic products are substantive to wool and nylon. Nonionic softeners, if water-soluble, have very low substantivity for any substrate and are easily lost by washing. Insoluble types may be substantive to polyester or cellulose acetate, as well as wool and nylon. The degree of softening with the nonionic products is only moderate but their nonionic nature makes them convenient for application simultaneously with any class of dyes or fluorescent brightening agents. The low-substantivity agents are preferable for repeat application in domestic washing.

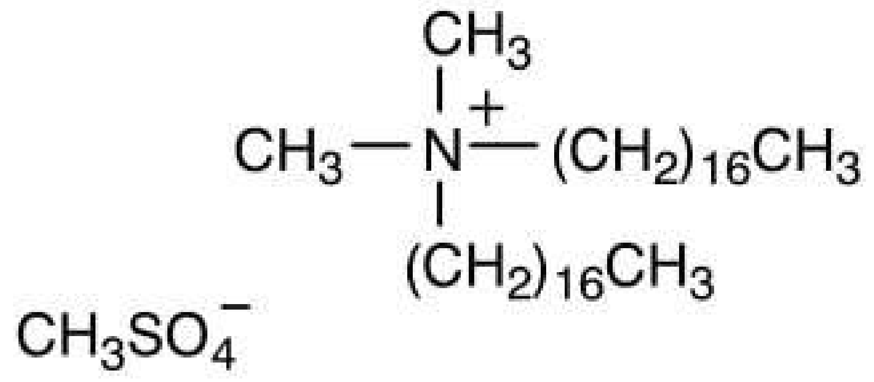
There has been a trend towards so-called multifunctional softeners in which account is taken of various other factors such as hydrophilicity, sewability, antistatic behaviour, lubrication and shearing stability [482]. For example, in jet dyeing a product will require, in addition to softening power:

- extremely high emulsion stability to cope with high pump and nozzle shearing forces at high temperatures
- a suitable defoaming system
- good substantivity to ensure adequate exhaustion.

Conversely, if good sewability is required, suitable products need to have good lubrication behaviour.

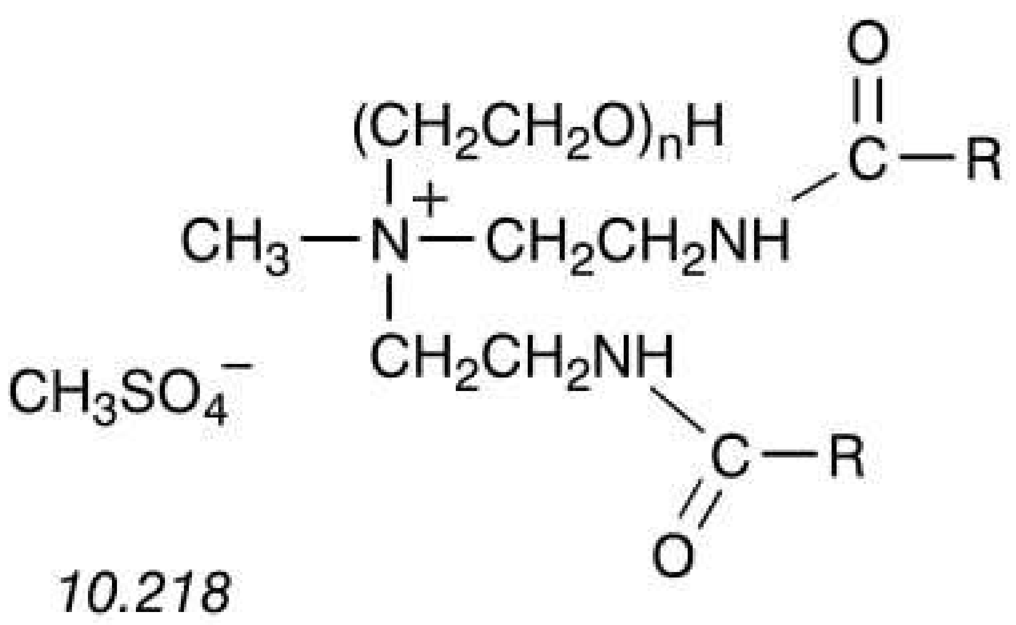
Quaternary ammonium compounds and other cationic softeners

Organic cationic softeners, as opposed to silicone derivatives, are usually quaternary alkylammonium compounds, the most important over many years being dimethyldistearylammonium methosulphate (10.217), on grounds of economy and availability. There are obviously many possible variants of such structures but typically the long-chain substituents are within the range C_{16} to C_{22} and may be fully or partially saturated [483]. These softeners possess aqueous solubility, substantivity for various fibres and, to some extent, antistatic and water-repellency properties. These properties can be modified by varying the substituents on the quaternary nitrogen atom. The softening effect is especially good. The balance of properties can be controlled more precisely using analogous ethoxylated or propoxylated amines (10.218), in which the degree of ethoxylation can also be varied. These are more expensive but provide high-quality industrial softeners. Further compounds available include quaternised imidazolines (10.219) and diamides or diurethanes containing a protonated amino group (10.220; R = alkyl or alkoxy).

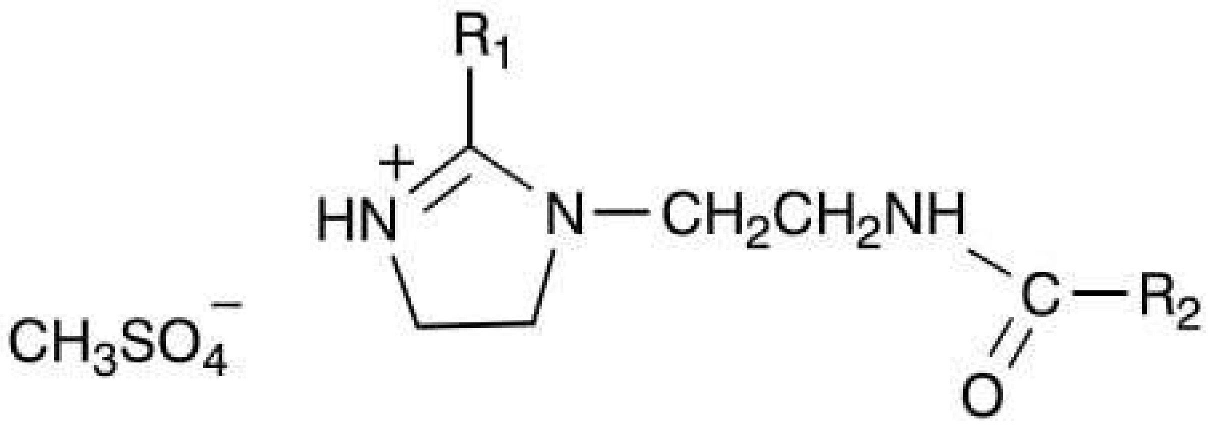


$$\mathrm{CH_3-\overset{CH_3}{\underset{(CH_2)_{16}CH_3}{\overset{+}{N}}}-(CH_2)_{16}CH_3 \qquad CH_3SO_4^-}$$

10.217



10.218



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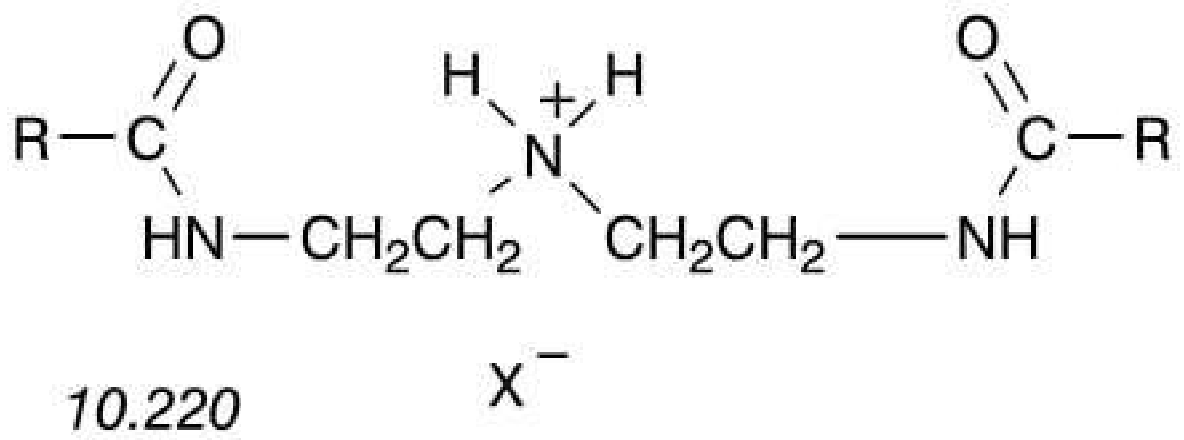
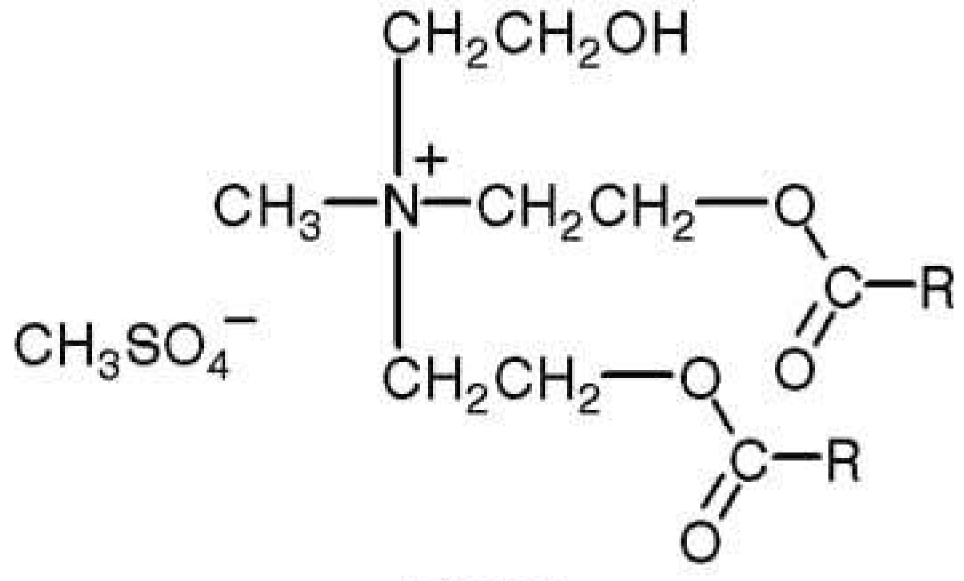


10.220

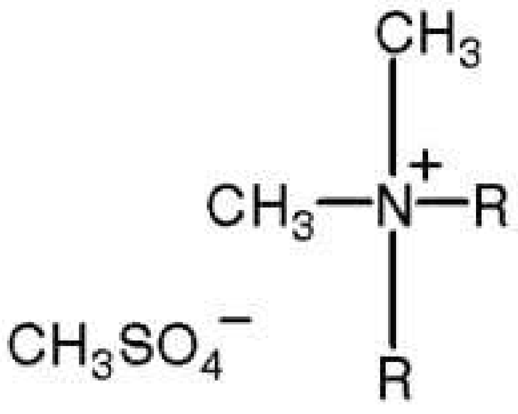
The specific properties of such compounds obviously depend on the precise nature of the substituents but in general the degree of softening decreases as follows: dialkyldimethylammonium compounds > imidazolinium salts > aminoalkyl diamides or diurethanes [480]. In the case of the quaternised compounds the preferred anions are methosulphate or ethosulphate, since these have a less corrosive effect on steel vessels than the chloride salts. These compounds generally show maximum cation activity at around pH 3.5 but are usually applied at higher pH values. In some cases the cationic softening agent is mixed with a nonionic surfactant to serve as a lubricant/antistat, this being particularly common in fabric softeners for domestic use. It is also worth noting that most quaternary ammonium compounds have a degree of antibacterial activity.

From a detailed study of three quaternary ammonium softeners based on hydrogenated tallow oil (10.221–10.223), adsorption of these softeners by cotton and acrylic fibres is shown in Figure 10.56. Adsorption of the three softeners by cotton did not vary greatly, apparently following a Donnan equilibrium mechanism. On the acrylic substrate a saturation point was reached at about 2 μmol of each softener per gram of fabric. A twenty-member panel using tactile sensation found no significant difference between the products for softness on either fibre. Measurement of bending rigidity indicated the following results for the same quantity of applied softener:

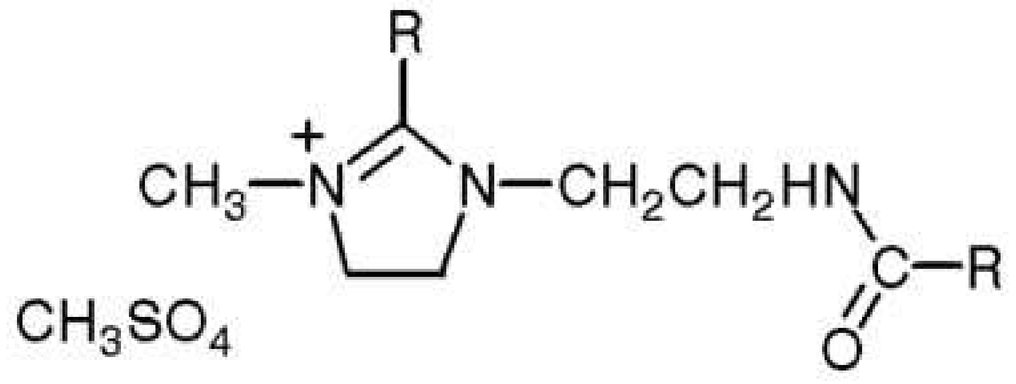
on cotton fabric: imidazolinium quat > ester quat or alkyl quat
on acrylic fabric: ester quat or imidazolinium quat > alkyl quat.



10.221



10.222



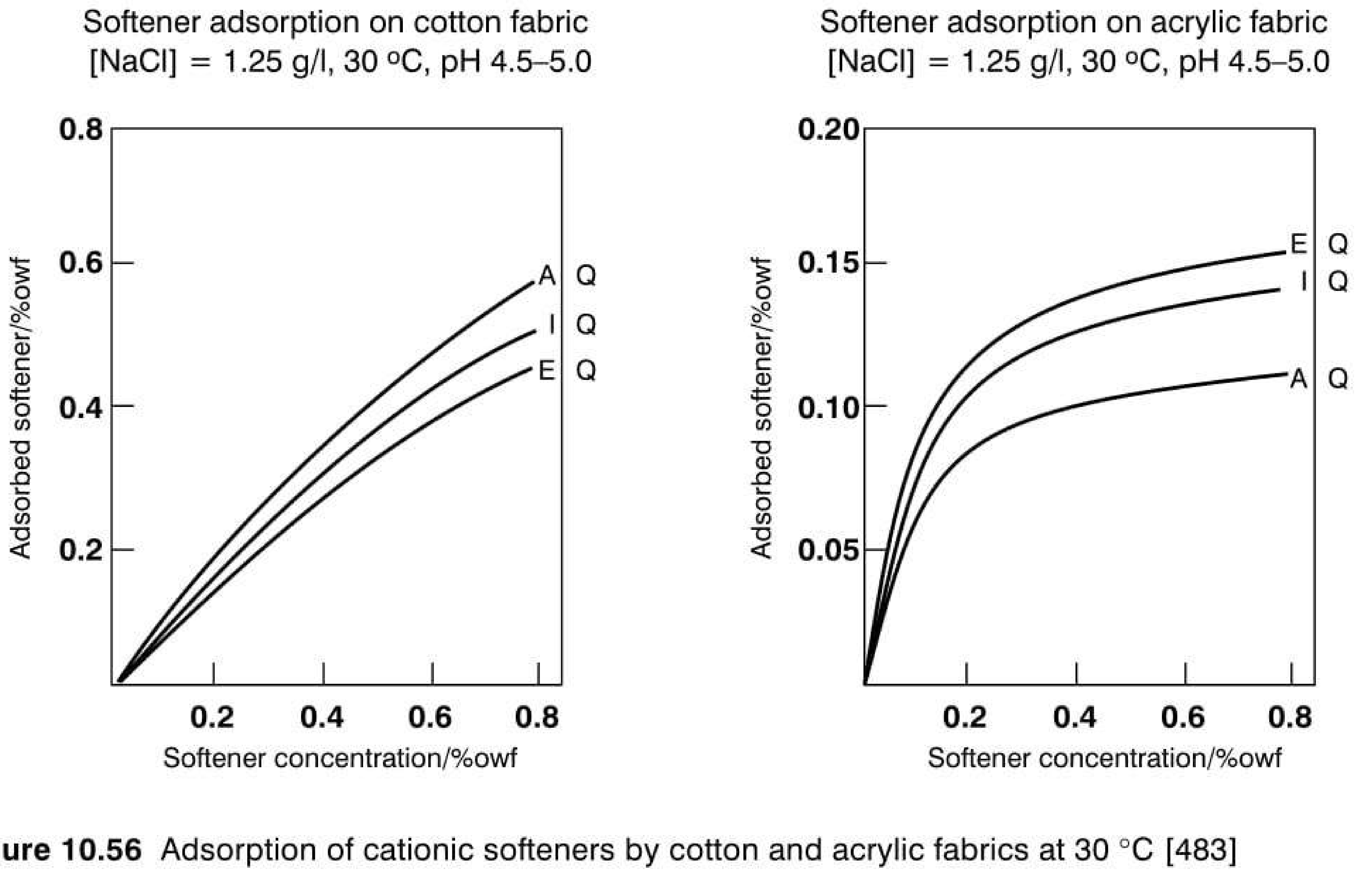
10.223

R = Hydrogenated tallow

Ester quat
N,*N*-bis(acyloxyethyl)-*N*-2-hydroxyethyl-*N*-methylammonium methosulphate

Alkyl quat
N,*N*-dialkyl-*N*,*N*-dimethylammonium methosulphate

Imidazolinium quat
1-acylaminoethyl-2-alkyl-3-methylimidazolinium methosulphate



Softener adsorption on cotton fabric
[NaCl] = 1.25 g/l, 30 °C, pH 4.5–5.0

Softener adsorption on acrylic fabric
[NaCl] = 1.25 g/l, 30 °C, pH 4.5–5.0

Figure 10.56 Adsorption of cationic softeners by cotton and acrylic fabrics at 30 °C [483]

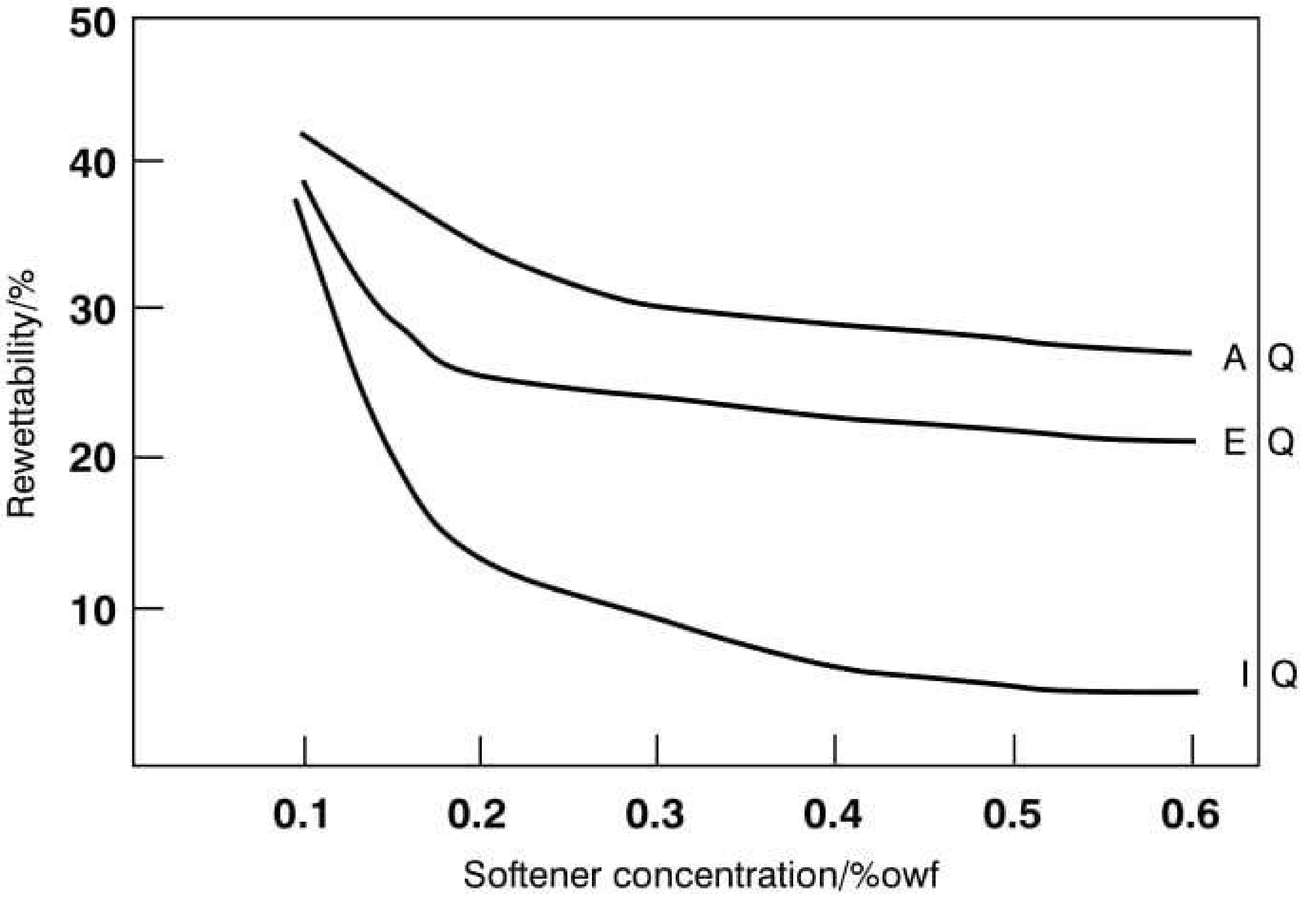


Figure 10.57 Effect of cationic softeners on the rewettability of cotton fabric [483]; 20 °C, 60% relative humidity

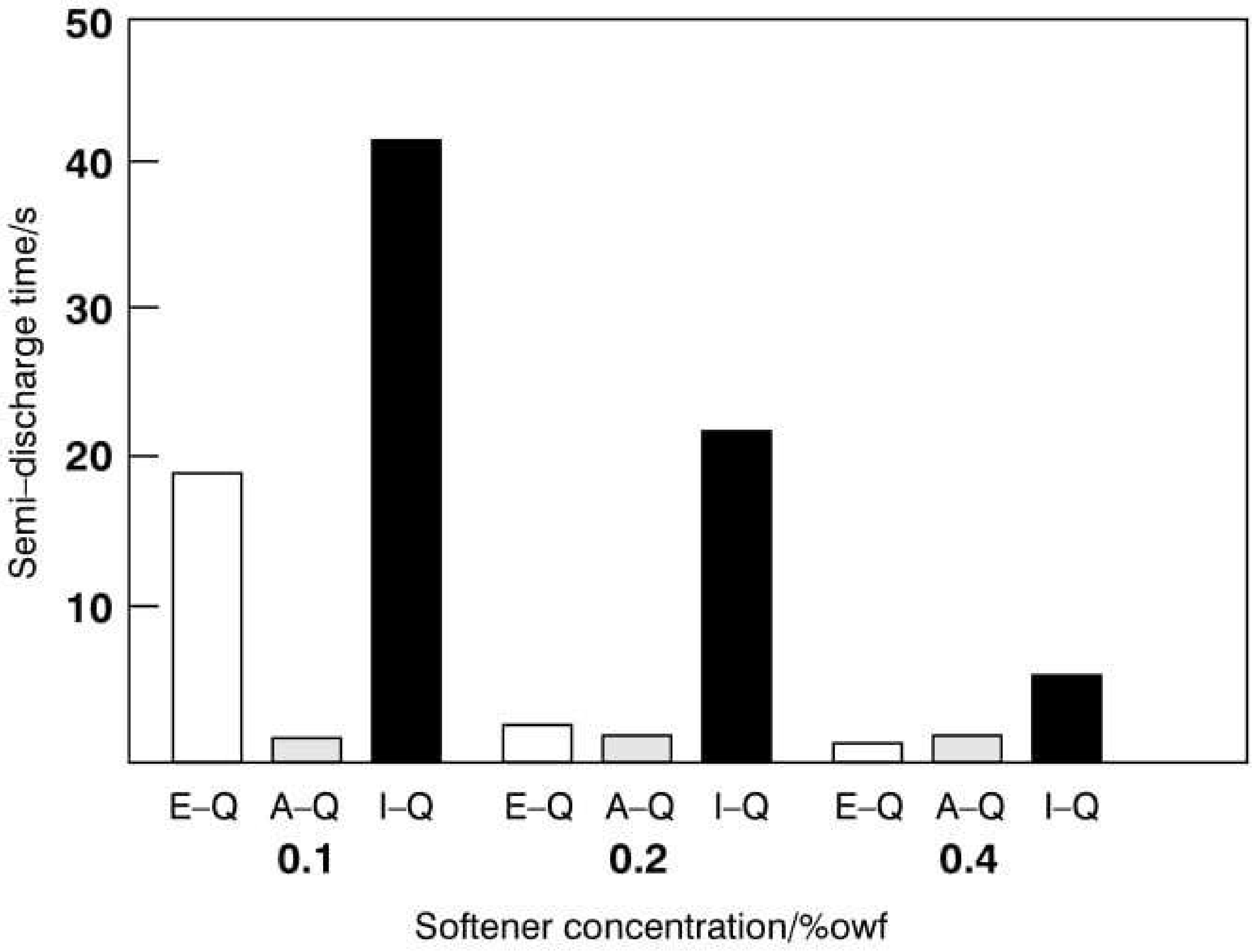


Figure 10.58 Effect of cationic softeners on the antistatic behaviour of acrylic fabric [483]; 20 °C, 60% relative humidity

A problem associated with quaternary ammonium softeners is that they increase the hydrophobic nature of the fibre and thus interfere with rewetting, this effect being cumulative with each successive application of the softener. The rewettability of a cotton fabric treated with the above three softeners is shown in Figure 10.57, wettability being affected somewhat less by the alkyl or ester quat than by the imidazolinium quat. Antistatic effects on the acrylic fabric are illustrated in Figure 10.58, showing wide variations between the softeners at low concentrations [483]. Surprisingly, none of these softeners induced significant thermomigration of three disperse dyes on polyester [483].

Micro-emulsion formulations of cationic softeners are available and are claimed to have superior fibre penetration properties [484]. Figure 10.59 shows the sorption of a micro-emulsion formulation of dimethyldistearylammonium (10.217) chloride. Similar results were obtained with micro-emulsion formulations of *N*,*N*-dialkyl-*N*-2-hydroxyethyl-*N*-methylammonium methosulphate (10.224) and *N*,*N*-bis(stearamidoethyl)-2-methylimidazolinium methosulphate (10.225), although the highest rate constant values were observed with the imidazoline derivative and the lowest with the dialkylhydroxyethylmethylammonium methosulphate (Table 10.46). Cotton washed 50 times in hard water absorbed the softeners rather more strongly than unwashed cotton. It is thought that this may be due to adsorption by the cotton of inorganic salts from the hard water and of acidic residues from the detergent used.

Yellowing can occur with quaternary cationic softeners and this limits their use on white fabrics. This problem can be overcome to some extent, provided drying or fixation temperatures are not too high, using so-called pseudo-cationic softeners [482]. These products are analogous to the so-called weakly cationic surfactants described in section 9.5.

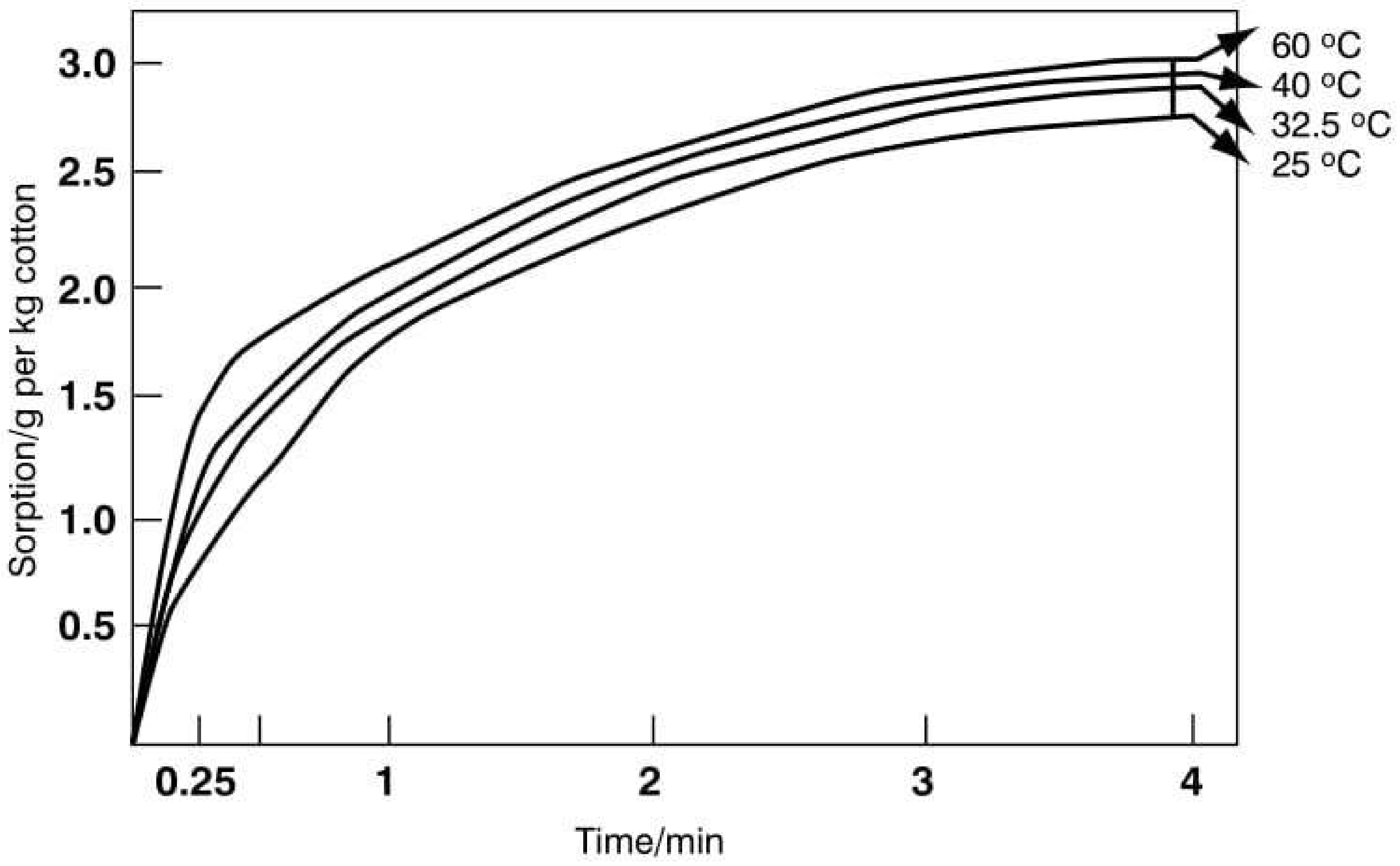
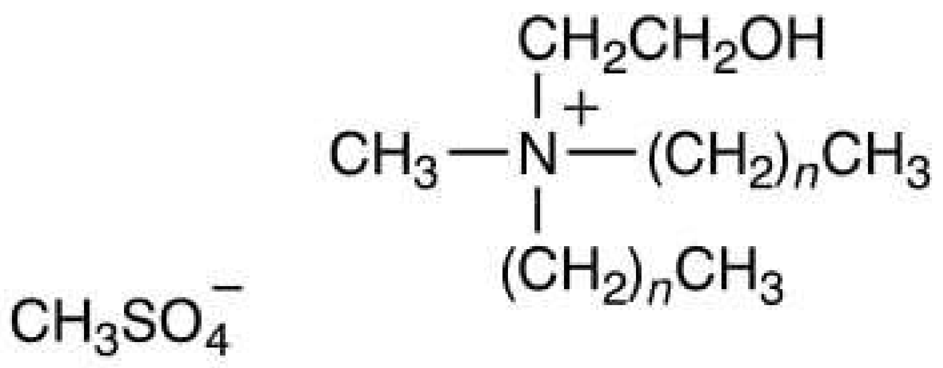
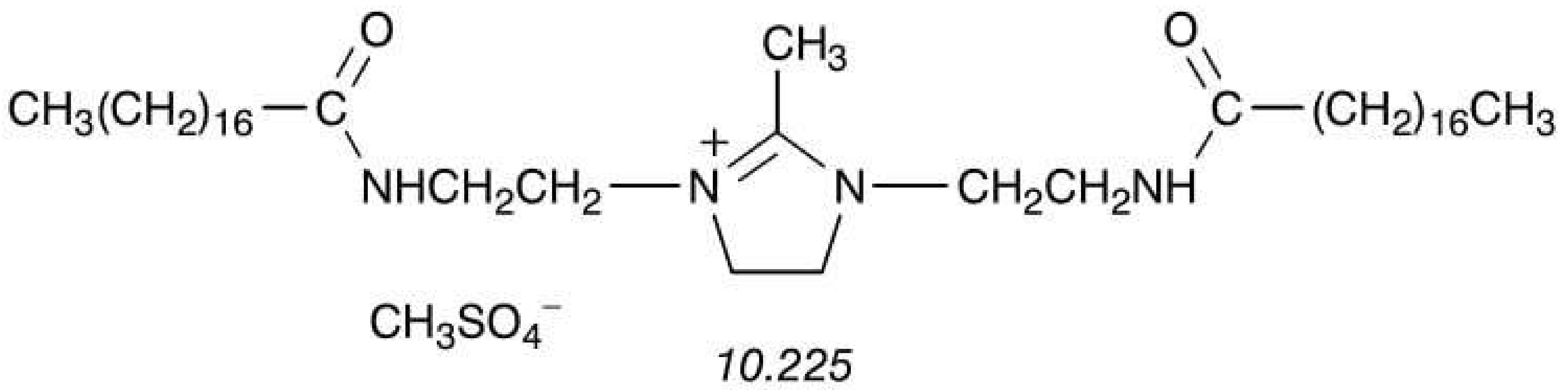


Figure 10.59 Sorption kinetics of micro-emulsion cationic softener formulation at different temperatures on cotton fabric [484]. Initial concentration 3 g/kg fibre, liquor ratio 15:1



$$CH_3-\underset{(CH_2)_nCH_3}{\overset{CH_2CH_2OH}{N^+}}-(CH_2)_nCH_3 \qquad CH_3SO_4^-$$

10.224



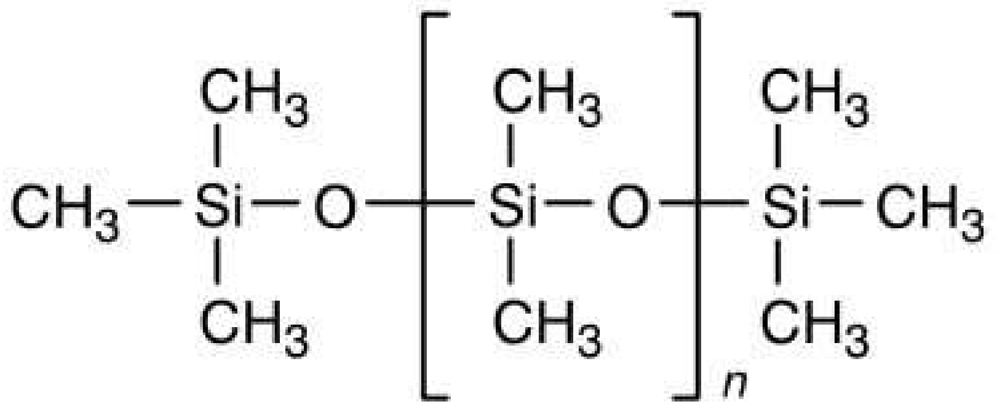
10.225

Table 10.46 Rate constants for sorption of cationic softeners at various temperatures on unwashed and washed cotton [484]

Softener	Temperature (°C)	Rate constants	
		Unwashed cotton	Washed 50 times
Dimethyldistearylammonium (10.217) chloride	25	0.42	0.72
	32.5	0.55	0.79
	40	0.64	1.14
	60	0.83	1.70
Dialkylhydroxyethylmethylammonium methosulphate (10.224)	25	0.46	0.57
	32.5	0.50	0.63
	40	0.55	0.71
	60	0.61	0.81
Bis(stearamidoethyl)methylimidazolinium methosulphate (10.225)	25	0.73	0.95
	32.5	0.80	1.10
	40	0.91	1.16
	60	1.03	1.47

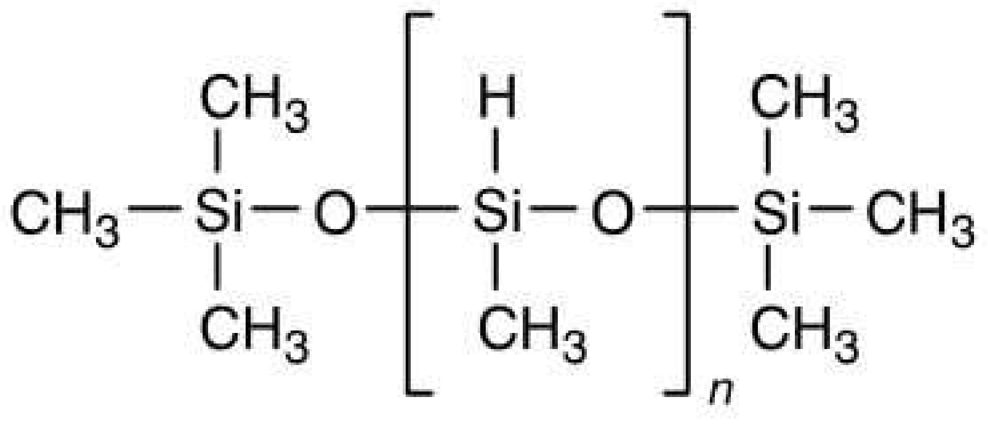
Silicone softeners

Poly(dimethyl siloxane) (10.226) represents the simplest of the silicone softeners, which are usually applied from emulsion. This polymer, however, is unreactive and is not substantive to fibres. Therefore it is not fast to washing and is little used nowadays. More durable softeners can be derived by modification of this fundamental siloxane. The so-called 'conventionally reactive' silicones were the first to be introduced, typical examples being those containing activated silanic hydrogen (10.227) or silanol (10.228) groups. Such polymers react with crosslinking agents (10.229 being a typical example) during a curing process with an organometallic catalyst, typically a zinc or zirconium alkanoate. A crosslinked polymer network of high molecular mass is formed on the fibre, this being the mechanism necessary to achieve a soft finish of high durability.



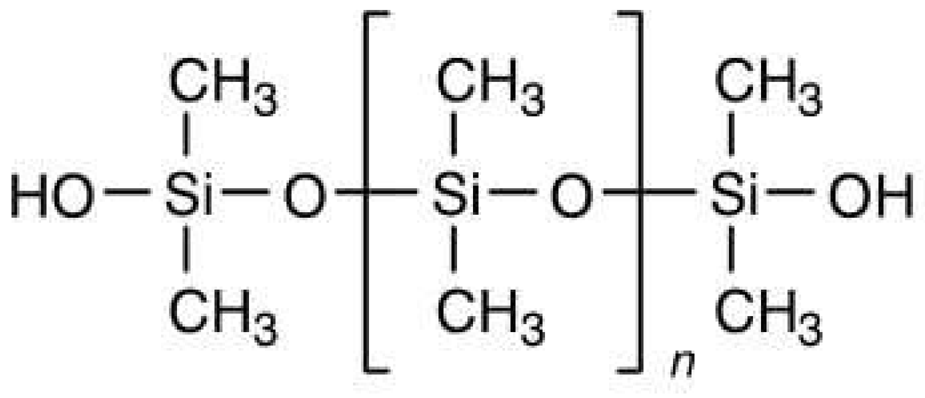
$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

10.226



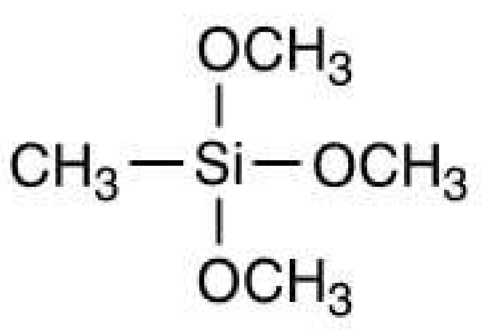
$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{H}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

10.227



$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-OH$$

10.228



$$CH_3-\underset{OCH_3}{\overset{OCH_3}{Si}}-OCH_3$$

10.229

The next development arose in the late 1970s with the introduction of aminofunctional silicone softeners. These contain aminoalkyl groups attached to the poly(dimethyl siloxane) backbone, leading to improved orientation and substantivity for the fibre [482]. This favourable orientation, illustrated in Figure 10.60, leads to an extremely soft handle, often described as 'supersoft'. These polymers are highly cost-effective, very small amounts being required to obtain the desired properties, thus giving both economic and environmental benefits. Indeed, such are the advantages of these products that they have assumed a dominant role in the marketplace. Mainly based on a single type of amino group, more than 90% of all commercially available aminosilicone softeners are in fact aminoethyliminopropyl silicones (10.230) [485].

The softening effect of silicones results from their lubrication behaviour that affects both the surface and the interior of the fibre. The behaviour of polysiloxanes of the 10.230 type can be varied by adjusting the average values of x and y and the range of chain lengths present. Further variations are possible by varying the R groups. In view of the technical and

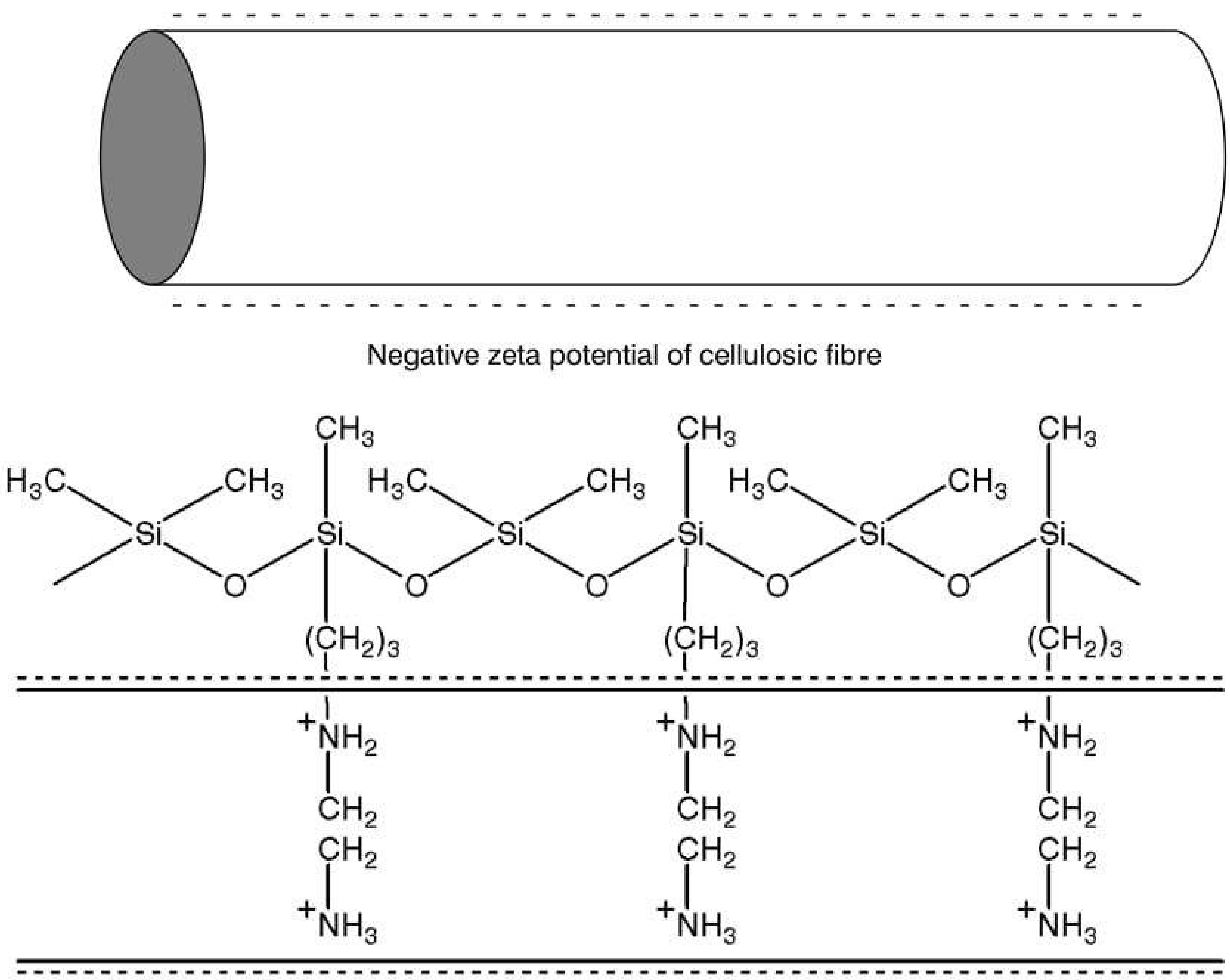
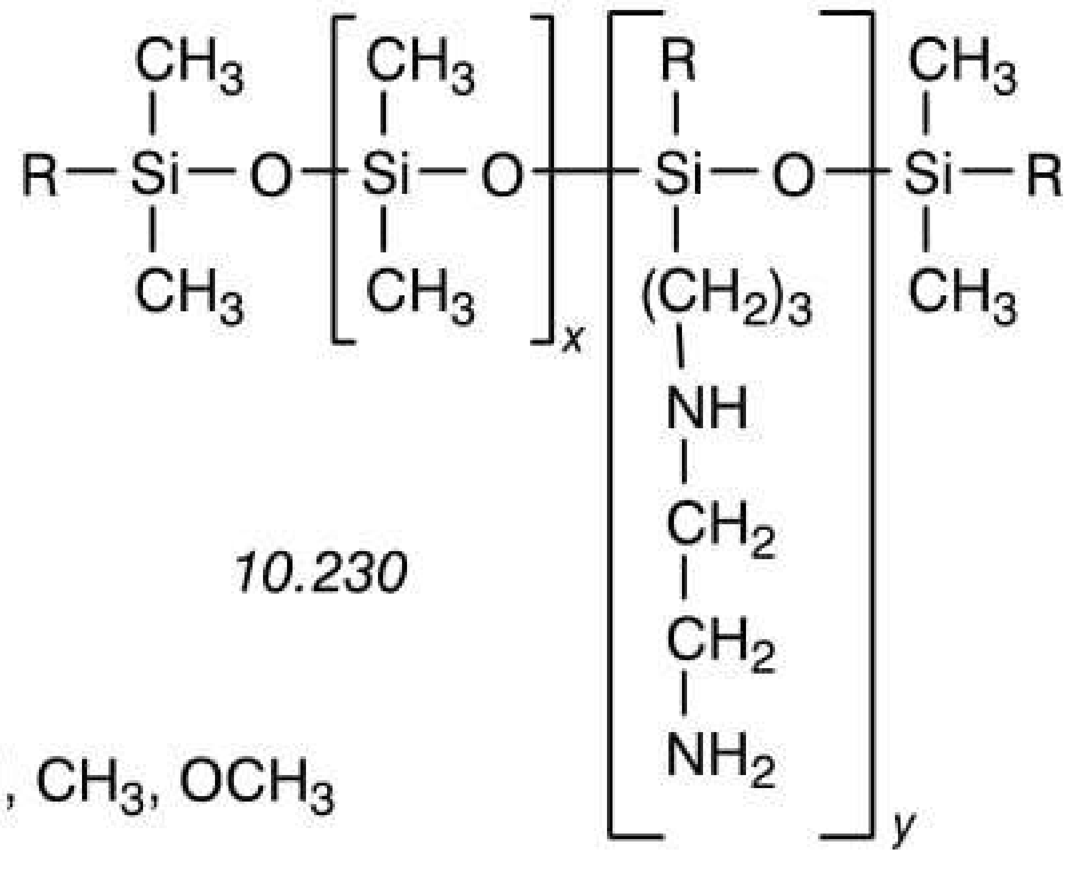


Figure 10.60 Attachment and orientation of an aminofunctional polysiloxane on a cellulosic fibre [482]



$$R-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_x-\left[\overset{R}{\underset{(CH_2)_3NHCH_2CH_2NH_2}{Si}}-O\right]_y-\overset{CH_3}{\underset{CH_3}{Si}}-R$$

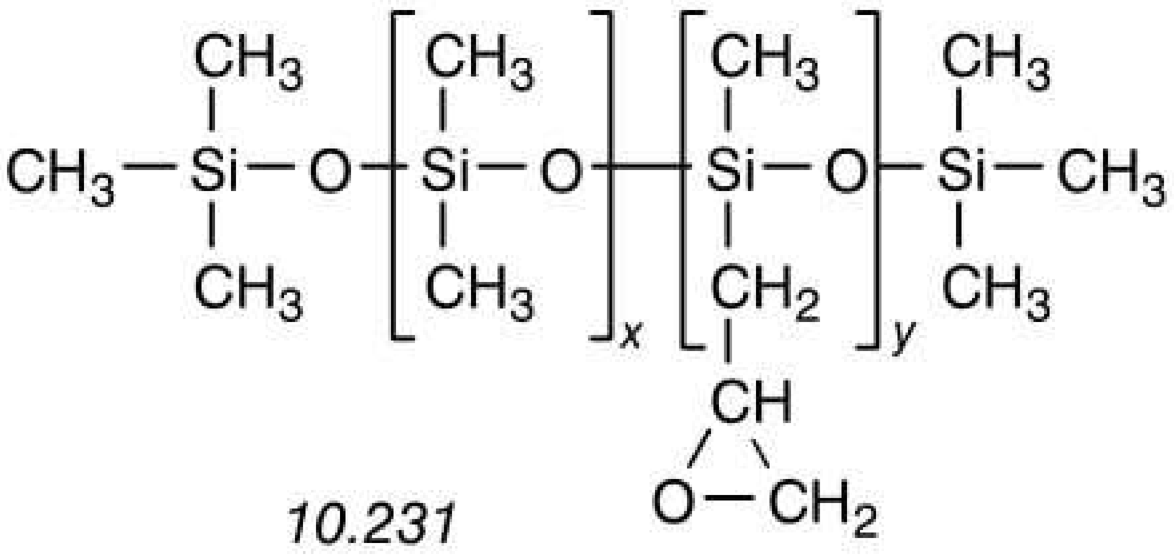
10.230

R = OH, CH_3, OCH_3

commercial importance of the aminofunctional polysiloxanes, it is worth exploring some structure/property relationships [485–489] even though there is as yet no conclusive correlation available for the most important aspect, that of softness as distinguished by tactile sensation.

The presence of the aminofunctional group appears to be necessary to obtain a 'supersoft' handle. In a study [488] of nineteen variants of the aminoethyliminopropyl polysiloxane structure (10.230) differing in amino group content (0 to 1.5 milli-eq./g), viscosity (300 to 21 000 mPas) and emulsion particle size (50 to 350 nm), good agreement was found between test parameters and amino group content, for which there was a strong substrate dependence. The cotton fabric softness showed a marked dependence on amino group content, giving an optimum value at about 0.3–0.4 milli-eq./g polysiloxane. Polyester/cotton blends (65:35 to 35:65) gave an optimum at about 0.2 milli-eq./g with a strong dependence on amino content, whereas a 100% polyester fabric showed a much weaker dependence together with a relatively high optimum at 0.5–0.6 milli-eq./g. Emulsion particle size and viscosity played subordinate roles, although it is known that very low viscosities (indicating short polymer chains) and very small particle sizes can be detrimental to softness effects under certain conditions.

Epoxyfunctional siloxanes are also useful as softeners. These may be derived from polysiloxane (10.231) or from aminopolysiloxanes (10.232). Further possibilities are represented by the polyalkoxylated epoxyfunctional silicones (10.233) and polyalkoxylated aminofunctional silicones (10.234). However, it has been pointed out [485] that the reaction of epichlorohydrin with aminopolysiloxanes is not very specific, since primary and secondary amine groups are usually randomly epoxidised resulting in viscous products that



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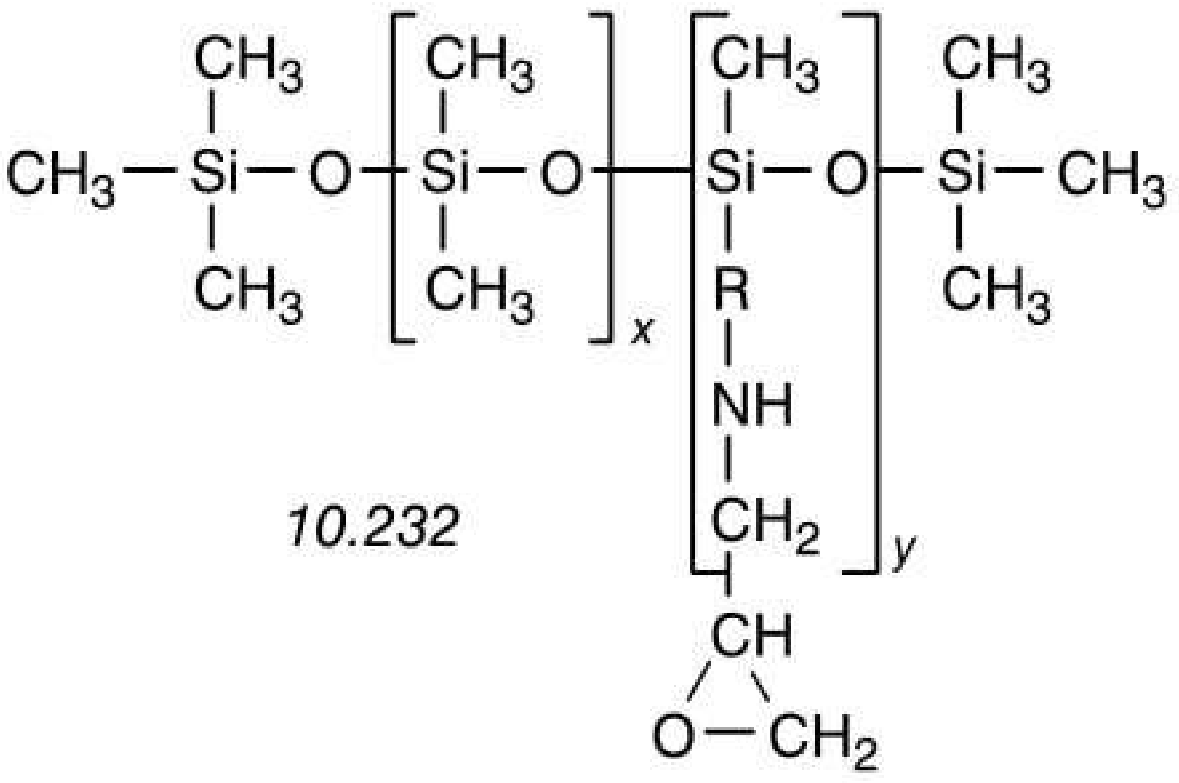

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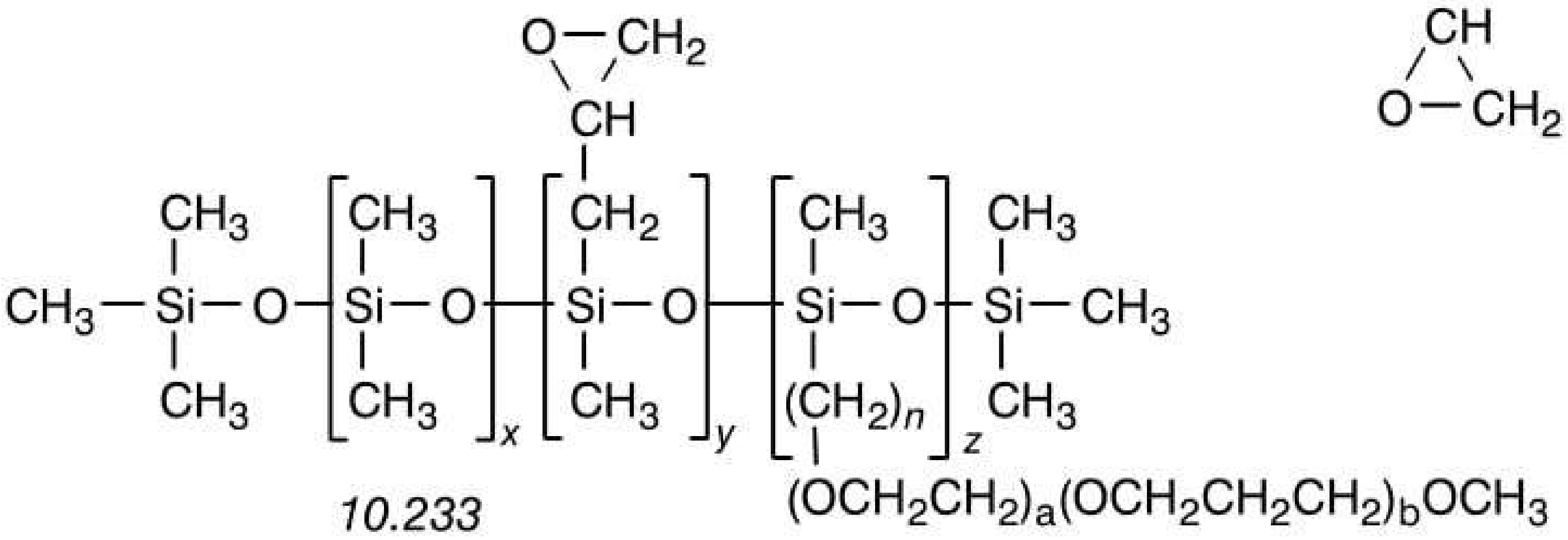

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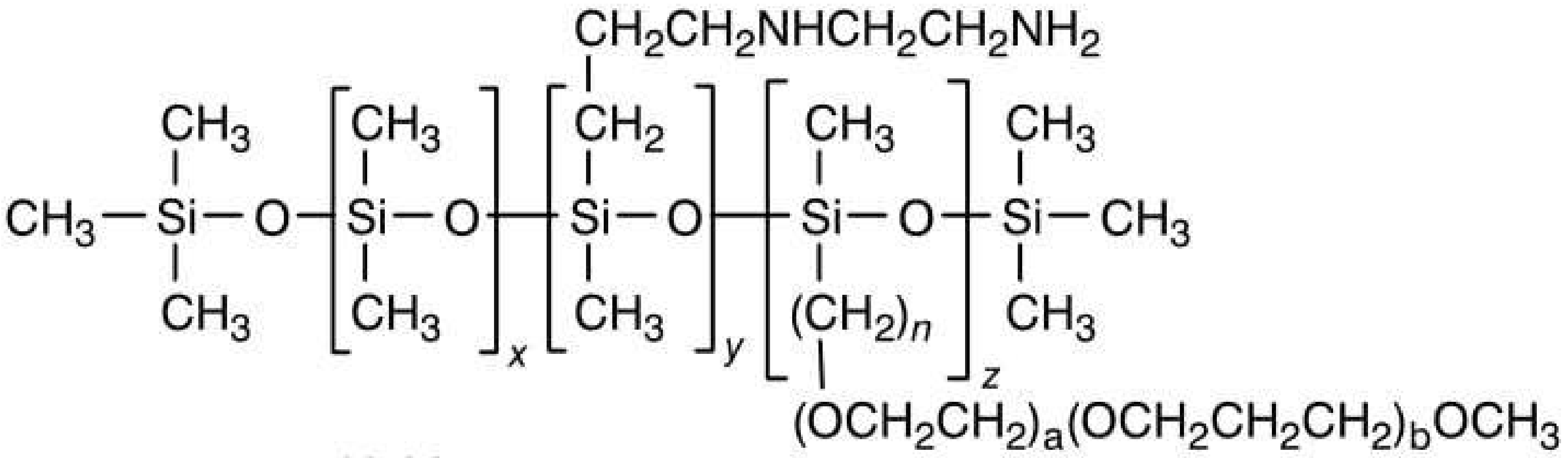
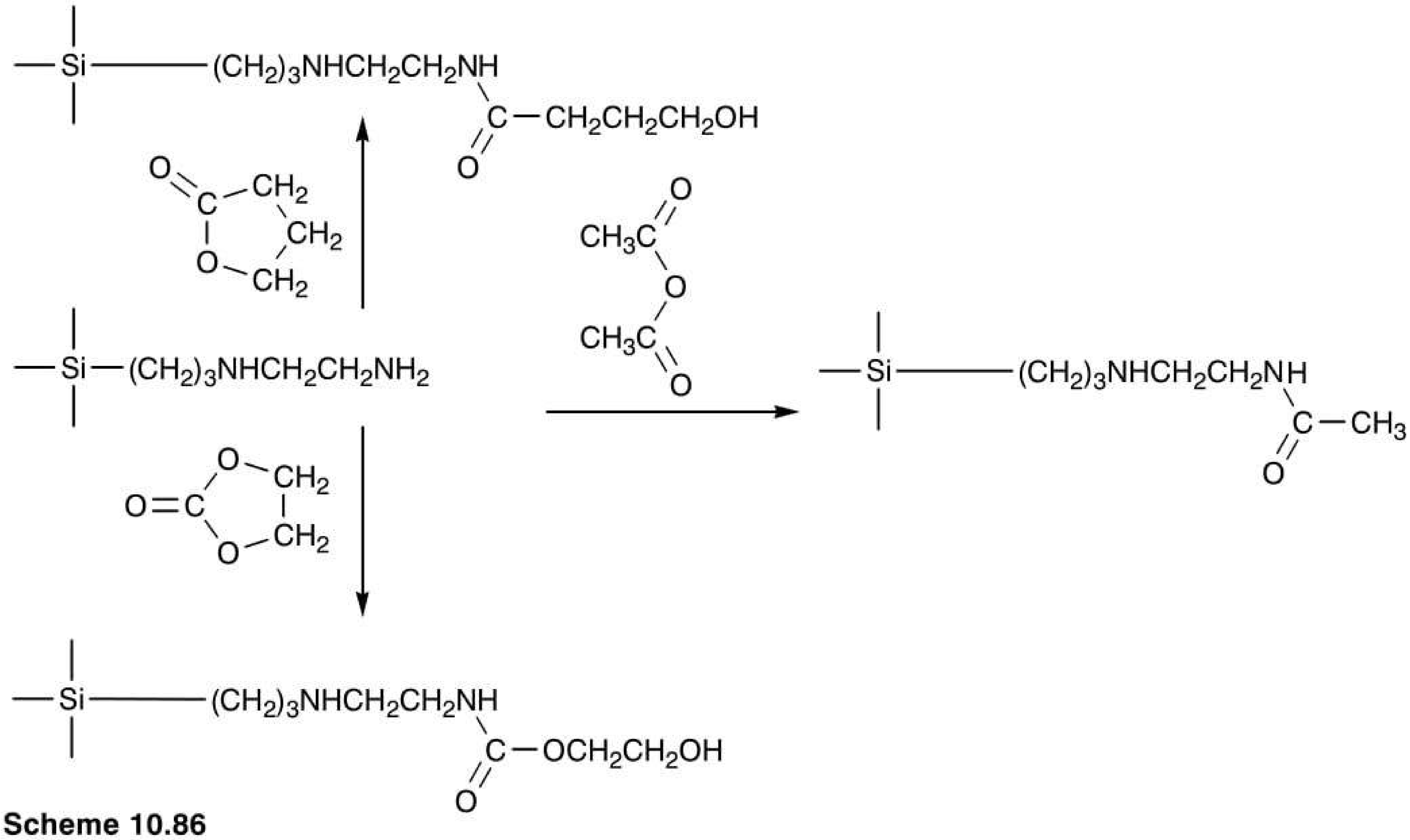


$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_x\left[\underset{CH_3}{\overset{CH_2CH_2NHCH_2CH_2NH_2}{\overset{CH_2}{Si}}}-O\right]_y\left[\underset{(OCH_2CH_2)_a(OCH_2CH_2CH_2)_bOCH_3}{\underset{(CH_2)_n}{\overset{CH_3}{Si}}}-O\right]_z\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}$$

10.234

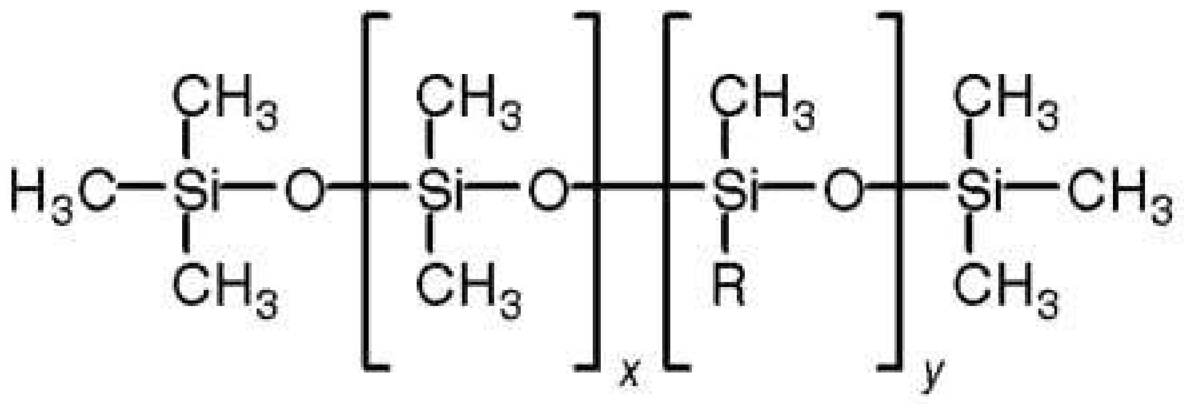
are difficult to emulsify. Thus they do not offer a significant improvement over the parent aminopolysiloxanes.

Promising products, offering a variety of structural possibilities, are obtained by acylation of aminopolysiloxanes [485]. Suitable acylating agents include anhydrides, lactones and carbonates (Scheme 10.86), of which acetic anhydride is the most economical. The optimum combination of effects is obtained by 30–70% acylation; more than 70% substitution can reduce the softening effect to the level associated with conventional poly(dimethyl siloxane). No significant differences have been observed with respect to handle, whiteness or water absorbency, depending on whether acylation is achieved using acetic anhydride, butyrolactone or ethylene carbonate as the acylating agent. A slight decline in softness of handle is observed with the acylated products compared with that from normal aminopolysiloxanes but this is compensated for by better whiteness, water absorbency and soil release properties. A major drawback of the standard aminoethyliminopropyl polysiloxanes is their tendency to show yellowing, resulting from the formation of chromogenic species by oxidative thermal decomposition of the aminofunctional group. Acylation largely overcomes this problem and also gives improvements in water absorbency and soil-release performance.



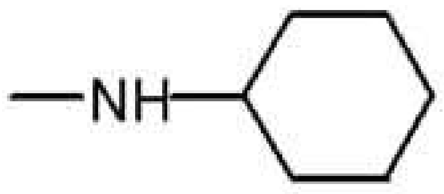
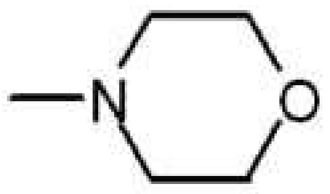
Scheme 10.86

Further fine tuning of the properties of aminopolysiloxanes can be achieved [485] by substitution of the siloxane units with primary, secondary or tertiary amino functions (10.235). Whiteness, water absorbency and soil release properties are improved with increasing degree of amino substitution from primary through to tertiary amines (Figure 10.61). The improvement in whiteness compared with the aminoethylimino reference product is particularly noteworthy, this being attributed to retardation of the oxidative thermal degradation because of the protective effect of alkylamino substitution. However, only the secondary amines show softness values as good as those of the aminoethylimino reference. The cyclohexylamino function, in particular, gives rise to a most useful



$H_3C-Si(CH_3)_2-O-[Si(CH_3)_2-O]_x-[Si(CH_3)(R)-O]_y-Si(CH_3)_2-CH_3$

10.235

Amine type	*R substituent*
Primary and secondary	$-NHCH_2CH_2NH_2$
Primary	$-NH_2$
Secondary	$-NHCH_3$
	$-NH(CH_2)_3CH_3$
	$-NH(CH_2)_{11}CH_3$
	
Tertiary	$-N(CH_2CH_3)_2$
	

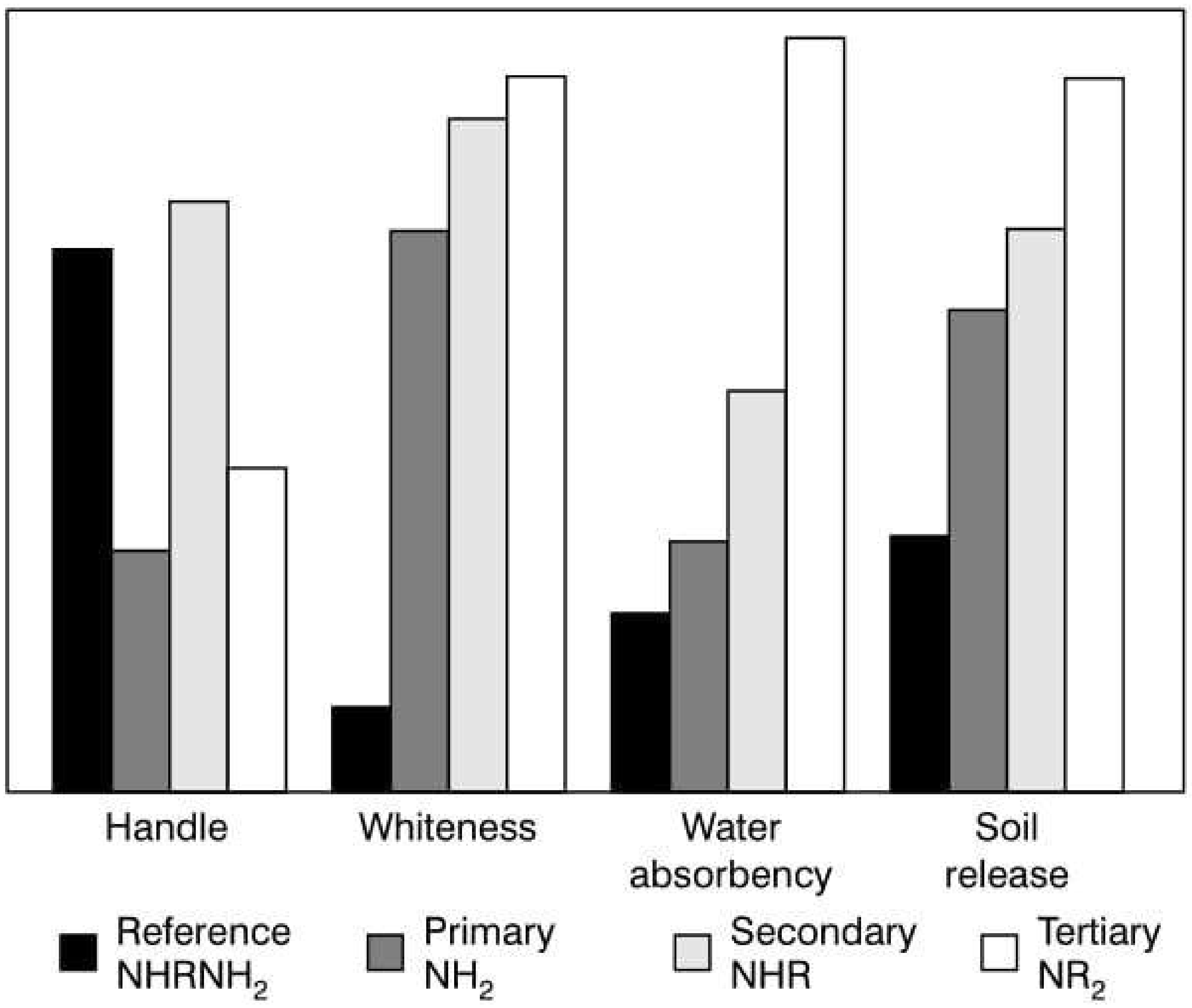
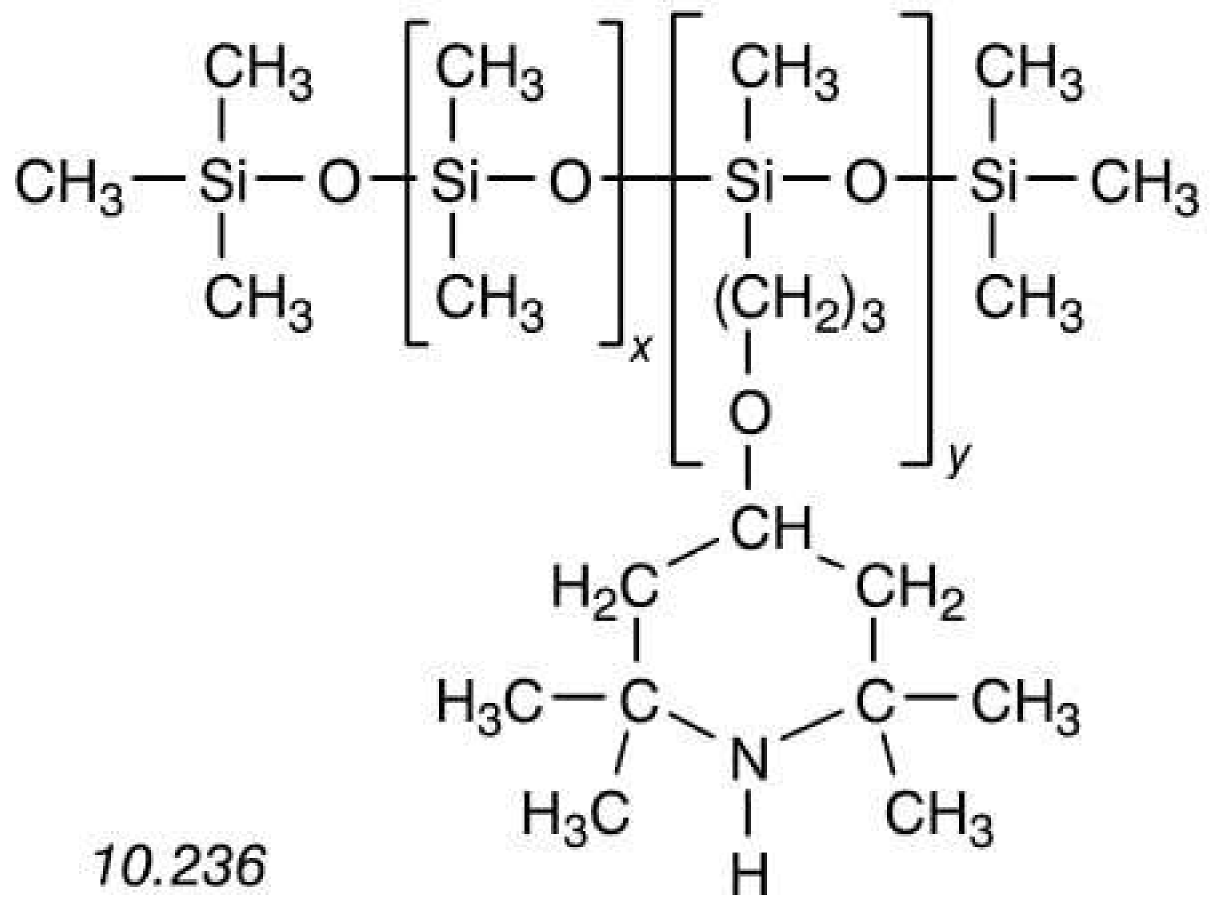


Figure 10.61 Effect of aminofunctional polysiloxanes on the physical properties of treated cotton fabric [485]



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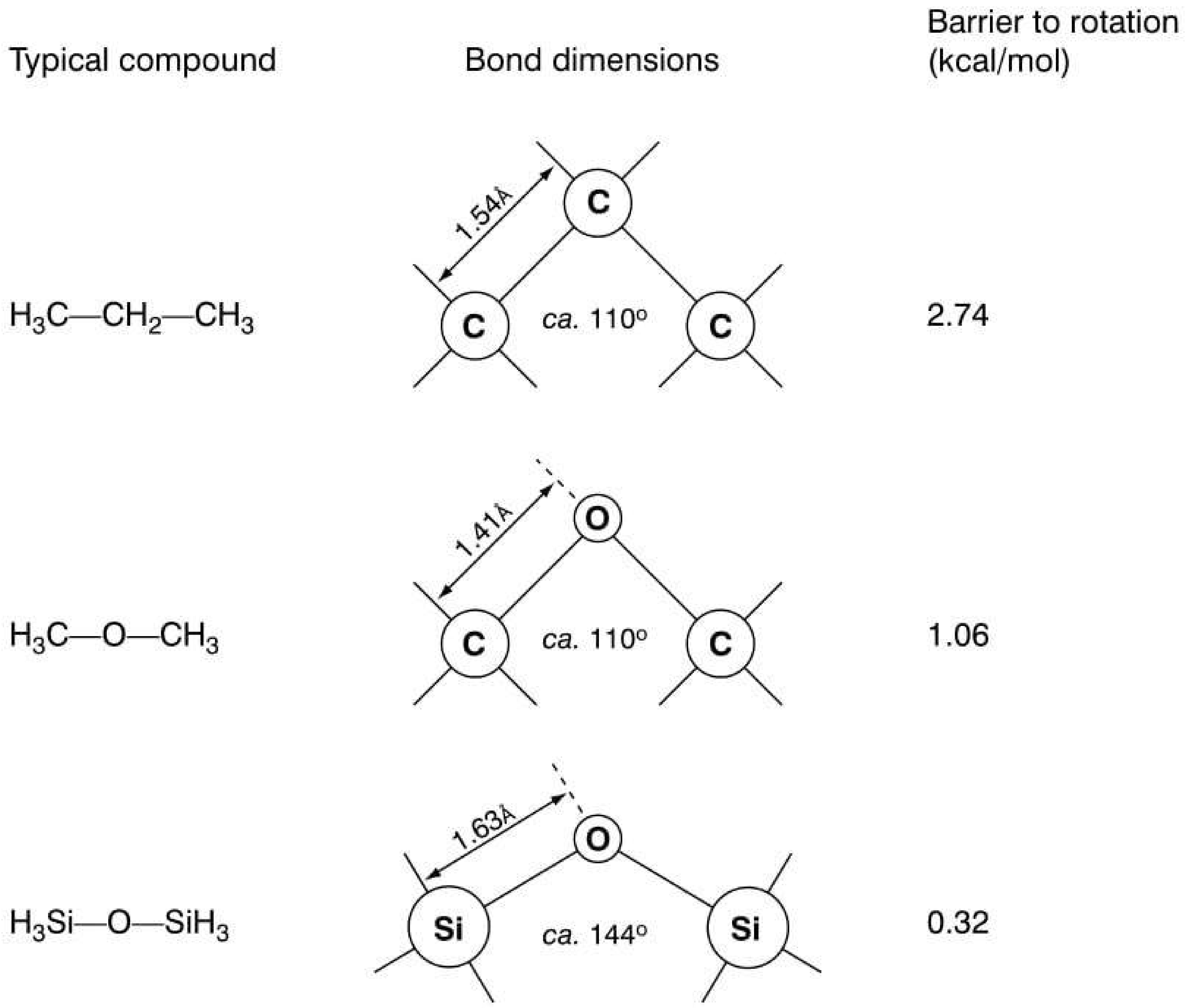


Figure 10.62 Molecular dimensions of alkane, ether and siloxane chain segments [489]

combination of effects: it gives optimum whiteness, as well as improved water absorbency and soil release (both properties superior to those of acylamino derivatives). In view of these results, it is not surprising to learn that hindered secondary amino substituents (10.236) also give rise to non-yellowing softeners [490].

An interesting attempt has been made to formulate a theoretical mechanism for the softening and fibre-substantivity characteristics of aminopolysiloxanes [489]. Their outstanding softening effects are the result of exceptionally high mobility of the polymer segments, this lubrication behaviour affecting both the surface and the interior of the fibre. Polyether chains are more flexible than polyalkyl chains, having a bond length of 1.41 Å and a bond angle of about 110° (Figure 10.62), thus providing a lower barrier to rotation.

Polysiloxane chains have a longer bond length and a larger bond angle, giving rise to an even lower barrier to rotation.

These softening agents have a binary nature; on the one hand there is the relatively hydrophobic polysiloxane backbone of the polymer, whilst on the other there is the aminoethyliminopropyl group capable of varying degrees of protonation. Increased protonation gives enhanced hydrophilicity and an increasing number of positive electrostatic charges. The hydrophobic backbone confers substantivity for hydrophobic fibres, whereas the protonated amino groups provide for electrostatic attraction to negatively charged fibres. These relationships are illustrated diagrammatically in Figures 10.63 to 10.68. In the case of poly(dimethyl siloxane) on cotton (Figure 10.63), the fibre–water hydrogen bonding forces are favoured and the weak polymer–fibre forces are inadequate to provide uniform deposition of a polymer film over the fibre surface. Thus the lubricating action to decrease fibre–fibre friction is inadequate and the handle of the finished fabric is firmer than untreated cotton.

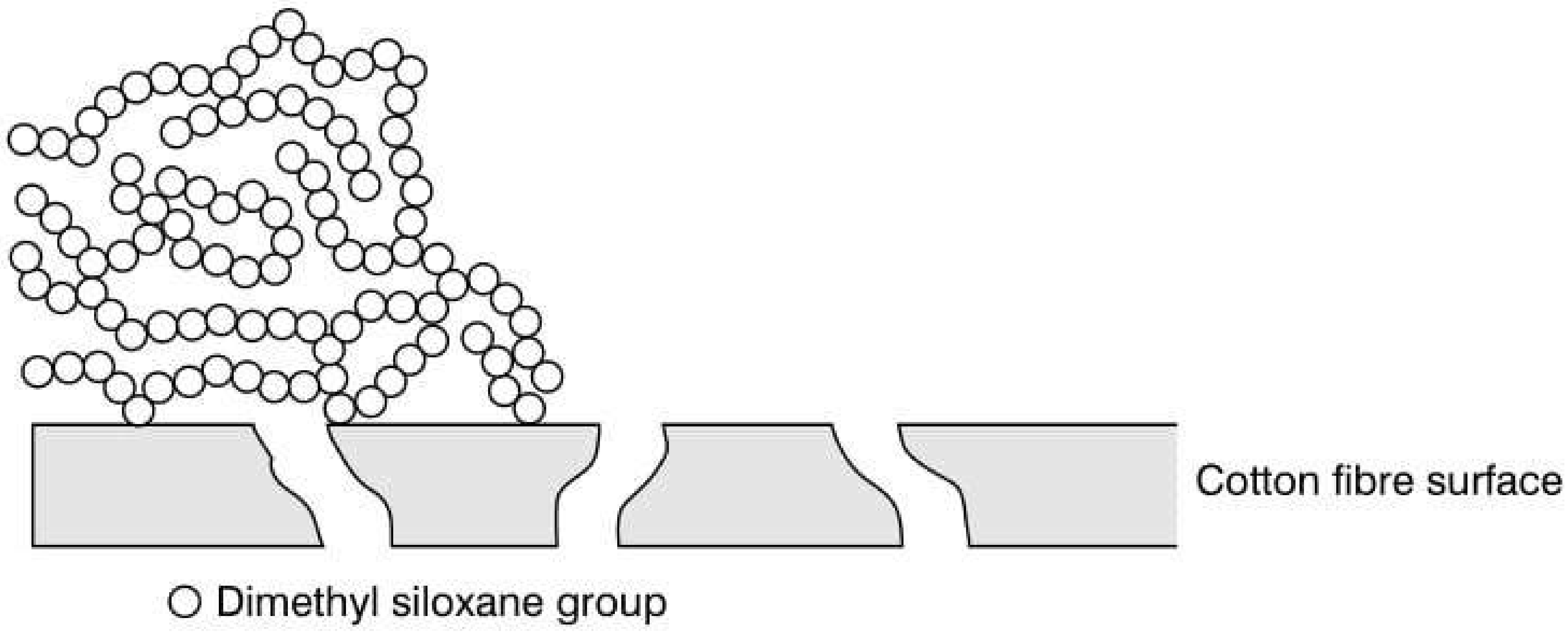


Figure 10.63 Poly(dimethyl siloxane) attached to cotton by weak polymer-fibre interactions [489]

Attachment to the cotton surface of an aminofunctional silicone containing relatively few partly protonated amino substituents is illustrated in Figure 10.64. The strong interaction between these groups and hydroxy groups in the cellulose does bring about some orientation of the silicone polymer segments close to the fibre surface but coverage of the latter is incomplete. The lubricating action of the polymer film, though more effective than in Figure 10.63, is somewhat limited and the fabric handle is not 'supersoft'. Figure 10.65 shows the much more effective distribution over the fibre surface of an aminofunctional silicone containing the optimum proportion of partly protonated amino substituents. Coverage is uniform and complete and the length of the silicone polymer segments between the anchoring amino substituents is sufficient to permit their high flexibility to contribute to optimum lubrication and a 'supersoft' handle. In the case of an aminofunctional silicone containing an excessive proportion of partly protonated amino groups (Figure 10.66), coverage is complete but the thin silicone film composed of short and inflexible polymer segments between the anchoring points is inadequate to provide a 'supersoft' handle.

Figure 10.67 indicates the probable distribution of a silicone containing the optimum content of aminoethyliminopropyl groups when applied to a polyester fibre surface. In this case the attachment is through hydrophobic polymer–fibre interaction and the mobility of the silicone chain segments is increased by electrostatic repulsion between neighbouring cationic groups. Dependence of softness of the treated polyester fabric on the proportion of

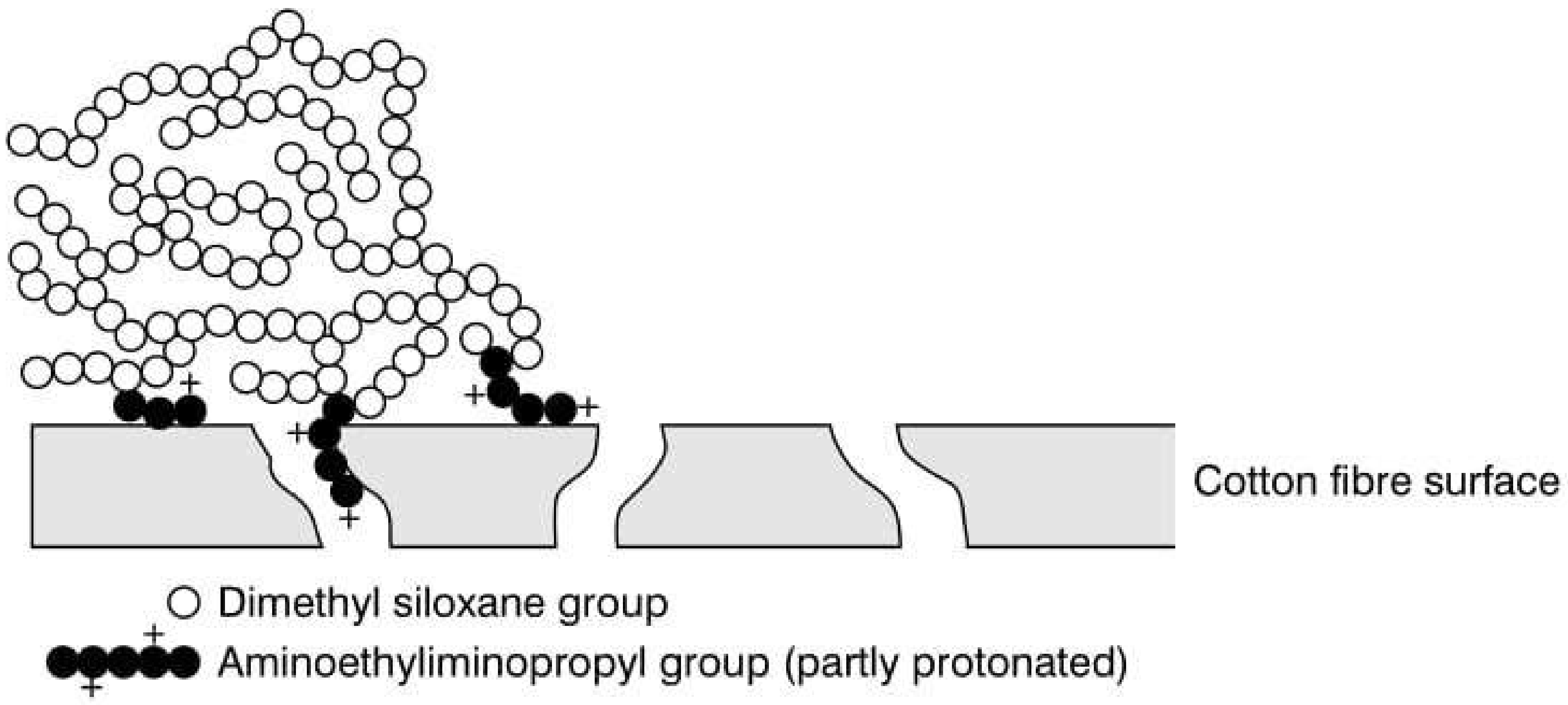


Figure 10.64 Aminoethyliminopropyl silicone attached to cotton by too few cationic amino groups [489]

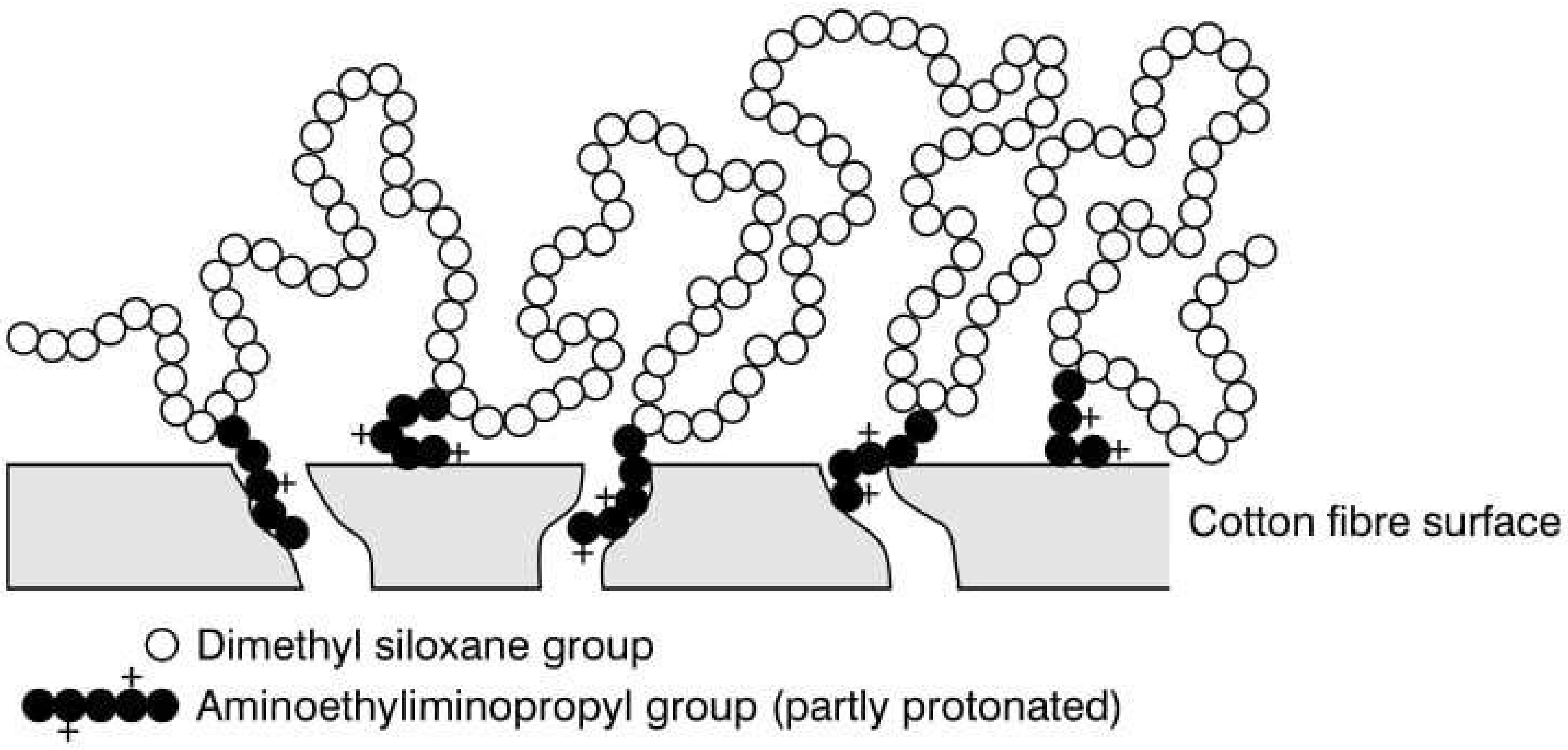


Figure 10.65 Aminoethyliminopropyl silicone attached to cotton by the optimum proportion of cationic amino groups [489]

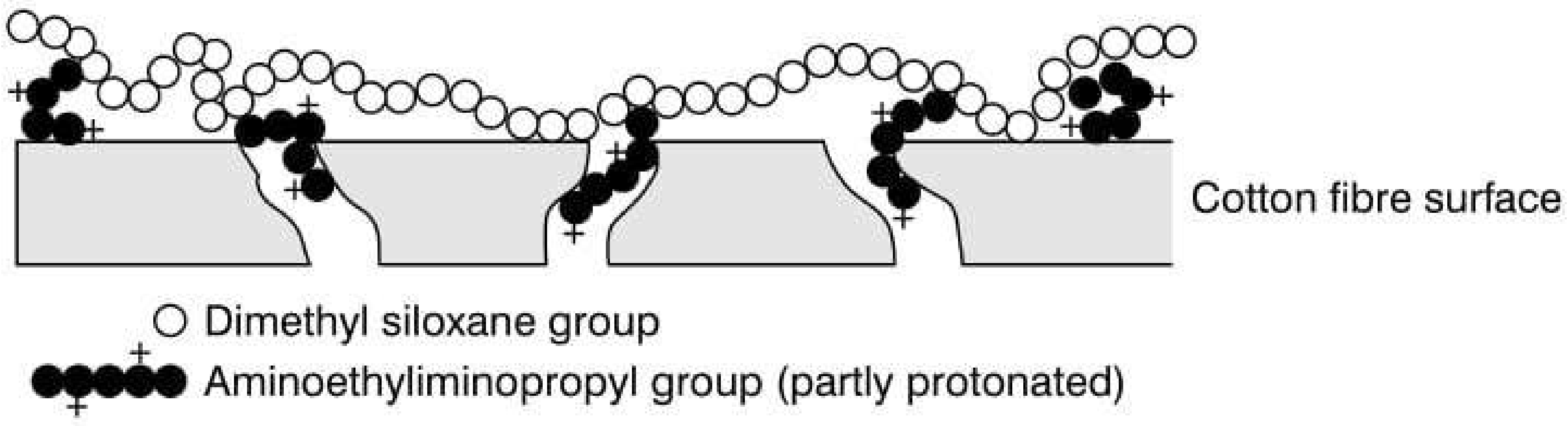


Figure 10.66 Aminoethyliminopropyl silicone attached to cotton by too many cationic amino groups [489]

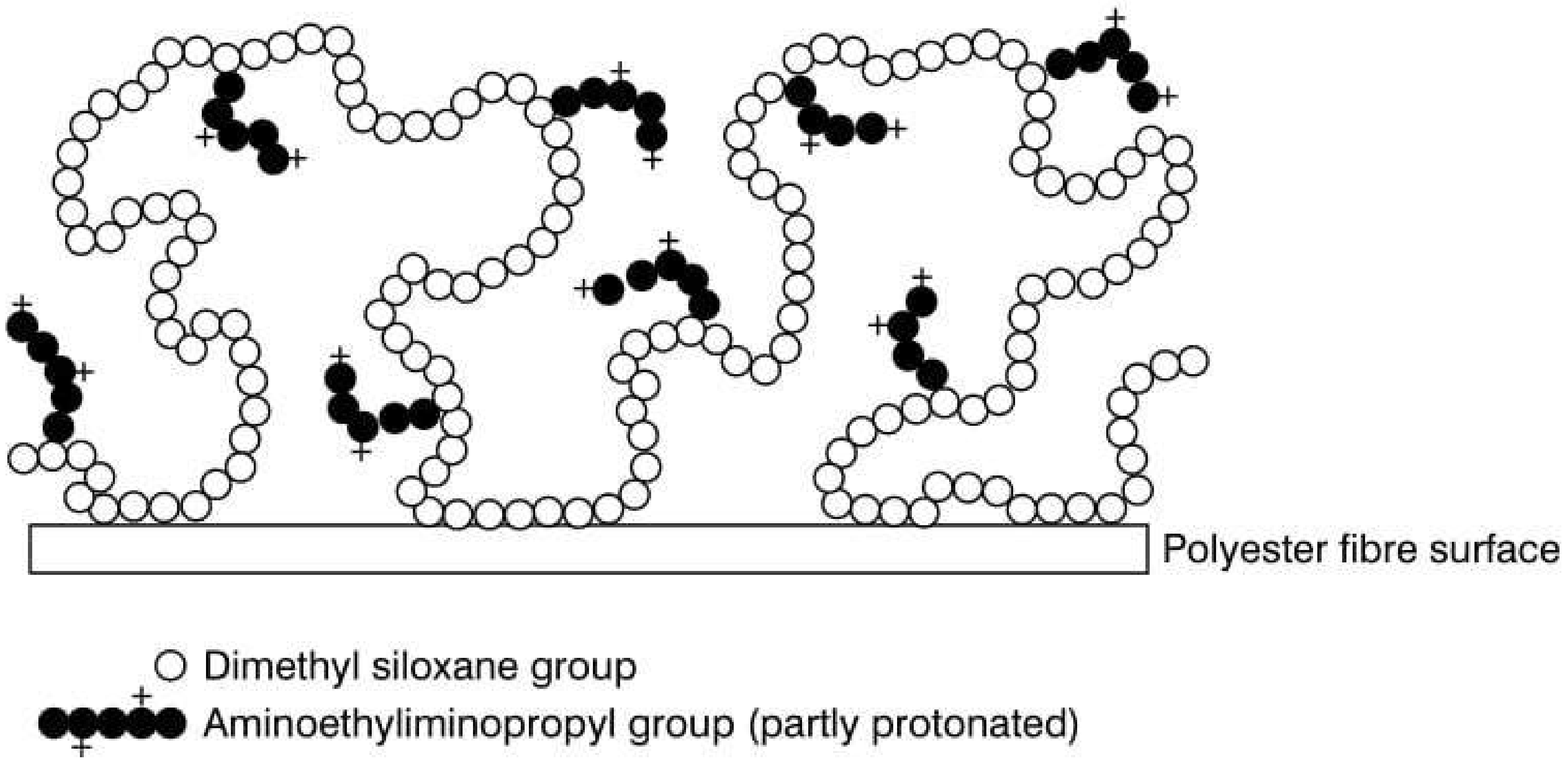


Figure 10.67 Probable orientation of an aminofunctional silicone on the surface of polyester [489]

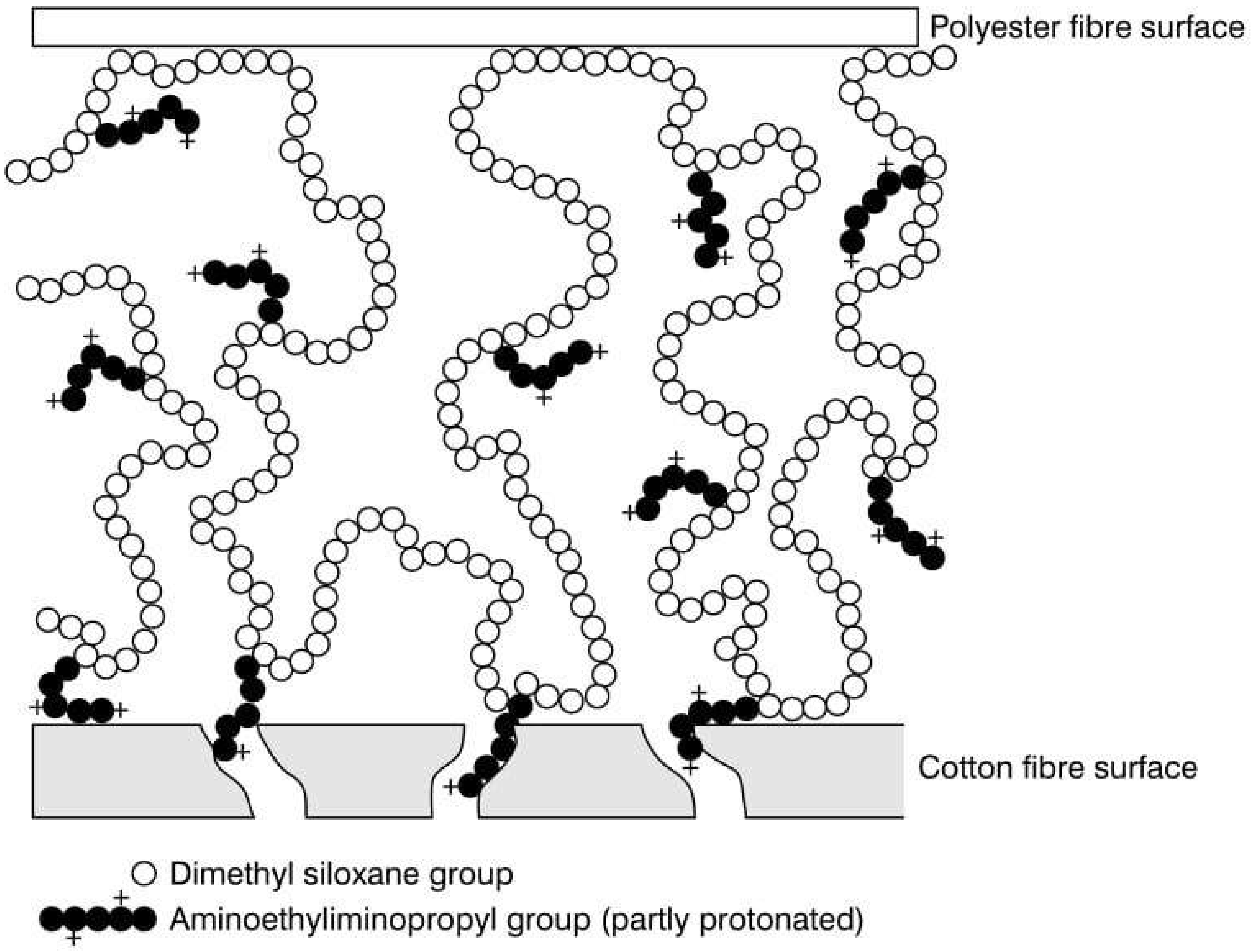


Figure 10.68 Probable orientation of an aminofunctional silicone between the surfaces of component fibres in a polyester/cotton blend [489]

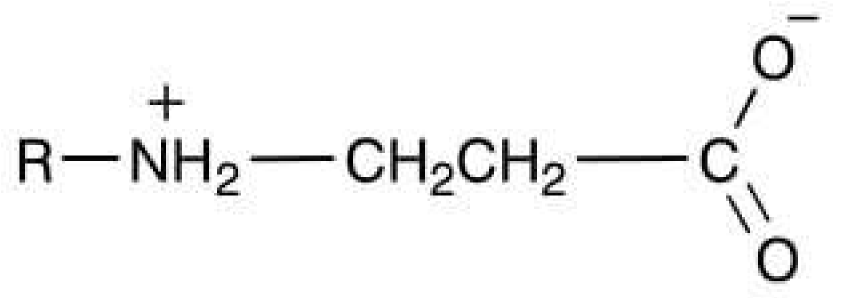
partly protonated amino groups present is less sensitive than in the case of cotton and the optimum level of softness is reached at a higher proportion on polyester than on cotton. These concepts are extended in Figure 10.68 to the behaviour of an aminofunctional silicone applied to a polyester/cotton blend fabric. Hydrogen bonding and coulombic forces of interaction between the partly protonated aminoethyliminopropyl groups of the silicone and hydroxy groups at the cellulose surface are reinforced by hydrophobic interaction between the dimethyl siloxane units and the polyester fibre surface. The mobility of the silicone polymer segments is favoured by electrostatic repulsion between neighbouring cationic groups and the optimum degree of softness is achieved at a relatively low proportion of these groups, somewhat less than the corresponding optimum on cotton.

Although fabrics made from microfibres generally have a softer handle and better drape than those from conventional fibres, these properties can be further improved to a significant extent by the application of silicone softeners, the best results being obtained with aminofunctional polysiloxanes [491].

Miscellaneous softening treatments

Many other products can be used as softeners but are less important commercially because of greater cost and/or inferior properties. Examples are anionic surfactants such as long-chain (C_{16}–C_{22}) alkyl sulphates, sulphonates, sulphosuccinates and soaps. These have rather low substantivity and are easily washed out. Nonionic types of limited substantivity and durability, usually applied by padding, include polyethoxylated derivatives of long-chain alcohols, acids, glycerides, oils and waxes. They are useful where ionic surfactants would pose compatibility problems and they exhibit useful antistatic properties, but they are more frequently used as lubricants in combination with other softeners, particularly the cationics.

Some amphoteric softeners such as amino acids (10.237) and sulphobetaines (10.238) are more effective and durable than the nonionic types but less durable than the cationics; moreover, they tend to be expensive. Other amphoteric types include the zwitterionic forms of quaternised imidazolines (10.239); long-chain amine oxides (10.240) also exhibit softening properties.



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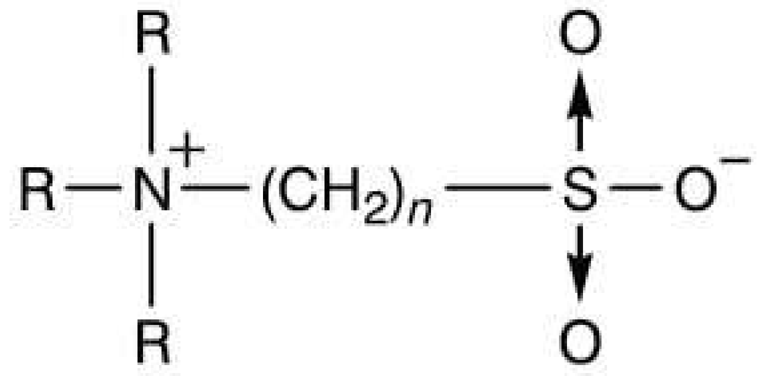

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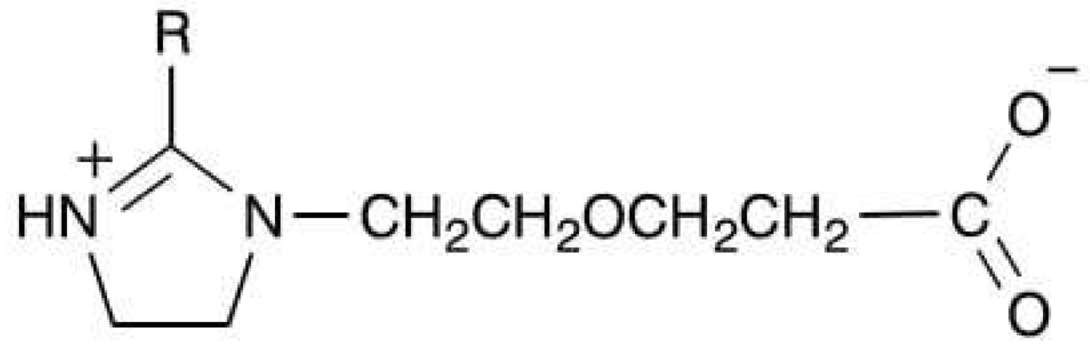

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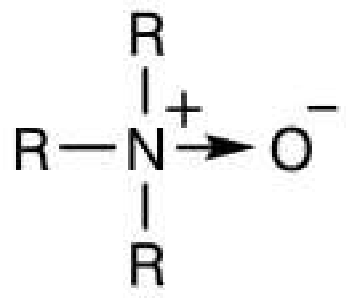
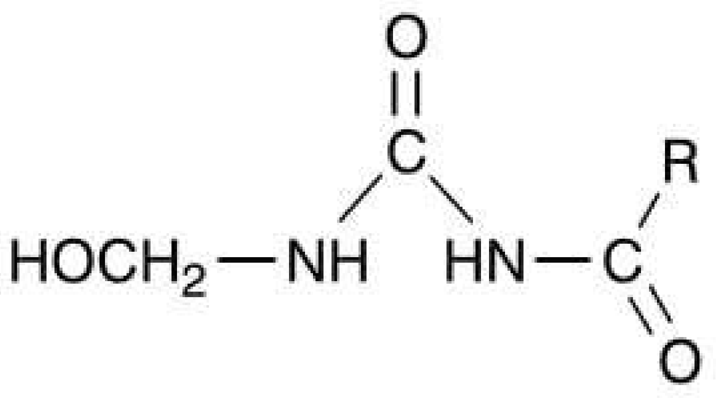


10.240

There are reactive softeners, some of which are *N*-methylol derivatives of long-chain fatty amides (10.241) while others are triazinyl compounds (10.242). The *N*-methylol compounds require baking with a latent acid catalyst to effect reaction, whereas dichlorotriazines require mildly alkaline fixation conditions. The *N*-methylol compounds are sometimes useful for combination with crease-resist, durable-press, soil-release and water-repellent finishes. In this context, the feasibility of using silane monomers such as methyltriethoxysilane (10.243), vinyltriethoxysilane (10.244), vinyltriacetylsilane (10.245) and epoxypropyltrimethoxysilane (10.246) in crosslinking reactions to give crease-resist properties and softness simultaneously has been investigated [492].



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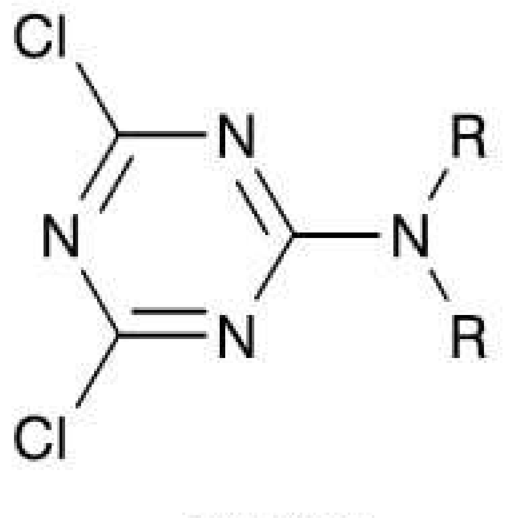

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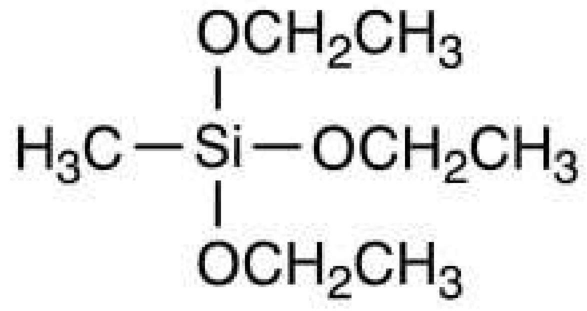

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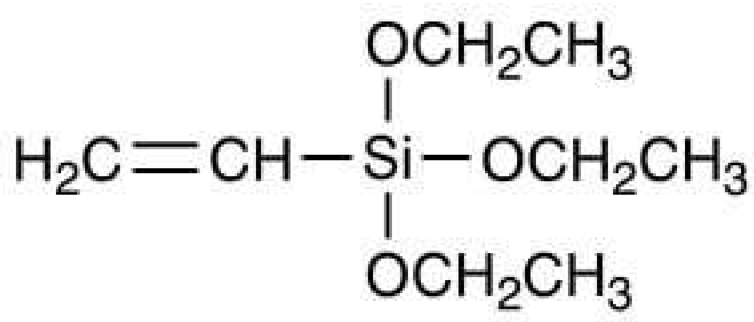

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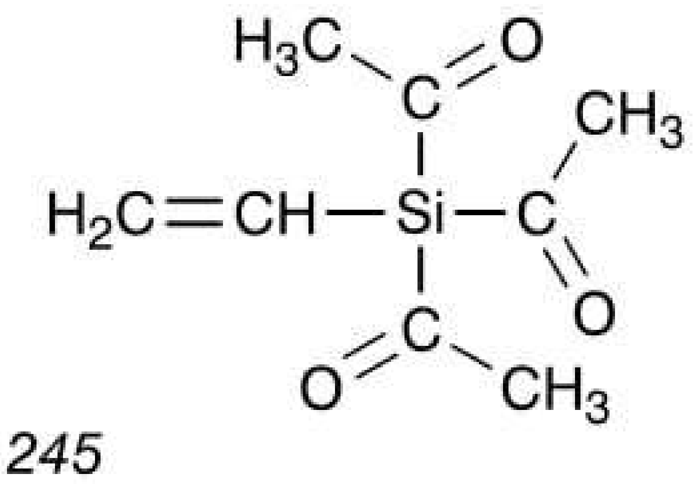

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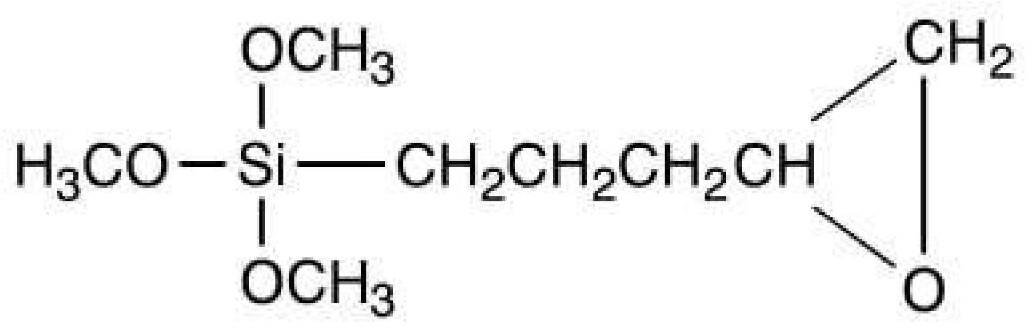


10.246

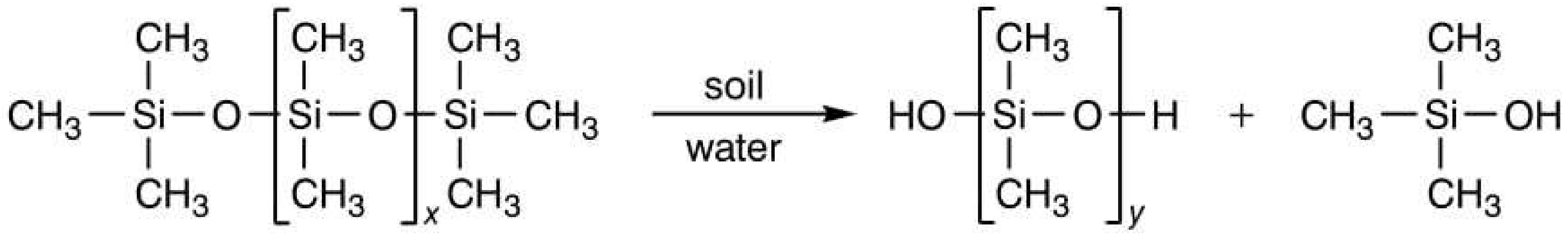
Softening treatments of a rather different nature include biofinishing enzyme treatments to modify the fabric surface. This has been dealt with already in section 10.4.2. Even more esoteric is the use of so-called telluric treatments using minerals (microliths) of precisely defined lithological and metamorphic properties. A detailed account of these complex materials is available [493]. In essence, an enzyme is micro-encapsulated within the mineral microlith. Under the action of strong mechanical forces this crystal structure is broken open, progressively releasing the enzyme. The process thus combines mechanical surface erosion of the textile with biochemical modification.

Environmental aspects of softening treatments

This account is concerned with environmental aspects of the application of softeners rather than their manufacture, although a discussion of environmental factors involved in the production of quaternary ammonium softeners is available [494]. Environmental aspects of cationic quaternary ammonium salts, nonionic surfactants and amphoteric compounds have been dealt with already in section 9.8.1. With regard to cationic quaternary softeners (Figure 10.56), it has been reported that the ester 10.221 can be considered to be biodegradable, in which respect it is superior to the tetra-alkylammonium salt 10.222 and the imidazolinium salt 10.223 [483]. A paradox has also been pointed out [494]: as the water solubility of quaternary compounds increases so does the rate of biodegradation and the fish toxicity, so that the requirement for the maximum rate of biodegradation can only be met by developing products that are more toxic to fish. Fish suffer through the interference of pollutants with gill breathing. In some mammals, however, there is a possibility of developing a subcutaneous toxicity that can cause neuromuscular problems and ultimately possible death. In this sense, quaternised silicone polymers can become highly toxic if certain neuronal distances are met, in the sense of a lock and key fit between them.

The environmental compatibility of silicone softeners is generally favourable [495,496]. The discussion here concerns only the silicone component of the formulation and not the supporting emulsifying system. For the most part this is nonionic, preferably based on linear ethoxylated fatty alcohols, although alkylphenol ethoxylates are still used in some countries [496]. The salient points regarding the environmental influence of silicones can be summarised as follows:

(1) Silicones are a minor part of discharges to waste waters.
(2) Although highly resistant to biodegradation by micro-organisms, poly(dimethyl siloxane) derivatives are very effectively degraded via natural chemical processes [495] such as catalysed hydrolysis and oxidation during soil contact to produce siloxanols and silanols of lower molecular mass (Scheme 10.87). These are then susceptible to both biological and abiotic decomposition, ultimately oxidising to natural silica.



Scheme 10.87

y = mainly 1

(3) Silicones are ecologically inert, having no effect on aerobic or anaerobic bacteria. Thus they do not inhibit the biological processes taking place during waste water treatment.
(4) Non-volatile silicones do not bioconcentrate in aquatic media. Their large molecular size prevents them from passing through the membranes of fish or other aquatic creatures. They readily become attached to particulate matter and are effectively

removed by the natural cleansing process of sedimentation. Elimination rates from sewage sludge are very high.

(5) Silicones give insignificant BOD values. Tests on aquatic plant and animal life revealed no measurable adverse effects even under highly exaggerated conditions. No significant change in growth rates of algae, plankton or other marine organisms has been found.

(6) Silicones have not been found to pose a threat to insects or birds.

(7) Volatile silicones are broken down by oxidative chemical processes on entering the atmosphere. The partially oxidised degradation products are less volatile and these are scrubbed out of the atmosphere by rain or deposited on the ground to be further diluted and degraded, the final products being natural silica, carbon dioxide and water.

(8) Volatile methylsiloxanes degrade quickly, the atmospheric lifetime being 10 to 30 days, and have no potential to interfere with the ozone layer.

(9) There is no risk of forming compounds that contribute to AOX values.

(10) Formaldehyde can be produced only if the degradation temperature exceeds 200 °C and even then the amounts produced are significantly less than those from carbon–carbon polymers containing methyl groups.

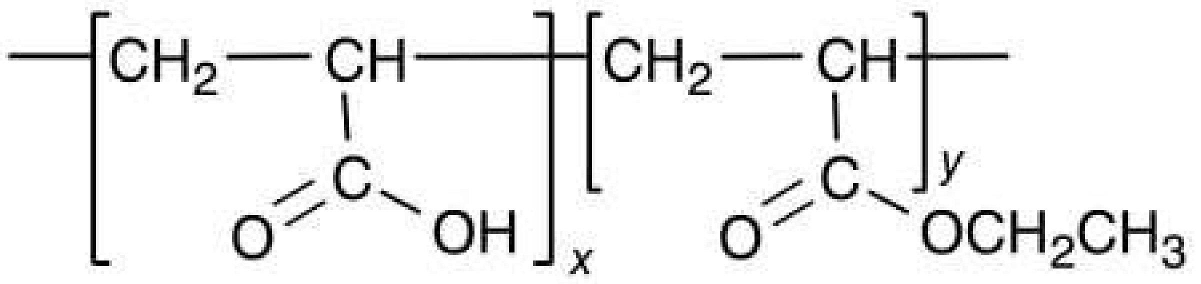
10.10.4 Soil-release, soil-repellent and water-repellent agents

Agents to protect against soiling were developed following the increasing use of hydrophobic fibres, particularly nylon and polyester, since experience demonstrated the tenacity of oily stains and oil-bound dirt for these fibres. Durable press cotton fabrics also tended to soil more easily than untreated fabrics. The subject of soiling and soil removal is more complex than might at first appear [476,497–500] and involves such aspects as soil resistance, soil adsorption, detergency, soil removal and soil re-deposition. We are concerned essentially with soils attracted to, and bound mainly at the fibre surface, as opposed to particulate dirt trapped within the interstices between fibres in the yarn. The primary objective is to modify the fibre surface (a) to increase the resistance of the fibre to soiling in the first place (soil repellency) and (b) to ensure that any soil that is deposited is more weakly bound and is hence more easily removed in washing (soil release). Most soils, as expected from a predominantly hydrophobic interaction, are held mainly by nonpolar bonding, although electrostatic forces may come into play with, for example, coloured anionic stains from food and beverages.

The essence of any soil-resistant treatment is to render the surface of the fibres more hydrophilic. It also helps if the coating of the fibre is such as to reduce surface irregularity and surface energy. Whilst the two aspects of soil repellency and soil release are interrelated, the actual balance of these properties varies from finish to finish according to requirements. In carpet treatments for example, which are normally given a shampoo rather than washed, the emphasis must be on repellency, whereas soil release becomes of much greater importance in textiles that are frequently washed.

Early soil-release agents, applied particularly to resin-finished cellulosic goods, were water-soluble polymers, many being related to thickeners (section 10.8) such as starch, hydroxypropyl starch, sodium carboxymethylcellulose, methylcellulose, hydroxyethylcellulose, alginates, poly(vinyl alcohol) and poly(vinylpyrrolidone). These functioned essentially as temporary barriers and 'preferential reservoirs' for soil, which was thus easily removed along with the finish in subsequent washing, when they then helped to minimise re-deposition. Obviously these finishes were only temporarily effective. More durable finishes have been developed and these are generally classified in three groups according to whether they feature (a) carboxyl groups, (b) oxyethylene and/or hydroxy groups and (c) fluorocarbon moieties. The fluorocarbon finishes in particular have also been developed as water-repellent treatments.

The carboxylated polymers [476,499] include acrylic, methacrylic or maleic acid polymers (all obviously anionic in character) applied mainly from aqueous emulsion and particularly in combination with crease-resist or durable press resins. This type of chemistry has already been discussed in section 10.8.2. A particularly common example is the copolymer of acrylic acid with ethyl acrylate (10.247). In general the best balance of properties is obtained with 75–85% ethyl acrylate (y) and 25–15% acrylic acid (x), with an average chain length of about 1300 (x + y) units; 65–85% ethyl acrylate with 35–15% methacrylic acid is also suitable. When the content of the acidic comonomer increases above about 30% the durability to washing tends to decrease, whilst longer chains tend to give a stiffer handle [499].

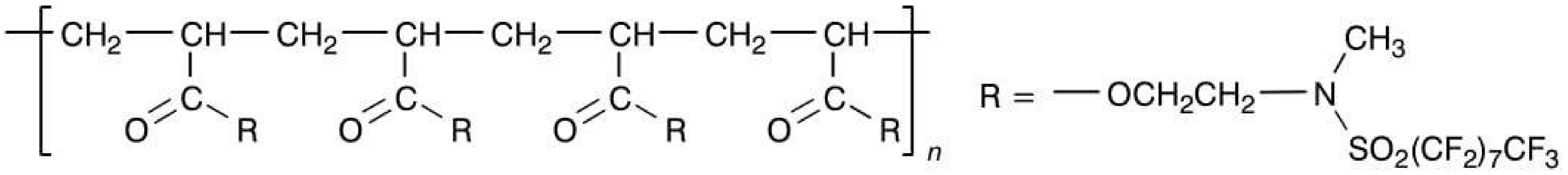


10.247

Soil-release products containing oxyethylene or hydroxy groups may be anionic or nonionic. Many less durable water-soluble polymers have been mentioned already, such as the hydroxy-containing finishes poly(vinyl alcohol), starch, and derivatives of starch or cellulose. When applied together with *N*-methylol reactants, as in easy-care finishing, they give more durable soil-release properties. Typical of the oxyethylene-containing compounds are poly(ethylene glycol) and poly(ethylene oxide) adducts of carboxylic acids, amines, phenols and alcohols, which may be combined with hydroxy-reactive functional agents as used in easy-care finishes, such as *N*-methylol reactants or isocyanates.

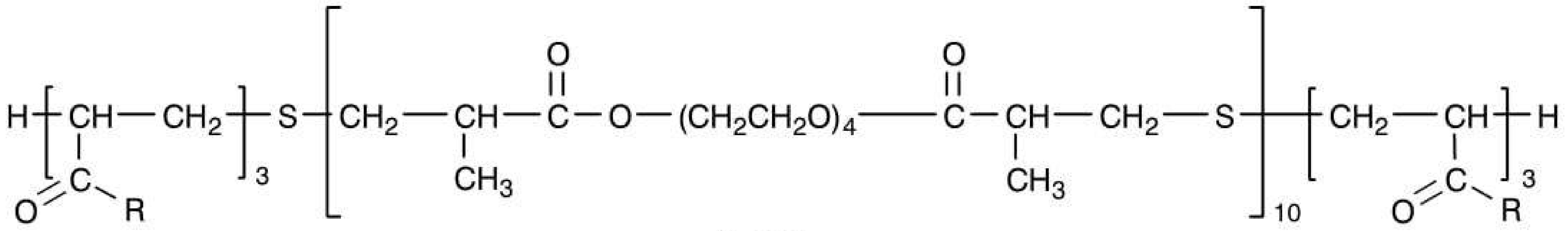
Essentially nonionic soil-release agents comprise polyesters, polyamides, polyurethanes, polyepoxides and polyacetals. These have been used mainly on polyester and polyester/cellulosic fabrics, either crosslinked to effect insolubilisation (if necessary) or by surface adsorption at relatively low temperature. Polyester soil-release finishes have been most important, particularly for polyester fibres and their blends with cellulosic fibres. These finishes, however, have much lower relative molecular mass (1000 to 100 000) than polyester fibres and hence contain a greater proportion of hydrophilic hydroxy groups. They have been particularly useful for application in laundering processes. These essentially nonionic polymers may be given anionic character by copolymerising with, for example, the carboxylated polymers mentioned earlier; these hybrid types are generally applied with durable press finishes.

Polyfluorinated chemicals now dominate in the fields of oil-repellent and water-repellent finishes. The earlier so-called conventional polyfluorinated products were of the type represented by poly(*N*-methylperfluoro-octanesulphonamidoethyl acrylate)(10.248) [499]. Such products presented a shield of closely packed fluoroalkyl groups at the fibre–air interface, thus giving low-energy surfaces with excellent oleophobicity. These showed excellent resistance to oil-based stains but were less satisfactory as soil-release agents during washing. The soil-release properties were subsequently considerably improved by copolymerising these conventional fluorochemicals with hydrophilic moieties [476,498,499] to give so-called hybrid block copolymers represented schematically by A–B–A–B–A–, where A represents the perfluoroalkyl-containing segment and B the hydrophilic segment. A typical example [498,499] is represented by structure 10.249, which is composed of alternating perfluorinated units of the type shown in structure 10.248 with hydrophilic oxyethylene moieties derived from the thiol-terminated copolymer of tetra-ethylene glycol dimethacrylate and hydrogen sulphide (10.250).



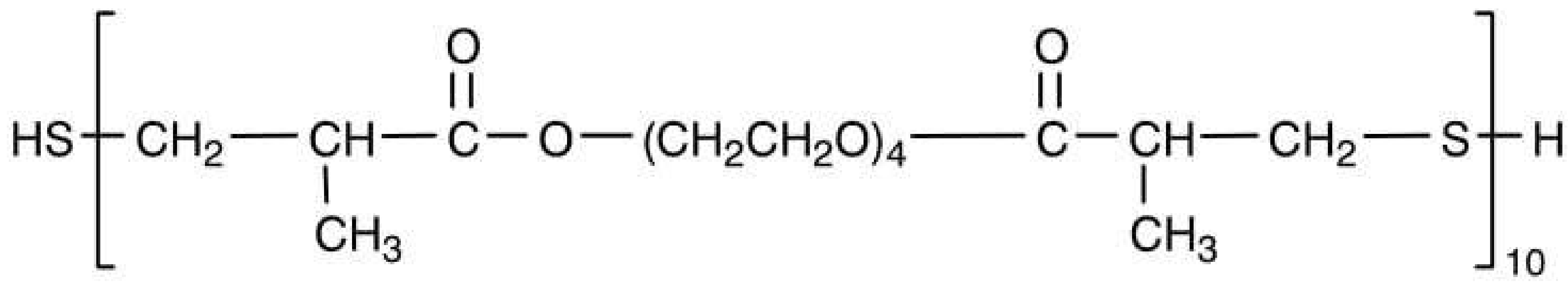
$$-\!\left[CH_2-CH(COR)-CH_2-CH(COR)-CH_2-CH(COR)-CH_2-CH(COR)\right]_n\!-\qquad R = -OCH_2CH_2-N(CH_3)SO_2(CF_2)_7CF_3$$

10.248



$$H\!\left[CH(COR)-CH_2\right]_3\!-S-\!\left[CH_2-CH(CH_3)-C(=O)-O-(CH_2CH_2O)_4-C(=O)-CH(CH_3)-CH_2-S\right]_{10}\!-\!\left[CH_2-CH(COR)\right]_3\!-H$$

10.249



$$HS-\!\left[CH_2-CH(CH_3)-C(=O)-O-(CH_2CH_2O)_4-C(=O)-CH(CH_3)-CH_2-S\right]_{10}\!-H$$

10.250

Once again these are only average schematic structures, in this case representing a block copolymer of alternating segments. The hydrophilic segments in themselves show no significant oil repellency and are not very effective as soil-release agents, yet when incorporated into such hybrid structures they considerably improve the soil-release properties without inhibiting the inherent soil-repellency of the perfluorinated segments. This is said [499] to result from the capability of these hybrid polymers to orient a specific moiety at the surface, depending on the polarity of the fibre–environment interface. Thus in air the fibre–air interface is dominated by the closely packed perfluoroalkyl chains, promoting good oil repellency, whilst in aqueous wash liquors it is the hydrophilic segments that orient at the fibre–liquid interface, thus enhancing soil release. In either case the non-active moiety is said to be collapsed below the surface. In this way, the lowest interfacial energy, with respect to the particular environment, is attained in both cases.

The example used here incorporated a perfluorinated polyacrylate and a poly(oxyethylene) hydrophilic moiety. Other fluorochemical and hydrophilic moieties can be used providing they display similar alternating surface orientation characteristics with respect to air and water. The essential character of the hydrophilic unit is that it should have polar groups capable of strong interaction with water, preferably by hydrogen bonding; examples are hydroxy, carboxyl and ether oxygen. Usually C_5–C_{18} perfluoroalkyl groups are used, but individual products may contain a mixture of homologues. Thus there is tremendous scope for designing a great variety of these complex copolymers.

It is now opportune to consider the structure–property relationships of fluorochemical finishes in more detail [501,502]. Water repellency depends mainly on reducing the critical surface energy of the fabric surface. This parameter must be less than that of the wetting liquid in order to create a physico-chemical barrier against penetration of the fabric by the liquid. Table 10.47 gives critical surface energies for various chemical groups at the surface of a fibre from which it can be seen that the CF_3 group is by far the most effective for lowering this surface energy. Table 10.48 lists surface tension values of some liquids and surface energy values of various fibres.

Table 10.47 Critical surface energies for low energy surfaces [502]

Chemical groups on the surfaces	Surface energy (mN/m) at 20 °C
$-CF_3$	6
$-CF_2-$	18
$-CH_3$	21
$-CH_2-$	31

Table 10.48 Surface tension of a range of liquids and surface energies of a range of textile fibres [502]

Liquid	Surface tension (mN/m) at 20 °C	Textile fibre	Surface energy (mN/m) at 20 °C
Water	72	Nylon	46
Peanut oil	40	Wool	45
Olive oil	32	Cotton	44
Petrol	26	Polyester	43
n-Octane	22		
n-Heptane	20		
Fluorocarbons	10–15		

It is evident from these two tables that a high density of CF_3 groups at the fibre surface will lower the critical surface energy sufficiently to create a barrier to penetration of all the liquids listed, particularly against water. It is also evident that perfluoroalkyl groups are essential to guarantee resistance to oily liquids. Thus the presence of CF_3 terminal groups is crucial. Equally important, however, is the overall structure of the molecule [502]; the perfluorinated segments should be long enough to maximise the CF_3 group density on the surface. It is this aspect that polyacrylic and polyurethane supporting structures have been able to satisfy, the longest chains producing the lowest surface energies (Figure 10.69). The results shown in Table 10.49 show how an increase in the perfluorinated segment length gradually enhances the resistance to oils and, to a lesser extent, to water. It is these considerations that have led to the preferred use of perfluoro-octyl or longer perfluorinated segments. Silicone emulsions, by comparison, typically give a surface tension of 25 mN/m and hence act only as water repellents.

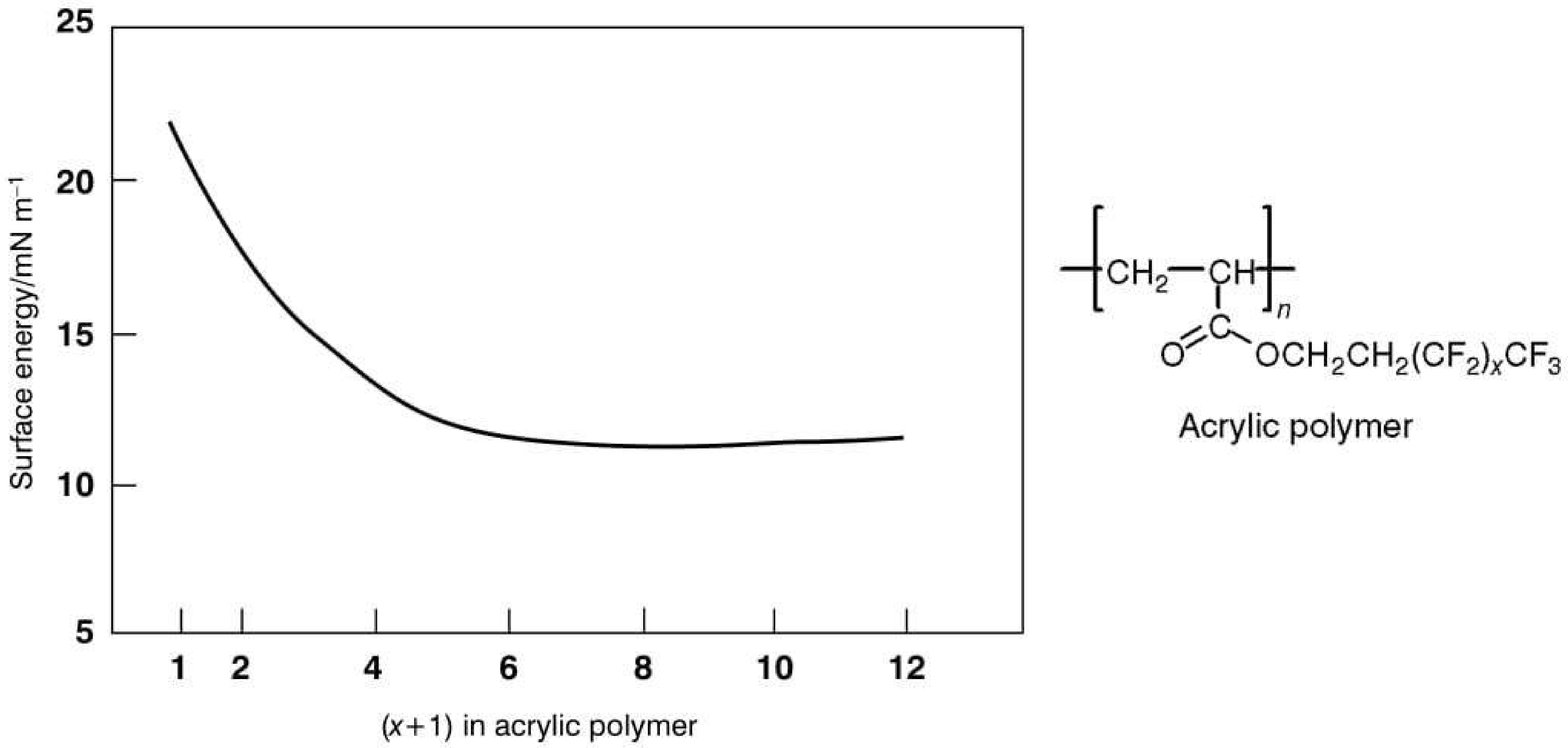
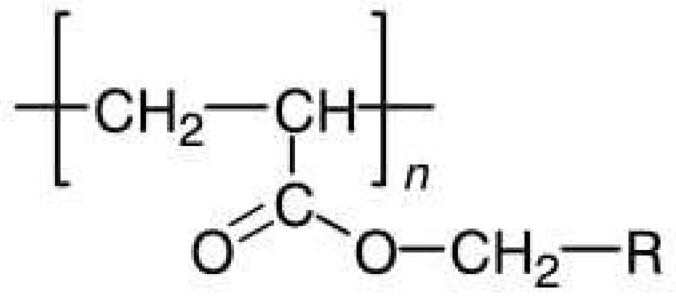
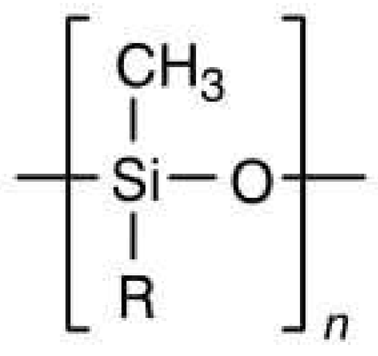


Figure 10.69 Change in critical surface energy with length of the perfluoroalkyl groups in acrylic polymers [502]

Table 10.49 Oil and water repellency of cotton fabrics treated with perfluorinated acrylic polymers [502]

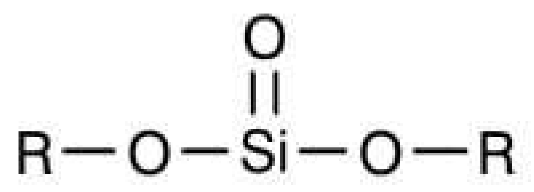
Acrylic polymer	1% Polymer applied to printed cotton	
		
Perfluorinated group R	Oil repellency (AATCC 118)	Spray test (ISO 4920)
$-CF_3$	0	50
$-CF_2CF_3$	3–4	70
$-(CF_2)_2CF_3$	6–7	70
$-(CF_2)_4CF_3$	7–8	70
$-(CF_2)_6CF_3$	7–8	70
$-(CF_2)_8CF_3$	8	80

A rather more novel yet logical development in fluorochemicals has been the emergence of fluoro-silicone hybrid polymers [503,504]. A series of products (10.251–10.253) has been extensively evaluated [503] for various properties, including liquid and solid surface energies, micelle formation, wetting, contact angle, film-release and antifoam behaviour. A similar type of product is tridecafluoro-octyltriethoxysilane (10.254). This has been applied to polyester and to cotton fabrics, fixation being achieved by drying at ambient temperature [504].



$$\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle R}{Si}}-O- \right]_n$$

10.251

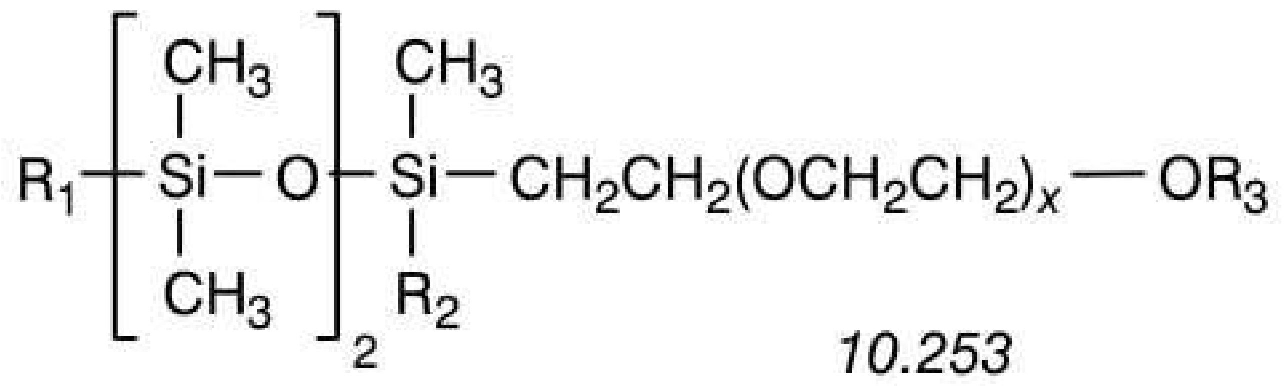


$$R-O-\overset{\displaystyle O}{\overset{\|}{Si}}-O-R$$

10.252

R = $—CH_2CH_2CF_3$ or

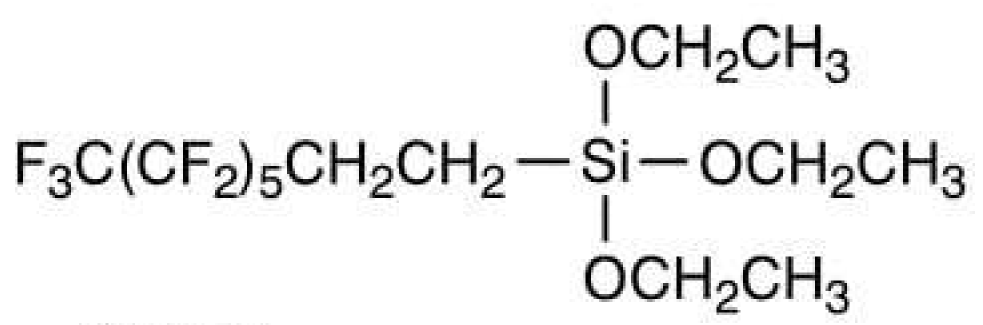
$—CH_2CH_2(CF_2)_3CF_3$



$$R_1\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O- \right]_2 \overset{\displaystyle CH_3}{\underset{\displaystyle R_2}{Si}}-CH_2CH_2(OCH_2CH_2)_x-OR_3$$

10.253

R_1	R_2	x	R_3
$—CH_2CH_2CF_3$	$—CH_3$	7	$—H$
$—CH_2CH_2CF_3$	$—CH_3$	12	$—H$
$—CH_2CH_2CF_3$	$—CH_2CH_2CF_3$	7	$—H$
$—CH_2CH_2CF_3$	$—CH_2CH_2CF_3$	12	$—H$
$—CH_2CH_2(CF_2)_3CF_3$	$—CH_3$	7	$—CH_3$
$—CH_2CH_2(CF_2)_3CF_3$	$—CH_3$	12	$—CH_3$



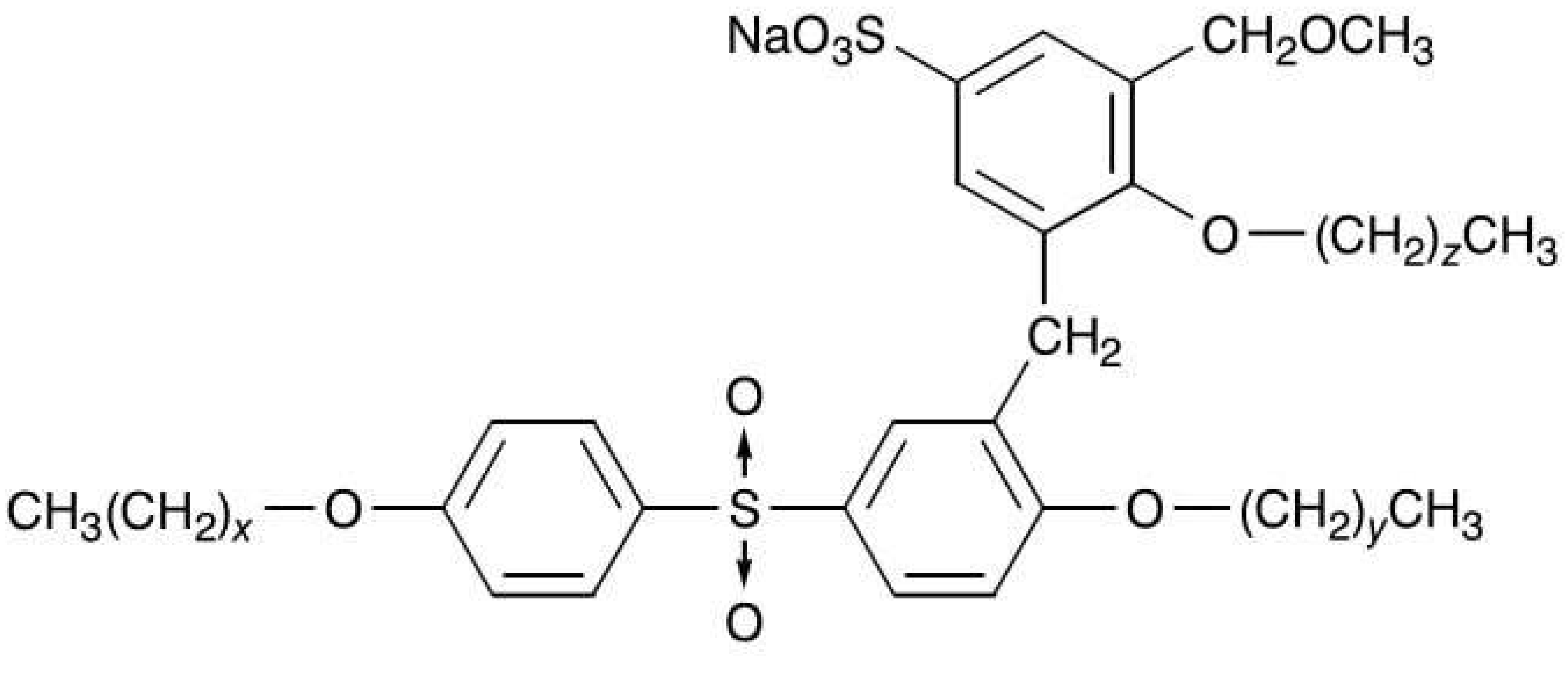
$$F_3C(CF_2)_5CH_2CH_2-\overset{\displaystyle OCH_2CH_3}{\underset{\displaystyle OCH_2CH_3}{Si}}-OCH_2CH_3$$

10.254

For application of these fluorochemical finishes to textile fabrics, an extremely important factor is their formulation into suitable aqueous emulsions or dispersions. The quality of the formulation has a critical influence on stability during storage and application, as well as the efficacy of treatment and durability [501,502]. In particular, the choice of surfactant(s) for emulsifying or dispersing must ensure good stability with freedom from deposition on rollers, yet must not impair the water and oil repellency of the finished fabric. No individual product fulfils all requirements; hence specifically formulated products are available for certain fibre types.

Application is mainly by padding followed by curing at 150–180 °C, although minimum add-on techniques such as slop padding, spraying and foam application have been successful. They can also be applied by discontinuous methods, such as exhaust or dip-spin [501].

These fluoropolymers are also used as the basis of so-called stain-blocking treatments, applied especially to nylon floorcovering and upholstery [505–508]. In general, the fluorochemical is used in conjunction with an anionic syntan resist agent of the type described in section 10.9.4. The latter functions by blocking the cationic protonated amine sorption sites in nylon. Thus the fluoropolymer repels oil-based soils and facilitates their removal during cleaning, whilst the syntan inhibits electrostatic interaction between the cationic sites and many coloured anionic substances in food, drinks and human/animal excreta. The two product types may be applied later in the dyehouse, in which case the



10.255

$x, y, z = 1–5$

effect is less durable. For maximum efficacy the two component types must be carefully chosen after much empirical screening. Fluorochemicals having perfluoroalkyl groups containing 10–12 carbon atoms and yielding an overall concentration level of 200–800 ppm of fluorine on the weight of fibre appear to be optimal [508]. The syntans are typically formaldehyde–phenolic condensation products; one product has the structure 10.255, which is interesting in that all the hydroxy groups have been converted into alkylaryl ethers [508].

Polymers of methacrylic acid or maleic acid, either alone or as a blend or copolymer with the sulphonated aryl–formaldehyde condensation products, have also been evaluated as stain-blocking chemicals [508,509]. An interesting development is the use of a polystyrene–maleic acid copolymer, this being unusual because of the absence of sulphonic acid groups [508,510]. Although the maleic and methacrylic acid polymers do not have the durability of the conventional syntans, they have the advantage that they are non-yellowing.

Although stain-blocking treatments were originally developed for nylon, there has been a good deal of emphasis over the last decade on extending their use to wool carpets [511–515]. Whilst syntans similar to those used on nylon are also suitable for wool, larger amounts are required to block the greater number of dye sites in wool [512].

Environmental aspects of fluorochemical finishing agents

In certain circumstances, organofluorine compounds can lead to the generation of AOX values, although a satisfactory method of measuring specific AOF values has yet to be developed [516]. Typical results of the environmental analysis of twelve fluorochemicals are shown in Table 10.50.

10.10.5 Bactericidal and insecticidal agents

There are three areas to consider:

(1) The use of insecticidal agents on wool to prevent attack by moth and beetle larvae.
(2) The use of bactericides to prevent biodegradation of chemicals such as thickening agents.
(3) The use of bactericides to inhibit bacterial activity on textiles.

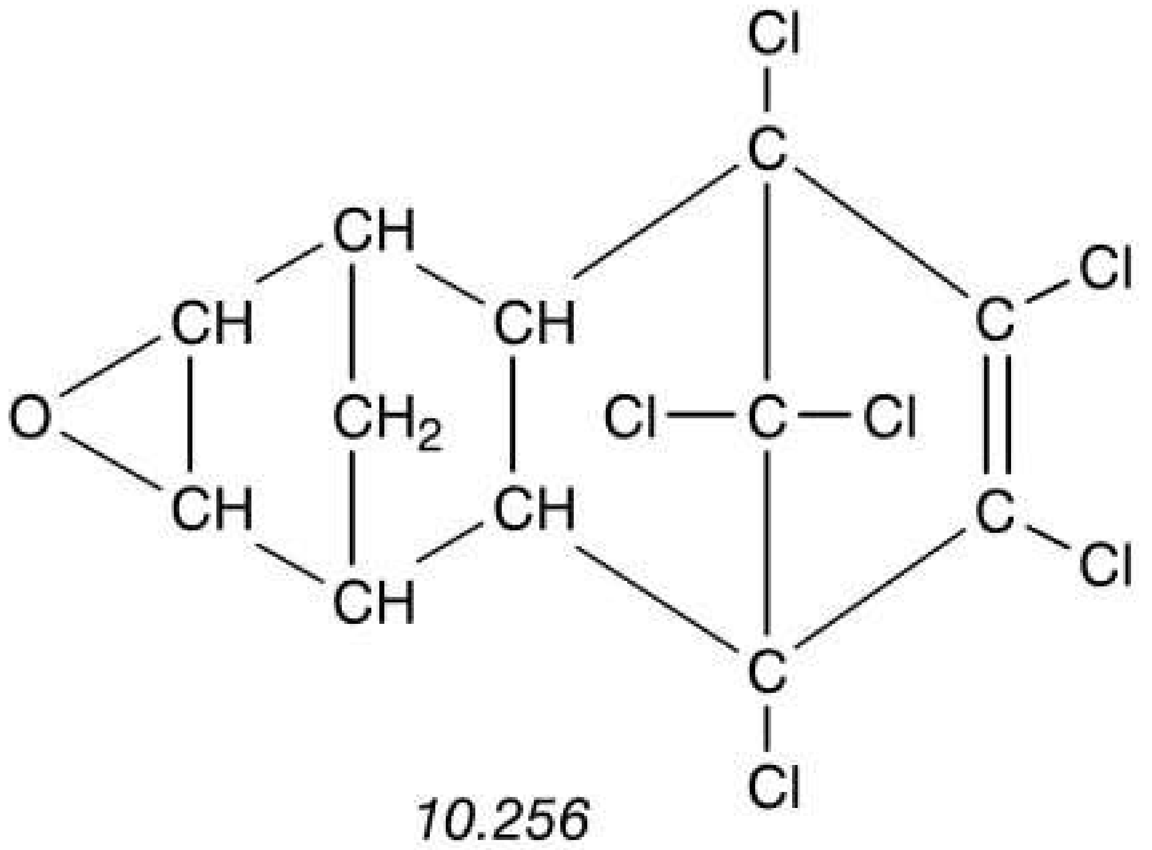
Insecticidal agents for wool

Lists of the principal types of insect that lay their eggs in wool are available [11,517]. Damage to the fibre is caused by the larvae that emerge from these eggs. Hence any

Table 10.50 Environmental analysis of fluorochemical agents at a product concentration of 1 g/l [516]

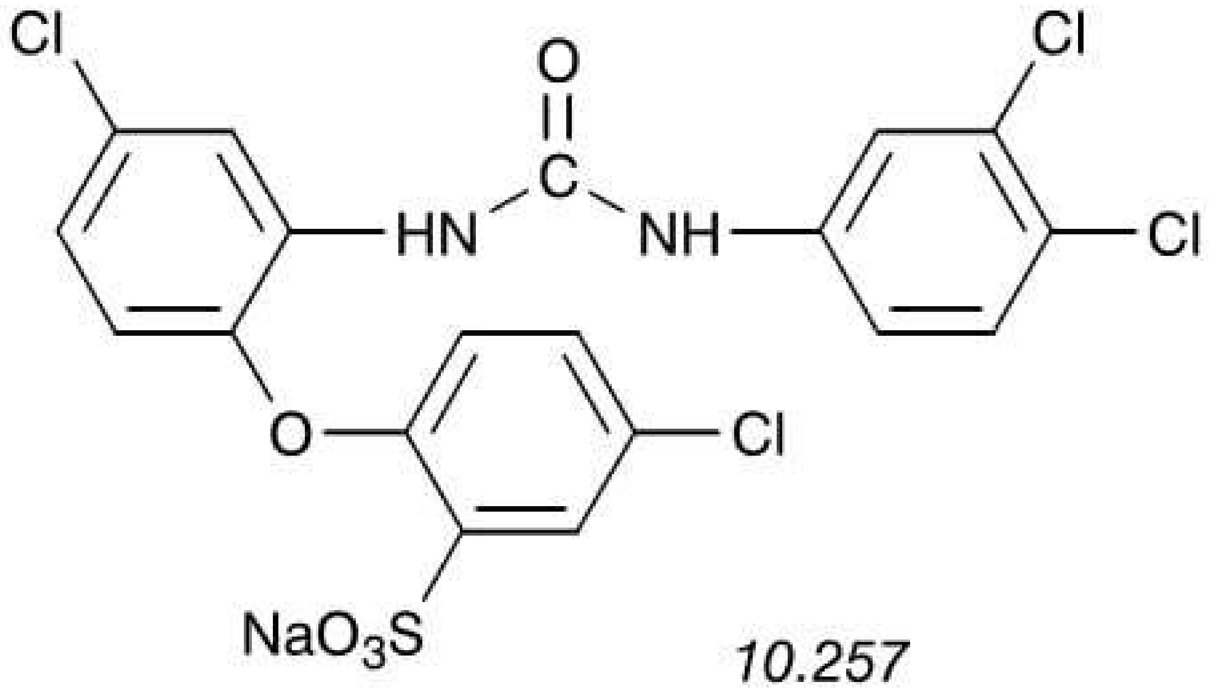
Product no.	Solids content (%)	AOX value (mg/l)	COD value (mg/l)	BOD_5 value (mg/l)	Bacterial toxicity (% resistance)
1	21.2	0.18	275	140	26
2	40.9	5.6	620	15	18
3	20.3	0.18	250	60	21
4	18.7	<0.05	345	30	66
5	5.3	1.3	305	160	6
6	17.0	<0.05	300	55	23
7	18.5	0.10	510	45	20
8	18.0	0.06	365	90	29
9	32.3	19.0	805	335	27
10	10.1	0.08	220	5	42
11	23.4	<0.05	425	55	50
12	31.2	0.06	355	85	54

insecticide used must be effective against these larvae. Since these products have no insecticidal effect on insects that do not consume the wool, it seems likely that such products act only through the digestive tract of the insect larvae. In addition to health and safety considerations, fastness properties also need to be taken into account. Fastness requirements on carpets are not so stringent as on machine-washable wool. Environmental, as well as health and safety factors, have resulted in an almost total ban on the use of dieldrin (10.256), the first compound to be used for this purpose. It proved to be toxic to man, animals, fish and birds, and was highly persistent in the environment.



10.256

Dieldrin

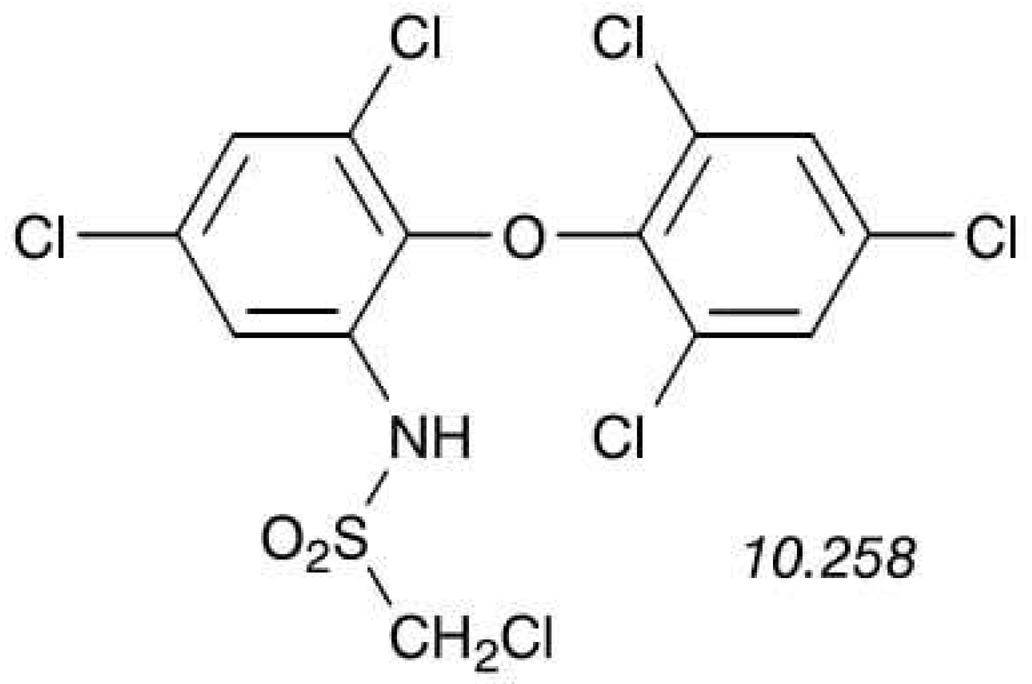


10.257

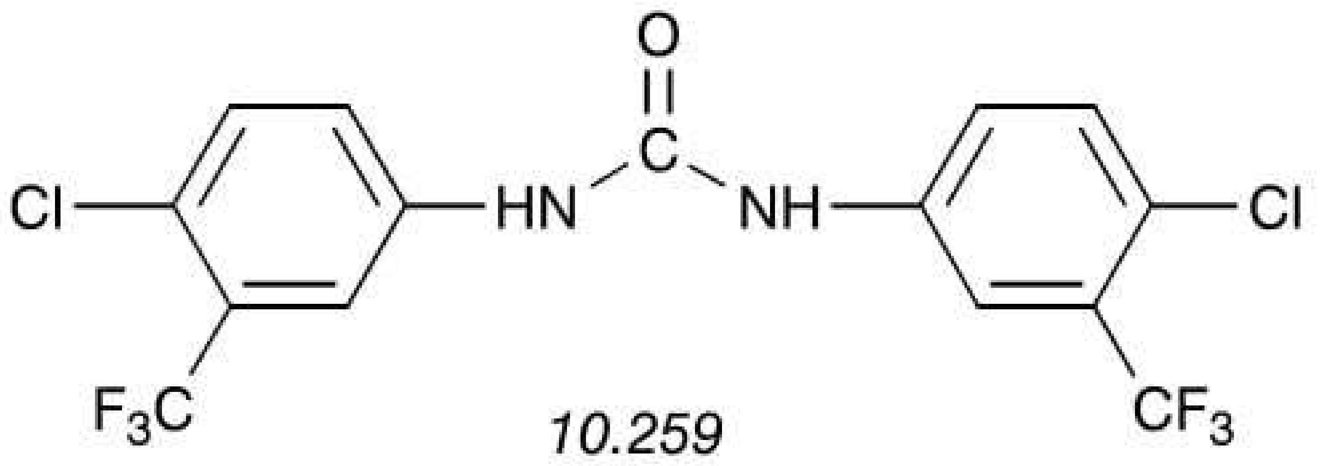
Sulcofenuron

Environmental factors coupled with the relatively small size of the market are acting restrictively against several other products that were formerly used. In an excellent review of this subject [517], the compounds that have found use are divided into two categories. The first category comprises those compounds that were developed specifically as wool mothproofing agents, most of these being anionic multichlorinated aryl compounds; some of these, for the reasons cited above, are no longer available. One of the best known is sulcofenuron (10.257). The sulpho group confers water solubility and exhaustion behaviour similar to those of an acid dye. This product is relatively expensive but has very good fastness to washing and light. Sulcofenuron, up to a concentration of 4 g/kg wool, is one of only three types of insect-resist agent permitted for the GuT scheme of ecolabelling [518].

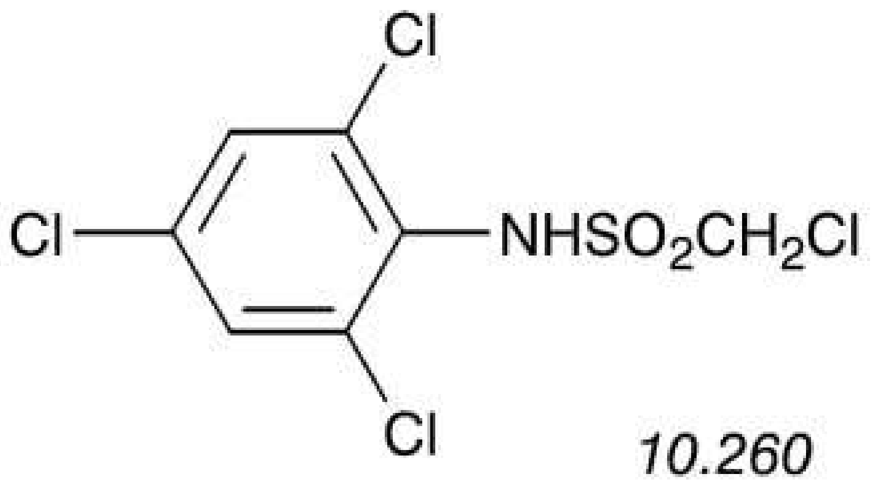
Chlorphenylid (10.258) has also provided insect-resist treatments but AOX generation during manufacture has led to the withdrawal of several such products since 1989. The chloromethylsulphonamido group requires at least pH 10 for aqueous solubility as the sodium salt. On acidification during application a dispersion of the free sulphonamide is formed and this is absorbed mainly through weak nonpolar interactions and hydrogen bonds. Combined chlorphenylid/sulcofenuron and chlorphenylid/flucofenuron (10.259) products were formerly used but have been withdrawn since 1989. Chloromethylsulphonamido-trichlorobenzene (10.260) has also been withdrawn since that date. Thus of the products developed specifically as insect-resist agents for wool only the sulcofenuron type remains in any significant use.


10.258

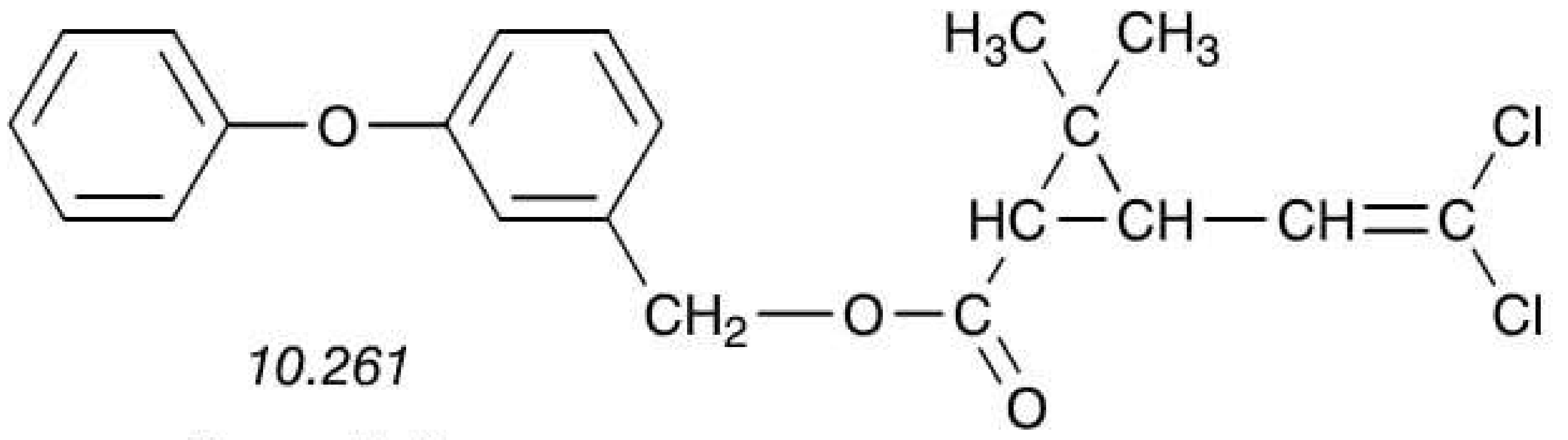
Chlorphenylid


10.259

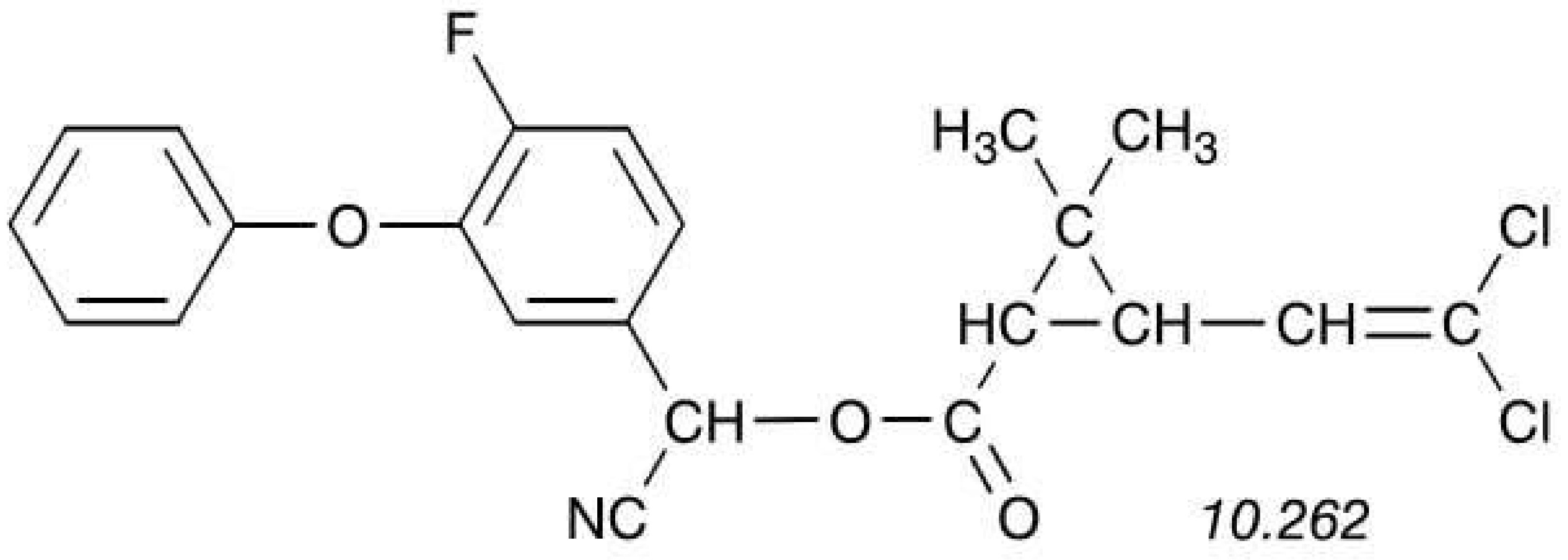
Flucofenuron


10.260

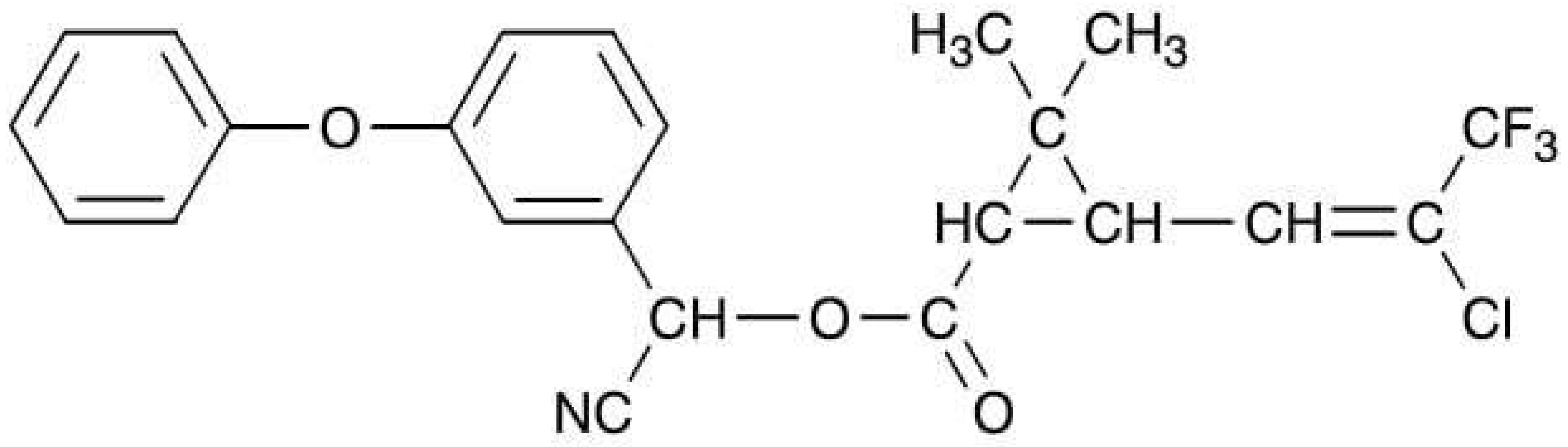
Compounds in the second group were originally developed as pesticides for agricultural use. These products have proved efficaceous and amenable to formulation as wool insect-resist agents. Most of them are pyrethroids, including permethrin (10.261), cyfluthrin (10.262) and cyhalothrin (10.263). A further effective compound is the hexahydropyrimidine derivative 10.264. Permethrin and cyfluthrin (together up to 210 mg/kg wool) are the other two types of insect-resist agent permitted for the GuT ecolabelling scheme [518].


10.261

Permethrin

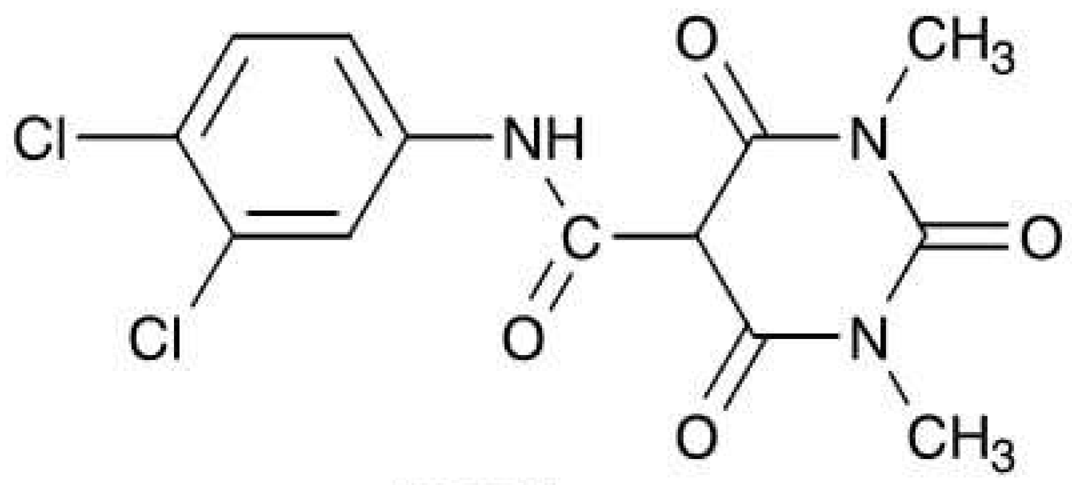

10.262

Cyfluthrin



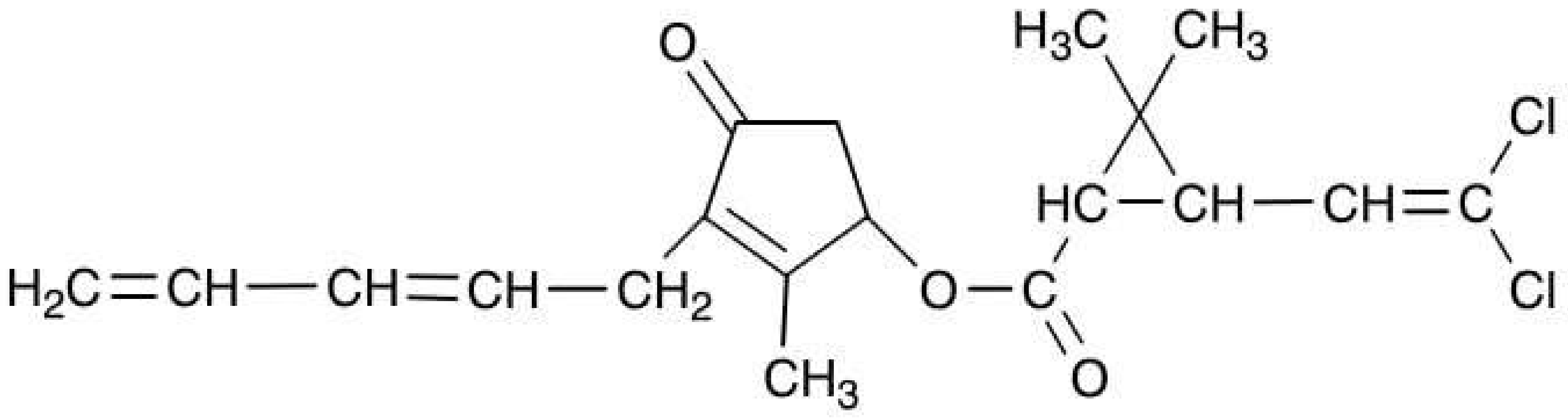
10.263

Cyhalothrin



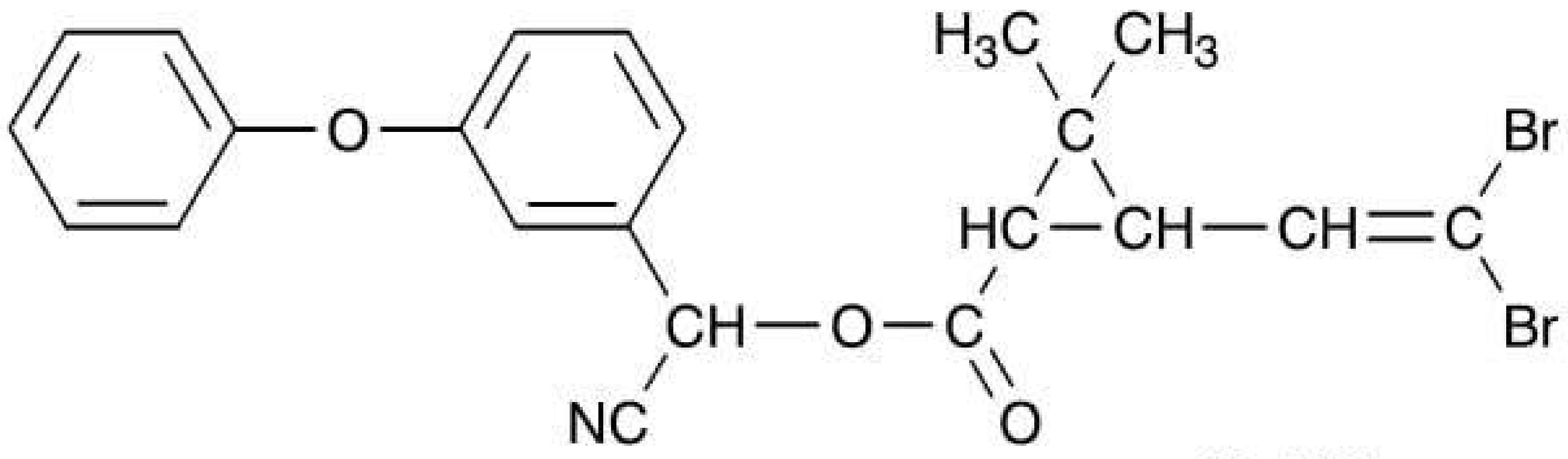
10.264

These synthetic pyrethroids mimic natural counterparts, of which the most important is pyrethrin 1 (10.265). Unfortunately, the natural products lack the photochemical and hydrolytic stability necessary for use as wool insect-resist agents. The synthetic products have the required stability, yet retain the low mammalian toxicity and low environmental retention of the natural products. Permethrin, however, is toxic to aquatic life and is therefore subject to increasingly severe discharge limits. There is some evidence that permethrin is less effective against larvae of a certain beetle. This can be compensated for by using a combination of permethrin with the hexahydropyrimidine derivative 10.264. Some possible alternative pyrethroids have been mentioned [517] as development products (10.266–10.269).



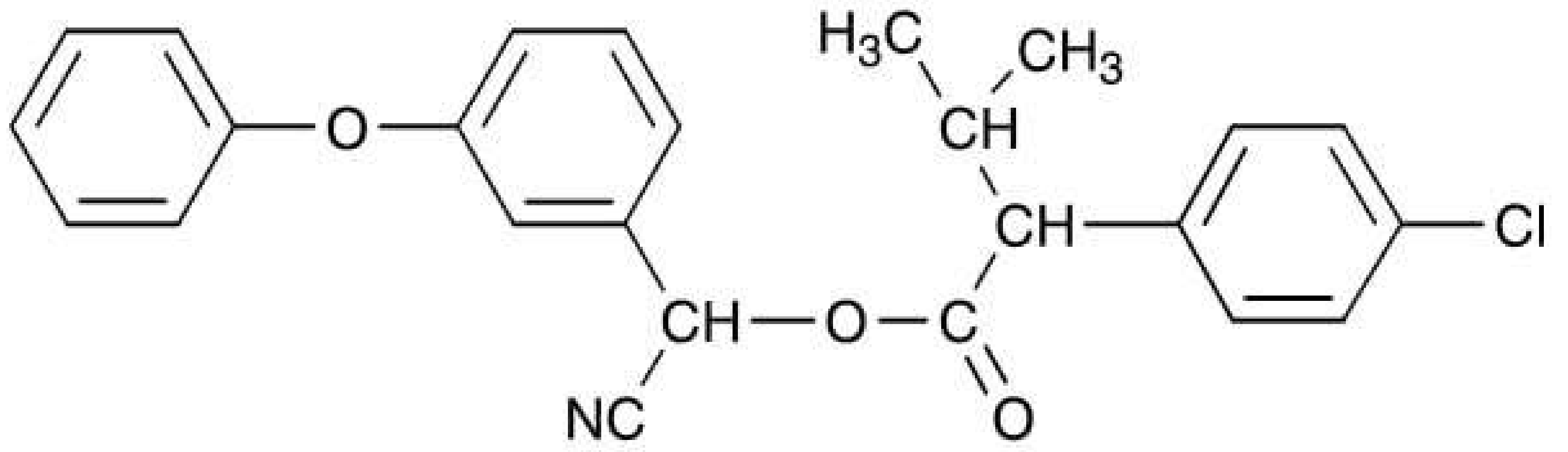
10.265

Pyrethrin I



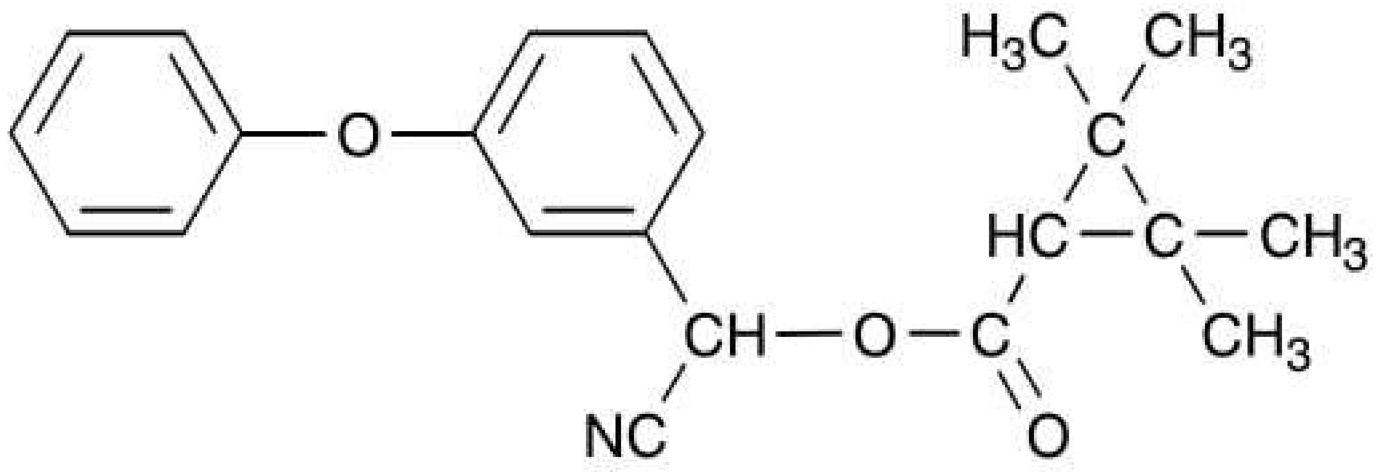
10.266

Deltamethrin



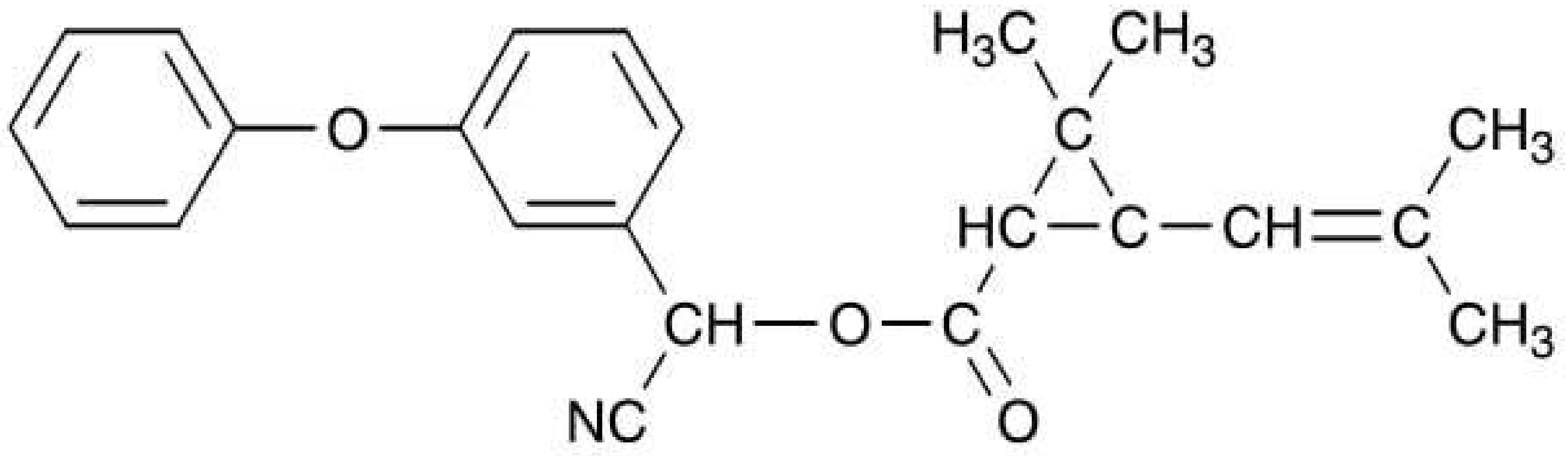
10.267

Fenvalerate



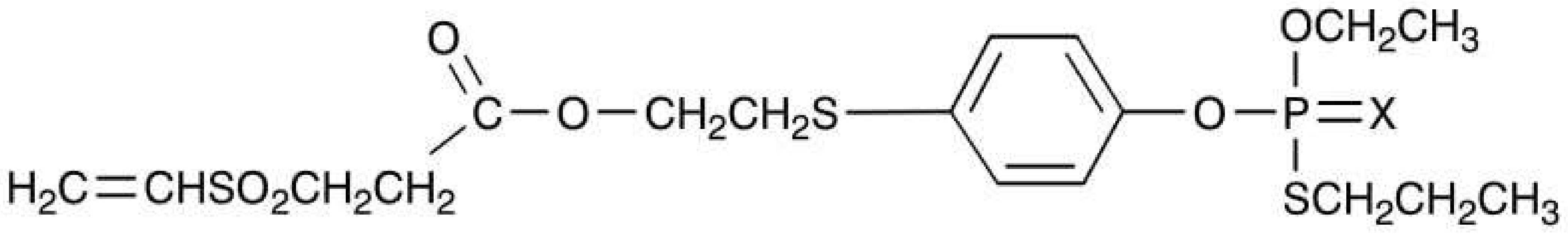
10.268

Fenpropathrin



10.269

Cyphenothrin



10.270

X = O or S

Other chemicals evaluated but not yet adopted commercially include organophosphorus compounds, triphenyltin compounds, quaternary ammonium salts, imidazoles, benzimidazoles, carbamates and the precocene anti-juvenile hormones [517]. Although none of the above has found use as an insect-resist agent, several have been used as antimicrobial agents for textiles.

Vinylsulphone fibre-reactive, insect-resist agents have been described, in which the insecticidal moiety is an organophosphorus grouping (10.270; X = O or S). The vinylsulphone group, by virtue of its nucleophilic addition reactions with wool keratin, confers excellent fastness. An interesting feature of these products is that they do not act as insecticides on wool until they become activated by hydrolysis of the ester bond during digestive processes within the insect.

A development reported recently [519] involves reduction of the cystine disulphide bonds in wool with either thioglycolic acid or tetrakis(hydroxymethyl)phosphonium chloride to form thiol groups, followed by crosslinking with bifunctional reactive dyes. This gave improved insect resistance but had adverse effects on physical properties such as strength, shrinkage and stiffness, thus limiting the potential of the process for commercial use.

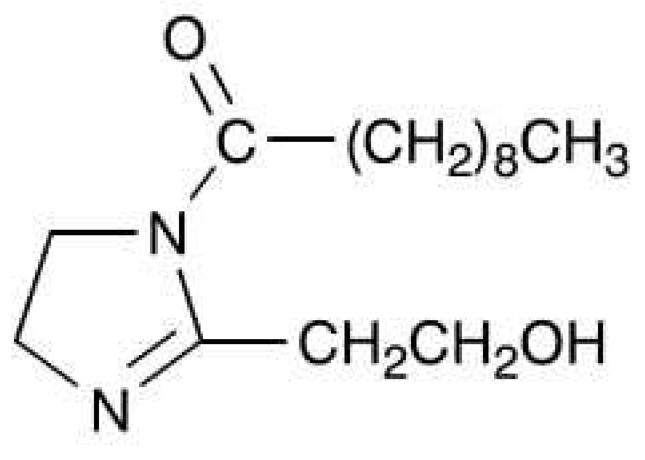
Despite these interesting developments, it has been pointed out [11,517] that because of the relatively small market and the costs of registration and ecotoxicological testing, it is currently unlikely that novel agents designed specifically for wool could be marketed economically. Any further advances are likely to be spin-offs from agricultural pesticide developments.

Application of these agents is best carried out from the dyebath to achieve the highest fastness ratings. This may not always be possible, however, and alternative stages (during scouring or application of spinning lubricants) are available [11,517]. Particular care is necessary in the choice and application level of insect-resist agents when applying them to fibre blends, since their partition behaviour between the component fibres varies. Pyrethroids, for example, tend to partition in favour of nylon in wool/nylon blends [520]. It is not surprising, given their aquatic toxicity, that these agents are under continual environmental scrutiny [521]. In order to comply with minimum discharge requirements, it is obviously helpful to be able to apply the minimum levels needed for adequate functionality and this has led to the development of appropriate machinery and methods [522–524].

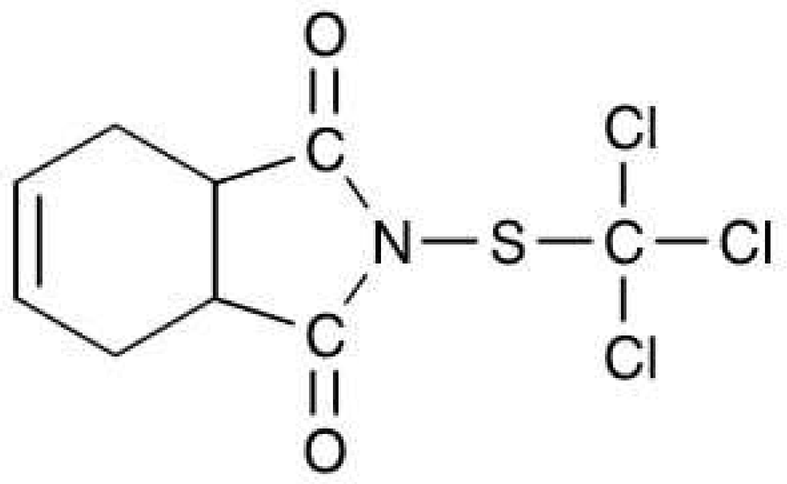
Bactericides for addition to fibres and other polymers

Bactericides can be added to microbially nutritious polymers, such as certain size polymers, dispersing agents and thickening agents, in order to protect them against biodegradation. For the same reason, they may be incorporated into man-made fibres for geotextiles and awnings. They may be applied to medical fabrics, hosiery, underwear and sports clothing for reasons of hygiene, in order to prevent infection, promote healing or prevent the development of odours. A comprehensive index is available [525]. Although this index covers all uses of antimicrobials, there is a section devoted to agents for textiles, in which the following are listed:

- Ammonium zirconium carbonate
- 1-Capryl-2-hydroxyethylimidazoline (10.271)
- *Cis-N*-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboximide (10.272; Captan)
- 2,2′-Dihydroxy-5,5′-1-dichlorodiphenylmethane (10.273; Dichlorophene)
- Diiodomethyl-*p*-tolylsulphone (10.274)
- Dimethylaminopropylricinoleamidobenzyl chloride (10.275)
- Lauryl/stearyltrimethylammonium bromide/chloride (10.276)
- Myristylamine (10.277)
- Sodium 2-mercaptobenzothiazole (10.278)
- 2,4,4′-Trichloro-2′-hydroxydiphenyl ether (10.279; Triclosan)
- Zinc 2-pyridinethiol-1-oxide (10.280; Zinc pyrithone).

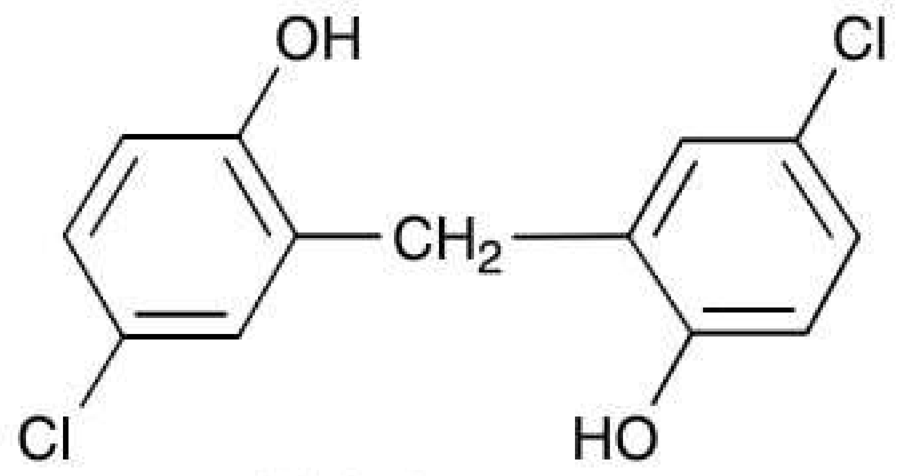


10.271



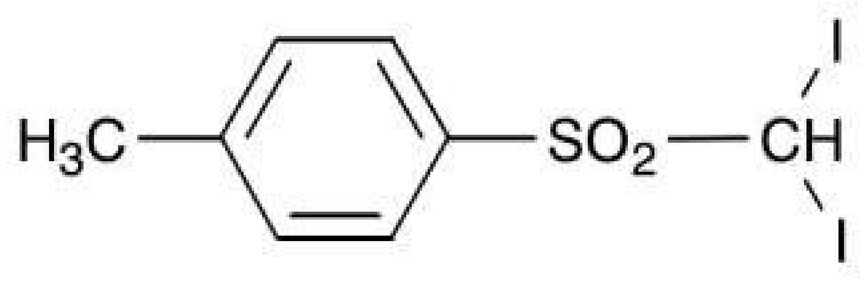
10.272

Captan

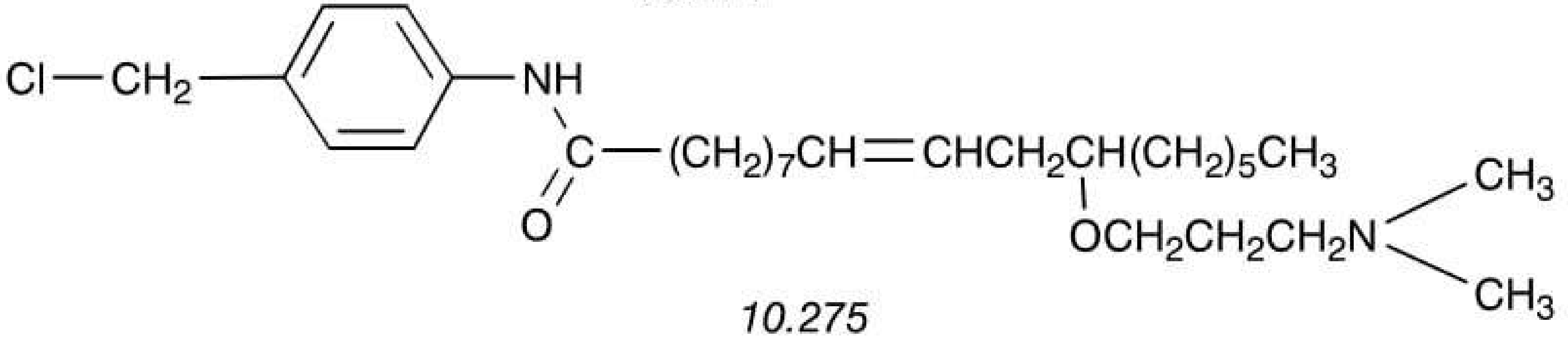


10.273

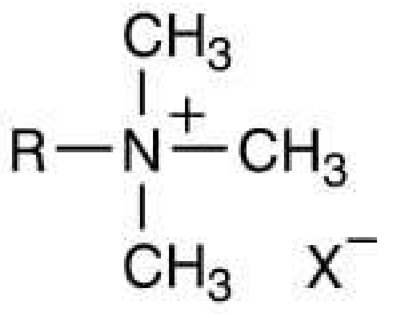
Dichlorophene



10.274



10.275



$R-N^{+}(CH_3)_3\ X^{-}$

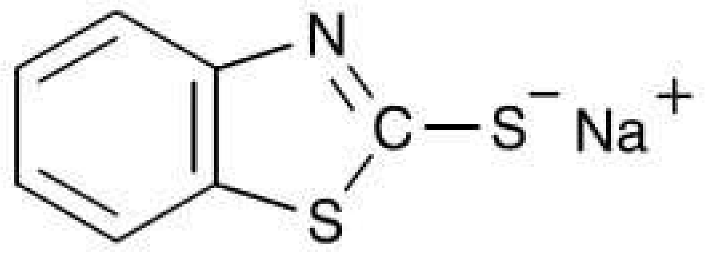
R = lauryl / stearyl
X = bromide / chloride

10.276

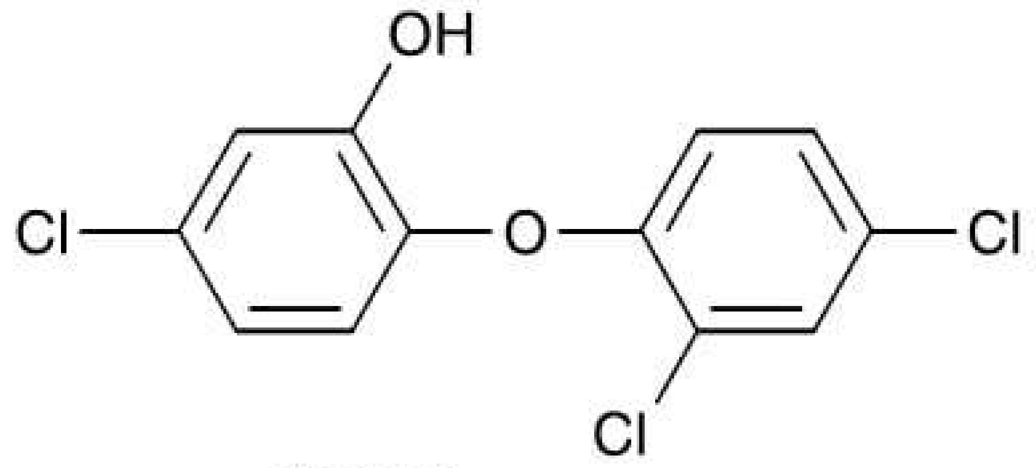
$CH_3(CH_2)_{13}NH_2$

10.277

Myristylamine

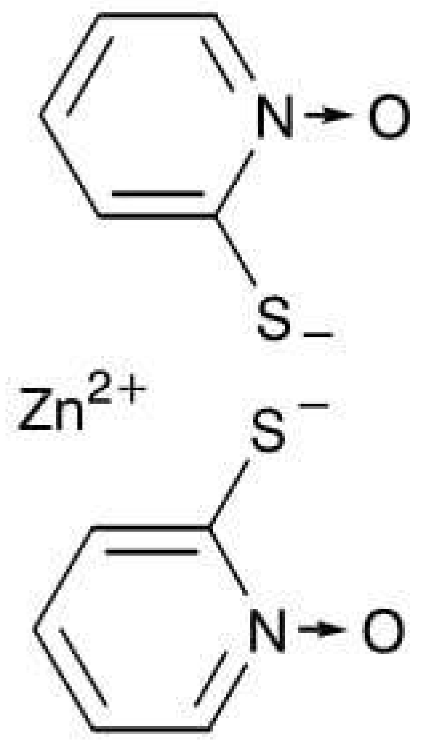


10.278



10.279

Triclosan



10.280

Zinc pyrithone

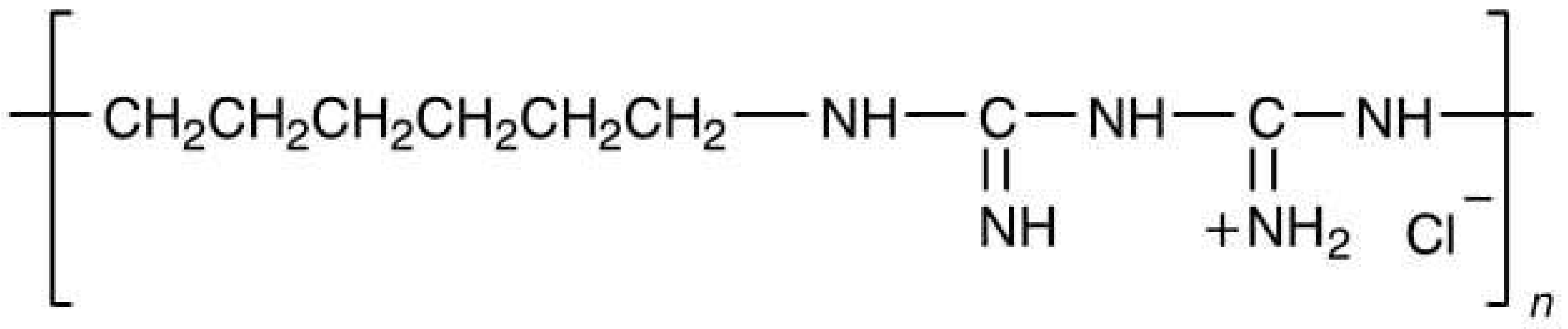
The environmental implications of adding biocides to polymers must always be borne in mind since, by definition, all effective biocides are more or less toxic. Thus addition of a biocide may render a normally biodegradable thickener less so. Hence biocides should be used at as low a concentration as possible. Natural size polymers, thickening agents and dispersing agents are particularly attractive targets for microbial attack, but degradation by this route is more rapid wet than dry. Thus printing pastes and liquid disperse dyes are sensitive targets. In the case of printing pastes, biological degradation on storage can lead to a significant loss of viscosity and rheological malfunction. Sensitive thickening agents, for example, can be protected by incorporating a biocide, usually at less than 0.1%, which is just about sufficient for effectiveness [383].

It has been suggested [383] that manufacturers of thickening agents will cease to incorporate preservatives in their products. The printer will then be responsible for selecting and using, in just the required amount, a preservative that is still just tolerable under the conditions of use. Formaldehyde has been widely used for this purpose but is now ecologically undesirable. Phenolic compounds such as sodium pentachlorophenate, *o*-phenylphenate or chloro-*m*-cresol have also been used. Such nucleophilic compounds can adversely affect the yield and hue of certain reactive dyes [390]. If absolutely minimal quantities are used, just sufficient for the required bacterial efficiency, it is possible for these residues to be washed out with much water to give extremely dilute waste waters. These traces no longer exert significant bacterial action and may even be biodegradable under these conditions.

Interest in the application of biocides to textiles has increased in recent years. They may in some cases be applied during manufacture of the fibre (in melt spinning) or as a finishing treatment. Although numerous papers on this subject have been published, many are unfortunately of little chemical interest as they disclose little other than commercial names. Poly(ethylene glycol) ($HO[CH_2CH_2O]_nH$) crosslinked with dimethyloldihydroxyethyleneurea has been reported to give fabrics with antibacterial properties suitable for nonwoven protective surgical apparel [526].

Triclosan (10.279) kills a wide range of bacteria that cause food poisoning, dysentery, cholera, pneumonia, tetanus, meningitis, tuberculosis and sore throats. It also prevents the development of bacterially related odours and kills the yeasts responsible for candida ulcers and athlete's foot. This compound can be incorporated during fibre manufacture to give durable antibacterial properties [527–529]. Despite the widespread use of Triclosan in toothpastes and acne creams, it is reported that it can cause allergic dermatitis in susceptible individuals, especially when used in products for the feet [525].

Poly(hexamethylenebiguanide hydrochloride) (10.281) has been used in the sanitisation of swimming pools. For textiles, it has been formulated into a finish capable of providing a range of antibacterial fabrics from medical products to odour-free socks [530,531]. This agent is mainly of interest for cotton; the polymeric cationic structure exhibits high substantivity for the negatively charged surface of the fibre. Application is by padding, optimally at pH 7–8, and the performance can be improved by subsequent wet-on-wet padding with an anionic fixing agent. No elevated curing temperature is required and approximately 1% of the antimicrobial agent on the weight of cotton is optimal for bactericidal performance. The product has a long history of use as a bactericide, exhibits low toxicity and is environmentally acceptable, being bioeliminated by adsorption.

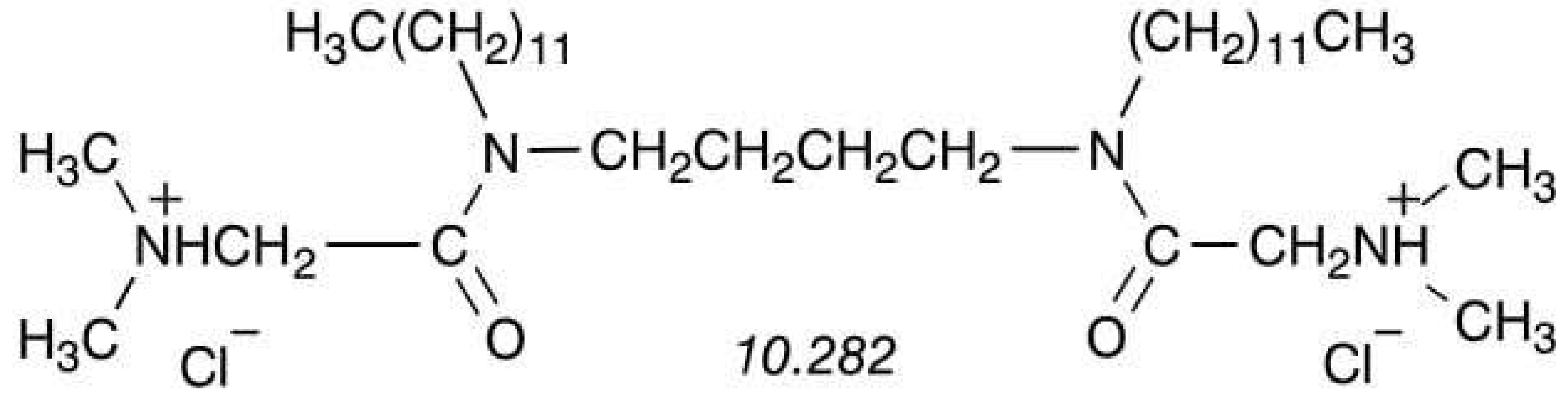


$$\left[-CH_2CH_2CH_2CH_2CH_2CH_2-NH-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{{}^{+}NH_2\ \ Cl^{-}}{\|}}{C}-NH-\right]_n$$

average $n = 12$

10.281

Novel bis-quaternary compounds have been reported for improving the microbial resistance of wool [532]. These products are described as a new class of bis-quaternary ammonium surfactants known as gemini quaternary ammonium compounds or bis-quats. They consist of two saturated hydrocarbon chains and a complex polar group consisting of two quaternary ammonium salts linked through an alkane spacer chain containing amide and optional disulphide bonds. Bacterial efficacy on wool was confirmed for two products: *N*,*N*′-bis(*N*-dodecyl-*N*,*N*-dimethylglycine)-1,4-diaminobutane dihydrochloride (10.282) *N*,*N*′-bis(*N*-dodecyl-*N*,*N*-dimethylglycine)cystamine dihydrochloride (10.283). These agents were applied at 0.0025–0.5% on the weight of wool by exhaustion from an aqueous solution at 40 °C.



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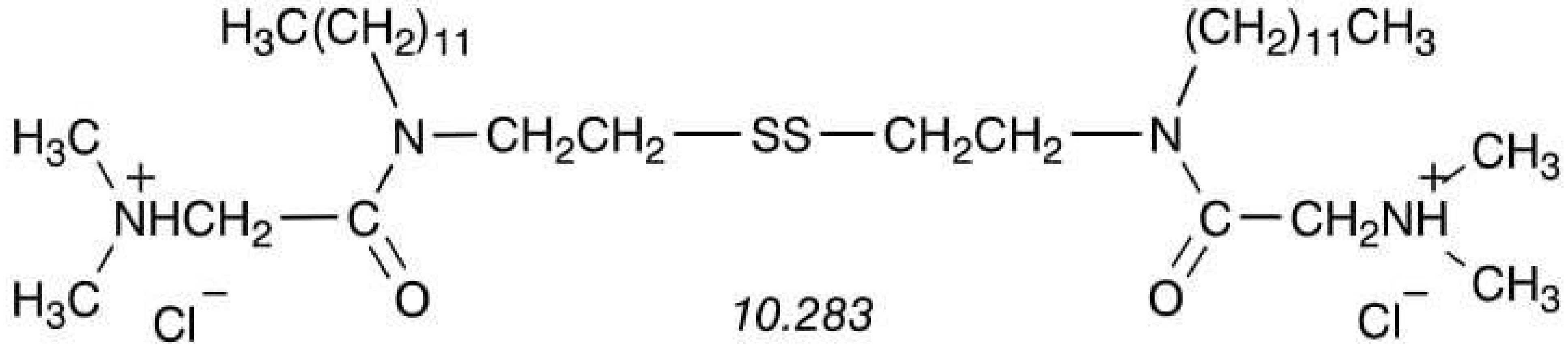


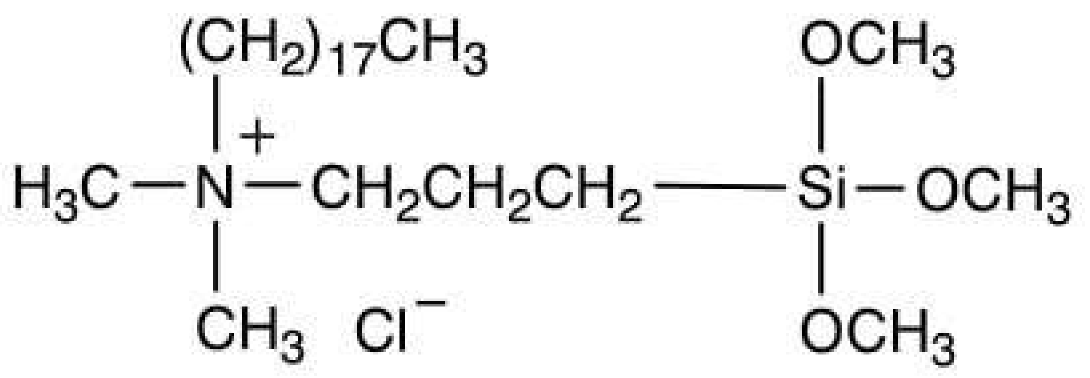
10.283

The bacterial resistance of silk fibroin can be improved by treatment at low pH values in aqueous solutions of metal ions and at high pH values in solutions of metal–amine complexes, using untreated silk or silk pretreated with an aqueous solution of tannic acid (10.183). Suitable metals include Cu, Zn, Ni, Fe and Ag [533]. It is to be expected that treatment with such metal compounds will be subject to restrictions in environmentally sensitive areas.

Antimicrobial agents may adversely affect the light fastness of nylon dyeings or cause yellowing of the fibre. The six antimicrobial treatments listed in Table 10.51 have been

Table 10.51 Comparison of antimicrobial finishes on nylon [534]

Finish	Chemical class(es)	Structure(s)
1	Silicone quaternary ammonium salt	10.284
2	Silicone quaternary ammonium salt	10.285
3	Organo-tin	10.286
4	Phenolics (mixture)	10.273/10.287
5	Phenolic and organo-tin	10.279/10.288
6	Organo-tin and quaternary ammonium salt	10.288/10.289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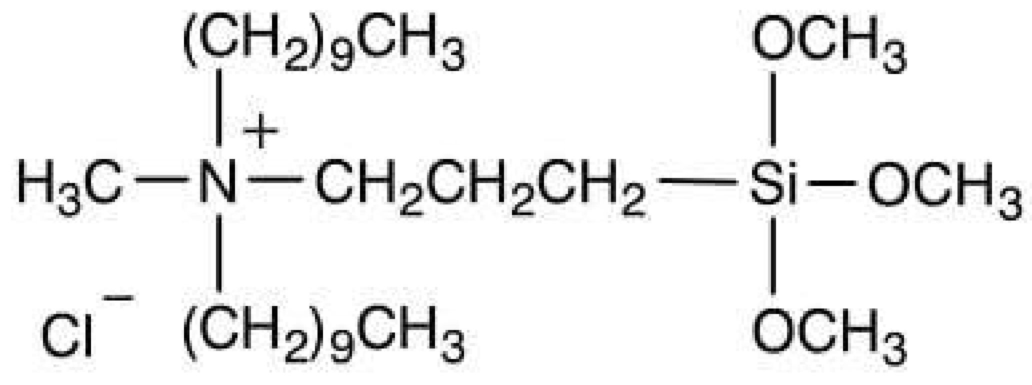
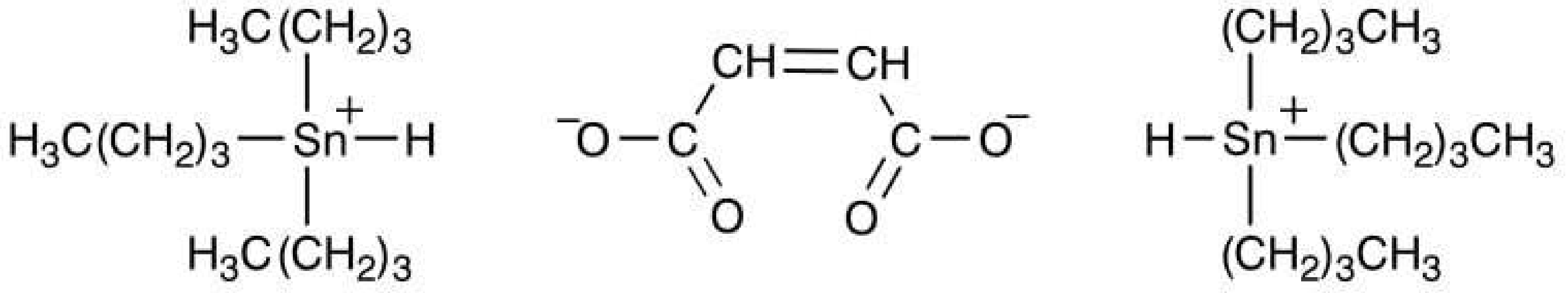
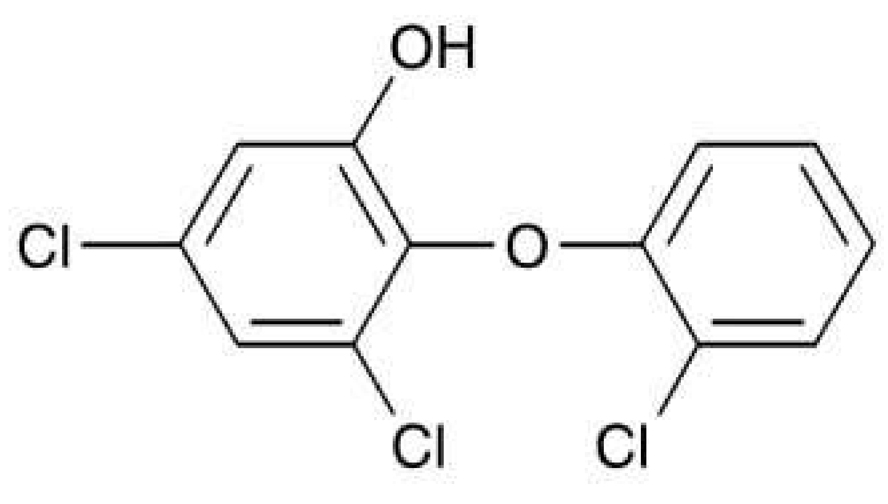
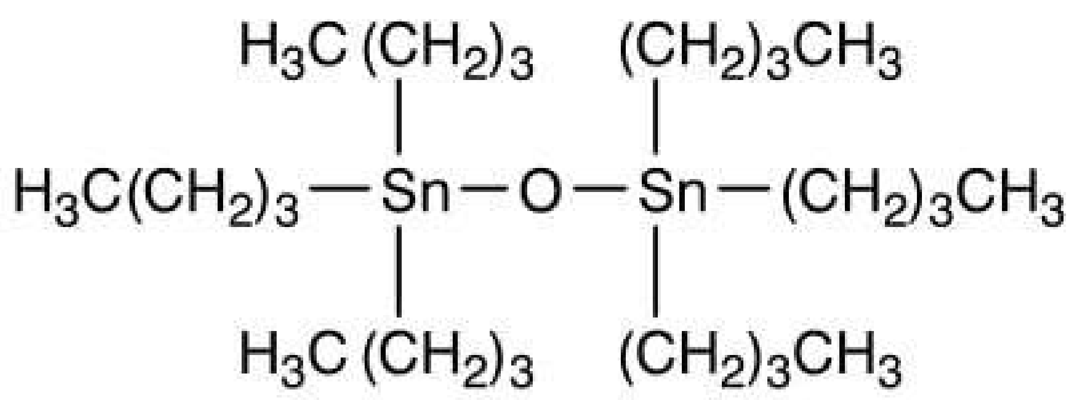
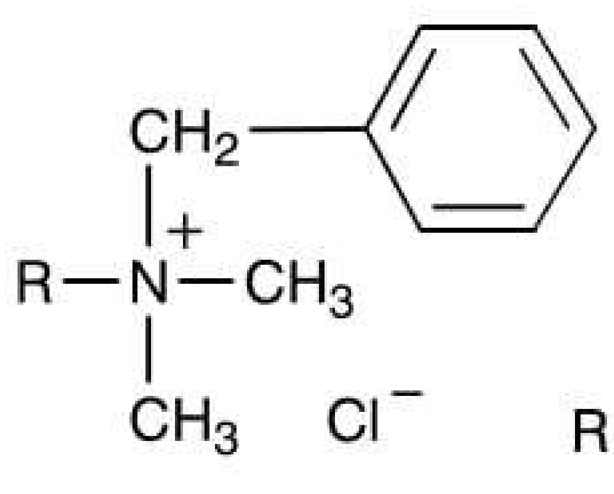

10.285


10.286


10.287


10.288


R = n-alkyl

10.289

evaluated in relation to these two factors, each being applied at the manufacturer's recommended concentration [534]. The effect on light fastness varied with each dye and only a few dyes were studied; some dyes were more sensitive to specific antimicrobial finishes. Overall, Finish 3 had the smallest effect on light fastness, followed by Finish 5. Finishes 6 and 4 gave the greatest reduction in light fastness, Finish 4 also causing appreciable discoloration of the undyed fibres.

10.11 FOAMING AND DEFOAMING AGENTS

10.11.1 Foaming agents

The idea of using a matrix of foam to transfer chemicals and colorants to textiles had its origin in the growing need to conserve thermal energy and water in the aftermath of the so-called oil crisis and recession of the early 1970s. In a sense, it was an antidote to the feverish work carried out in the late 1960s on solvent dyeing. Foam dyeing began with an elegant short-liquor (about 1.5:1) dyeing process developed in 1972 mainly for garment dyeing in rotary machines. The application of foams to textiles has been widely investigated subsequently, although the degree of commercial acceptance has proved limited. Nevertheless, potential exists for the foam-based application of lubricants, stiffening agents, waxes, size polymers, mercerising liquors, durable press resins, water/oil repellents, softening agents, shrink-resist resins, dyes and print pastes. Although continuous dyeing and printing, mainly of carpeting, has attained significant commercial use, most foam processing is confined to the application of finishes where concentration tolerances and evenness of application are much less critical. A major account of the properties of foams and their general industrial applications includes a chapter devoted to textile applications [535].

Apart from reproducibility and uniformity of application, one of the main problems associated with foam application is dissolving or dispersing relatively large quantities of the principal and auxiliary agents in a very small volume of water, followed by the difficulty of maintaining compatibility of the components and the density and stability of the 'loaded' foam under such conditions. For example, resin finishing can typically require the dissolution of about 600 g of resin, softener and catalyst in only 400 g of water. Nevertheless, foam processing does offer advantages, notably in the conservation of water and energy and the reduction of effluent problems.

The foam matrix used in textile wet processing is a stabilised air-in-water system. A foam cannot be made with pure water, however; a foaming agent, usually a surfactant, is needed to give a reasonably stable honeycomb matrix of air cells, each enclosed by a thin viscoelastic film of liquid. Clearly, a reduction in surface tension is one important factor in the creation of foam; others include the elasticity and viscosity of the film walls between the bubbles, and the size and uniformity of the bubbles themselves. Drainage, by gravity, of the liquid from the film walls leads to instability of the foam and tends to a maximum with larger spherical bubbles. In a system consisting of variously sized bubbles, the smaller ones tend to coalesce into the larger, which are thus further increased in size and become less stable because of the increased propensity for liquid drainage. Thus, for maximum stability, the bubbles should be as small and uniform as possible, leading to minimum diffusion of air from bubble to bubble, and maximum entropic and electrical double layer repulsion. The ideal state is not attainable in practice, however, and all foams are unstable to some degree. Nor is perfect foam stability particularly required in textile application, since at some stage during the process collapse of the foam is generally desirable to ensure maximum deposition of chemicals and/or colorants.

The foaming propensity of surfactants generally reaches a maximum at the critical micelle concentration, beyond which there appears to be little further contribution to foam density. Foam stabilisers are also added in some cases. The two important steps in the foam treatment of textile materials are generating the foam and applying it to the substrate:

(1) Generation is generally by high-speed rotors, with metered air and liquid flows and monitoring to control the density of the foam.
(2) Application of controlled amounts of foam to the substrate is by knife-on-roller, knife-on-blanket, floating knife, horizontal pad or furnishing roller with doctor blade, or by squeegee across a printing screen.

Subsequent collapsing of the foam is generally by collapse onto the fabric (controlled to some extent by the chemicals used), by vacuum suction of the foam into the fabric, or by means of a pad nip.

The most important auxiliary used is, of course, the foaming agent. In theory any surfactant that will form a stable foam can be used. In practice the choice is usually between anionics (generally cheaper), nonionics, or a mixture of both. Consideration must be given to overall compatibility as well as to foaming characteristics: for example, anionic agents should generally be avoided when applying cationic products. Long-chain alcohol sulphonates and ethoxylates, as well as sulphates and sulphosuccinates, have been used; a typical selection is given below, the first three being anionic and the others nonionic:

- sodium lauryl sulphate
- ammonium lauryl sulphate
- sodium dioctylsulphosuccinate
- lauryl alcohol poly(oxyethylene)
- decanol poly(oxyethylene)
- tridecanol poly(oxyethylene).

Particularly effective is a mixture of anionic and nonionic agents, such as a mildly anionic sulphated alcohol ethoxylate with a nonionic alcohol ethoxylate. Ideally, foaming agents should:

- generate consistent foam easily
- show optimum and uniform wetting
- cover a wide range of wettability so as to be adaptable for different situations
- show little or no effect on colour fastness
- be compatible with the other components
- be biodegradable.

The main function of the foam stabilising agent is to reinforce the intercellular film wall by contributing rheological characteristics of viscoelasticity. The increased viscosity may also assist handling. The aim, as so often with auxiliaries, is to achieve an optimum balance. If the bubbles are too thin and wet too quickly they will collapse prematurely, whilst too stable a film could hinder uniform application. Examples of products used as foam stabilisers include thickening agents such as the polysaccharides, hydroxyethylcellulose, methylcellulose, carboxymethylcellulose, poly(vinyl alcohol) and poly(acrylic acid), as well as other compounds such as sodium tripolyphosphate, sodium hexametaphosphate (detergent 'builders') and decanol. Ideally, foam stabilisers should increase the stability of the foam to the optimum controllable level whilst also allowing for subsequent controllable collapse. They should be compatible with the other components and effective at various concentrations, give pseudoplastic solutions, and should not affect the drape and handle of the fabric. Electrolytes can have positive or negative effects on foam stability [535]; for example, a low concentration of phosphate ions increases the stability of a sodium laurate foam, whereas sodium chloride decreases the stability.

10.11.2 Defoaming agents

All chemical systems, to varying degree, tend to reduce free energy and foams are no exception. Hence foams are thermodynamically unstable, yet their stability varies from almost instantaneous collapse to prolonged persistence. Although foam can be useful, there are still many circumstances where its presence and persistence is enough of a nuisance to create a need for foam-destruction products, known as defoaming agents or antifoams. An authoritative reference work on the theory and applications of defoaming is available and this includes a chapter on applications in textile dyeing [536]. Reference 535 contains a chapter on the science and technology of silicone antifoams.

Just as foams are stabilised by decreasing the rate of liquid drainage from the film walls, they can be destabilised by increasing this drainage, resulting in thinning and eventual rupturing of the film. Defoaming agents generally effect this by two mechanisms, the basic objective being to displace foam-stabilising substances from the liquid-air interface [537]:

(1) Spreading alone is sufficient with light foams of high blow ratio (those having a high air-liquid ratio); in this case surfactants of relatively low surface tension (i.e. powerful surfactants) will spread over the large surface area of the intercellular film and displace the surfactants that are tending to stabilise the foam.

(2) Denser foams of low blow ratio additionally require penetration of the thicker aqueous film by the defoaming agent. Such a defoamer consists of an emulsified hydrophobic substance, which when added to the foaming system disperses fine droplets of insoluble hydrophobic material within the liquid lamellar walls, thus entering the liquid-air interface, aided to some extent by the solubilising action of the foaming agent(s). This creates a weak link as a result of high interfacial tension, the foam then tending to rupture at the interface between defoamer and foamer. In practice, the system is a finely balanced one requiring careful formulation of the composite defoaming agent.

The main requirement of an effective defoamer [537] is that the agent should be insoluble in the foaming system and should have a high rate of spreading. Spreading will be favoured if the defoamer has a lower surface tension than that of the foaming system. The interfacial tension between defoamer and foaming system must be high, but not so high as to inhibit spreading. A low degree of attraction between defoamer and foaming system (i.e. a high interfacial tension) is achieved by nonpolar defoamer systems that do not contribute positively to the surface viscosity of the lamellar walls.

For maximum efficiency the defoamer should be added to the system as soon as foaming becomes troublesome, since its active life-span is inevitably limited by the system's thermodynamic instability. Its principal action is on the liquid-air interface; therefore there is little point in adding it before sufficient liquid-air interfaces are formed. Secondly, the insoluble active ingredient of the defoamer, given the nature of the system in which it is working, must eventually become more or less solubilised, or at least emulsified, into the bulk liquid system, thus losing its activity and in some circumstances actually promoting foaming.

Defoamers are generally anionic or nonionic systems and fall into two groups. The first group consists of water-soluble surfactants with polar and nonpolar moieties. These compounds are effective only over a narrow range of conditions, functioning simply as spreading agents, and are seldom used alone. Such surfactants are readily absorbed into the bulk of the foaming system where, not surprisingly, they contribute to the foaming problem. This system is more frequently used, however, as the vehicular or 'carrier' basis of the second group of defoamers, which are much more widely used. These more active defoamers are emulsions of water-insoluble silicones or organic-based compounds of low volatility and high spreading power.

The general requirements for an ideal defoamer can be summarised [536]:

- eliminates existing foam as well as preventing further foam from forming
- easy to disperse in the dyebath
- does not react or interact with dyes or auxiliaries present in the bath
- chemically stable under dyeing conditions
- no deposition on fabric or machinery causing spotting or staining of the fabric
- no colour
- no odour
- stable to storage
- safe both to humans and to the environment.

The active organic-based defoamers include:

(1) Fatty acids, their glycerides and other esters, including fats, waxes and oils such as mineral and vegetable oils; fatty alkylamines and acylamides. Alkaline earth metal or aluminium salts of fatty acids tend to leave deposits on machinery [536].

(2) Higher alkanols, including the isomeric octyl alcohols (2-octanol and 2-ethylhexanol), cyclohexanol, lauryl and cetyl alcohols. Aliphatic alcohols have relatively poor foam control and have an odour that can be nauseous [536].

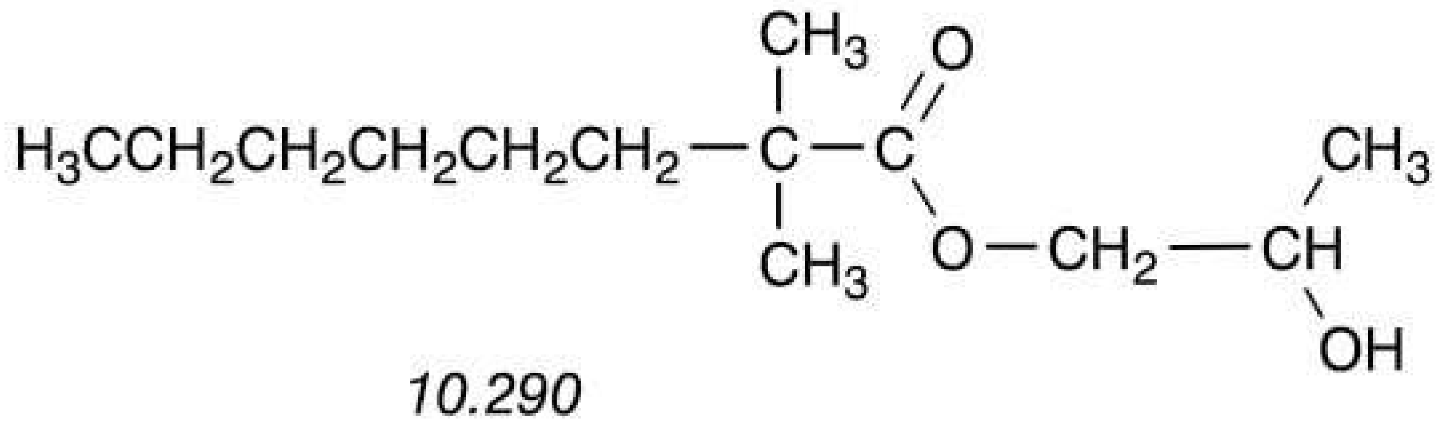
(3) Polyglycols, especially poly(propylene-1,2- or -1,3-glycol). Poly(oxyethylene) and poly(oxypropylene) block copolymers have relatively poor foam control [536].

(4) Insoluble alkyl esters of phosphoric acid, especially tributyl phosphate. These phosphate esters have relatively poor foam control [536].

Certain limitations of organic defoamers can be minimised by judicious formulation of mixtures. The following system is said to overcome some of the drawbacks associated with aluminium salts of fatty acids [536]:

- 87% Paraffin oil
- 6% 2-Ethyl-*n*-hexanol
- 4% Aluminium distearate
- 3% Phosphoric acid esterified with polyethoxylated *p*-nonylphenol.

In the case of an aliphatic alcohol such as iso-octanol, a similar level of defoaming activity together with a much less offensive odour can be achieved by using a propoxylated ester of a branched aliphatic acid, such as propylene-1,2-glycol mononeodecanoate (10.290).

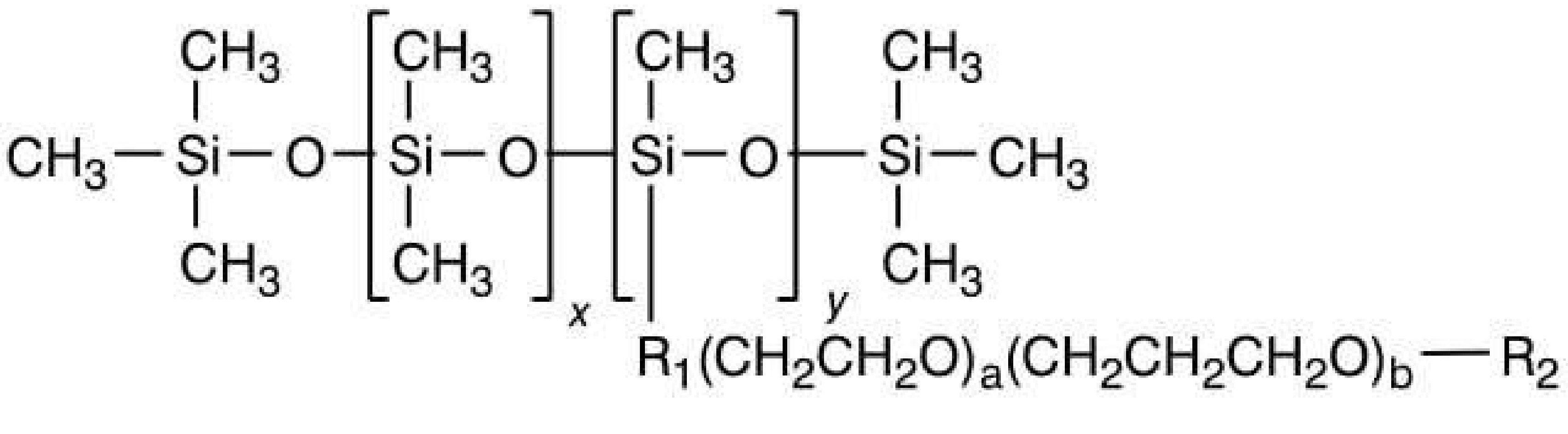


10.290

The active ingredients in silicone-based defoamers have traditionally been a poly(alkyl siloxane), especially poly(dimethyl siloxane) (10.226), and silica (SiO_2); the latter may be chemically bonded to the polysiloxane to render its surface hydrophobic. Some ‘spotting’ problems have been experienced with these defoamers owing to incompatibility of the antifoam emulsion with certain dye dispersions, especially at high rates of shear in the high-temperature dyeing of polyester with disperse dyes. This created a poor reputation for the early silicone antifoams in jet dyeing. The problems arose by destabilisation of the emulsion, resulting in cracking out of hydrophobic components which caused staining or spotting of the fabric, together with a drastic loss of defoaming action. The poly(dimethyl siloxane) products exert little foam suppression power alone. Their foam inhibition properties only become fully developed when combined with finely divided, hydrophobic silica particles [538].

Further improvements have been made to the emulsion system and to the silicone components themselves. Improved derivatives of poly(dimethyl siloxane) include [537] block copolymers with poly(oxyethylene) and poly(oxypropylene) segments represented schematically by structure 10.291. The solubility and other characteristics of these alkoxylated silicones (silicone polyglycols) can be adjusted by varying the proportions of dimethyl siloxane and oxyalkylene units. A specific advantage claimed for these compounds in high-temperature dyeing is their inverse solubility, analogous to the cloud point effect of nonionic surfactants. As the dyebath temperature approaches its maximum the solubility of the defoamer decreases, thus helping to maintain its effectiveness, whilst the increase in solubility on cooling after completion of the dyeing is claimed to overcome potential problems of subsequent spotting. The four most commonly used alkoxylated silicones are represented by structures 10.292–10.295 [536], where R is typically a methyl group, a is typically 1 and G is typically represented by formulae such as $-(CH_2)_3(OCH_2CH_2)_x(OCH_2CH_2CH_2)_yOR$ or $-(OCH_2CH_2)_x(OCH_2CH_2CH_2)_yOR$, where R is an end-capping group such as methyl.

A more recent development is the use of hybrid fluorochemical silicones, such as nonafluorohexyl-substituted siloxanes of the type represented by structure 10.296 [503].



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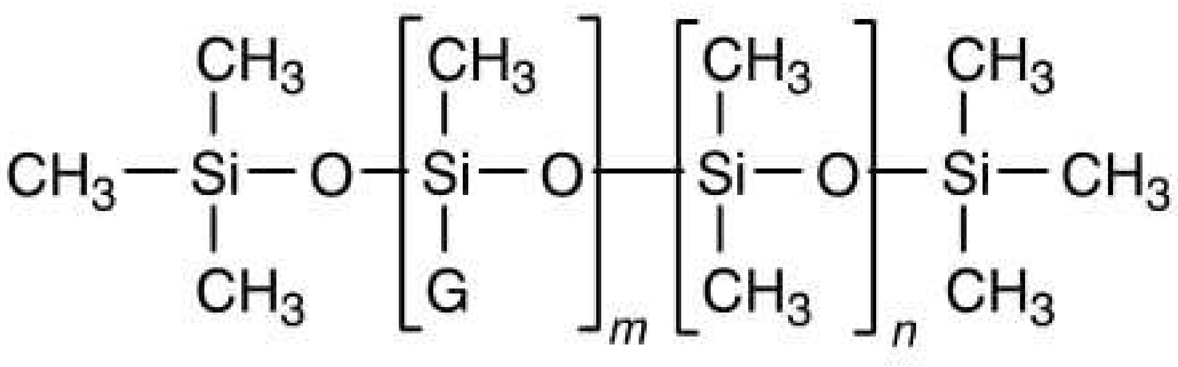
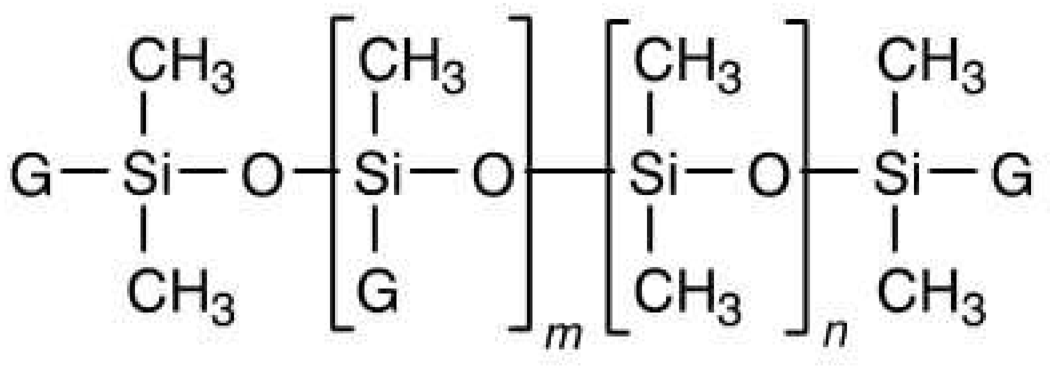


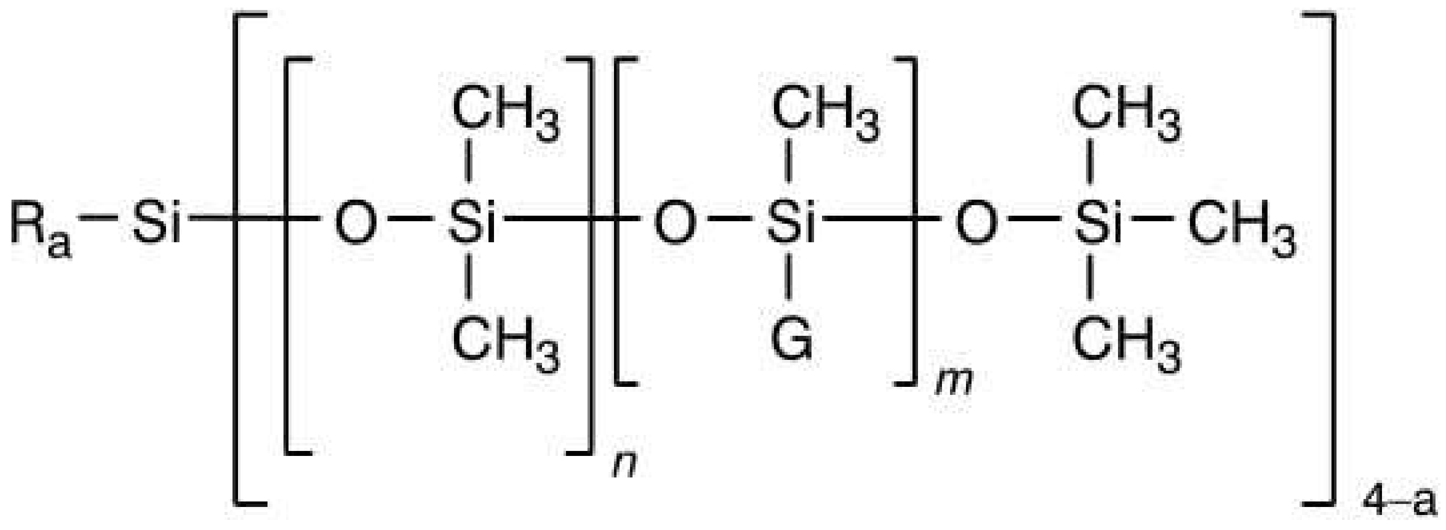
$CH_3-Si(CH_3)_2-O-[Si(CH_3)(G)-O]_m-[Si(CH_3)_2-O]_n-Si(CH_3)_2-CH_3$

10.292



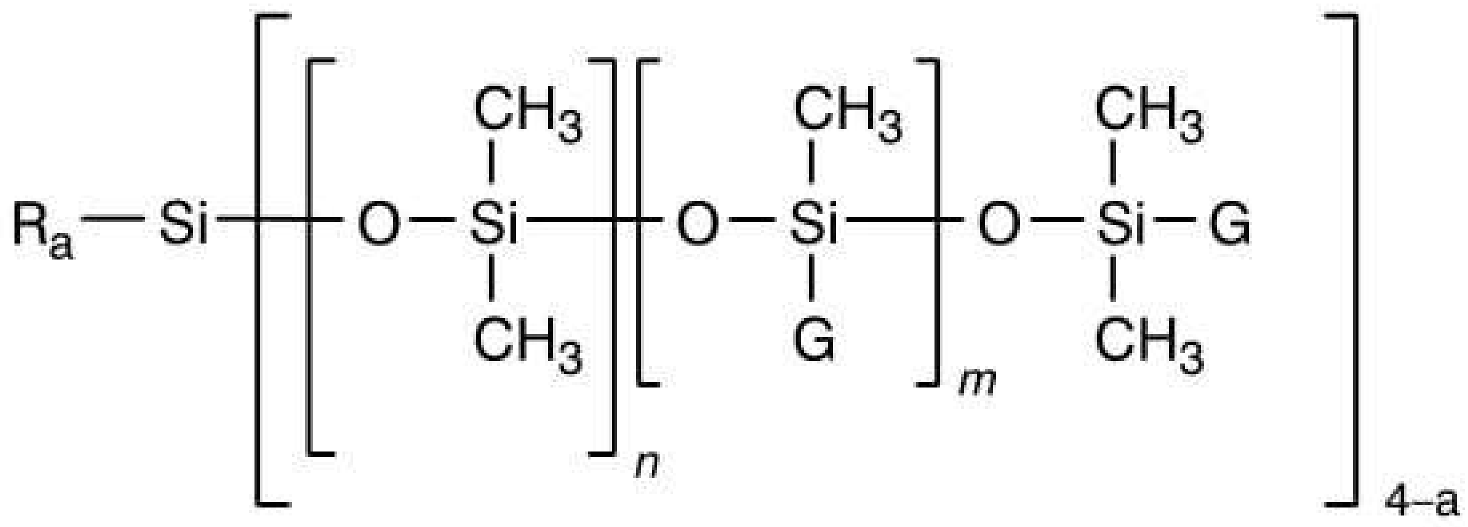
$G-Si(CH_3)_2-O-[Si(CH_3)(G)-O]_m-[Si(CH_3)_2-O]_n-Si(CH_3)_2-G$

10.293



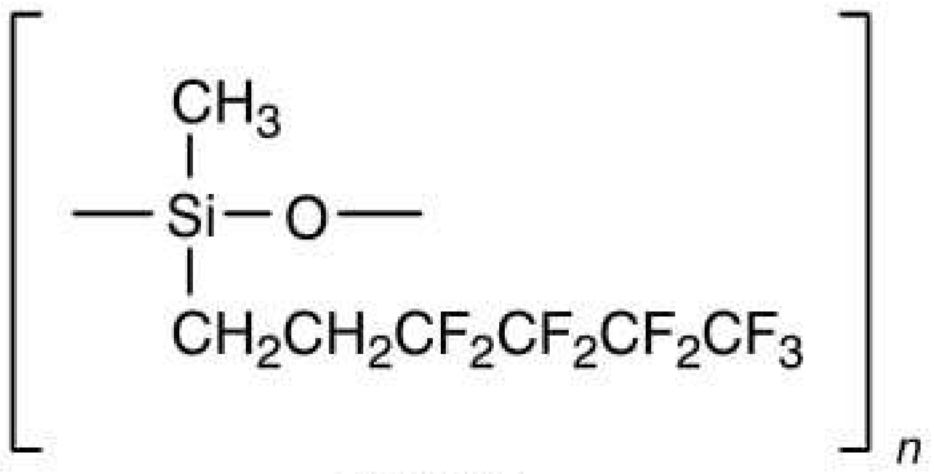
$R_a-Si\{[O-Si(CH_3)_2]_n[O-Si(CH_3)(G)]_m-O-Si(CH_3)_2-CH_3\}_{4-a}$

10.294



$R_a-Si\{[O-Si(CH_3)_2]_n[O-Si(CH_3)(G)]_m-O-Si(CH_3)_2-G\}_{4-a}$

10.295



$[-Si(CH_3)(CH_2CH_2CF_2CF_2CF_2CF_3)-O-]_n$

10.296

These copolymers have been mentioned already in section 10.10.4 as versatile and highly effective stain-resist, oil- and water-repellent finishing agents.

Antifoams are generally supplied for textile use as carefully formulated, relatively dilute aqueous emulsions; this ensures that the hydrophobic phase is uniformly distributed within the foaming system and also helps to safeguard against overdosing, with the attendant danger of spotting. A typical emulsion generally contains emulsifying agent(s) and thickening agent(s) in addition to water and the insoluble hydrophobic defoaming agent. For emulsification, the most common system [537] is a combination of a low-HLB surfactant with one of high HLB value, such as glyceryl monostearate or sorbitan monostearate with poly(ethylene glycol) monostearate. Obviously, the surfactants selected need to be low-foaming types and should provide an optimum level of emulsification, since over-emulsification will tend to negate the activity of the defoamer by inhibiting its interaction with the foaming system. The size of the defoamer droplets, largely determined by the emulsification system and the degree of comminution during manufacture, is critical in relation to the efficacy of the product; too small a size gives inadequate activity and if it is too large the stability of the emulsion is adversely affected. The optimum droplet size generally appears to be in the range 2 to 50 μm [537].

The function of the thickening agent is to increase the viscosity and so contribute to the stability of the product, the aim again being to attain an optimum level of viscosity. Thickening agents that do not gel at the high temperatures used in textile processing are essential; hydroxyethylcellulose, alginates and synthetic poly(acrylic acid) derivatives may be used. A small amount of a bactericide such as methyl *p*-hydroxybenzoate is often added to safeguard against biological degradation during storage, particularly in the case of natural thickening agents.

Typical formulations of commercial composite antifoams have been detailed [536,537]. There are many products on the market but evaluation of their relative efficacy depends on the foaming problems to be overcome. Not only does the chemical type of the active defoamer have to be considered, but its state within the emulsion and the intrinsic properties of the emulsion are also of crucial importance. Methods of evaluating defoamers have been described [539,540].

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