CHAPTER 7

Protein fibres

7.1 INTRODUCTION

Animal hair consists of complex proteins. The hair of sheep and goats is particularly important for textiles; wool is, by far, the major animal fibre in quantity, but cashmere and mohair are significant for their market value. This class of fibres also includes the fine double filament secreted by the silk worm. The entire range of protein fibres accounts for only about 6% of world fibre consumption, and the proportion is even less in many developed countries where synthetic fibres are readily available. Quality wools, fibres such as cashmere, and particularly silk, however, denote luxury and are priced accordingly.

Proteins are complex polyamides, also called polypeptides, produced by the biological polycondensation of a mixture of a specific type of amino acid with a variable side-group R (Scheme 3.3). The amino acid composition, and the sequence of the amino acid units along the polymer chain, characterise the structure of a protein molecule. Protein molecules, however, can adopt a variety of elaborate spatial arrangements. These include sheets of extended protein molecules laying side by side, or cord-like arrangements of individual helical molecules wound around each other. In globular proteins, such as enzymes, the protein molecules adopt even more complex, but characteristic, configurations. In living tissue, proteins are frequently associated with other types of biomolecules in complex cellular structures. It is only in fairly recent times that the detailed morphology (form and structure) of wool fibres, and the way in which it influences the dyeing process, has become clearer.

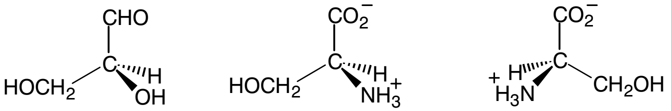
7.2 STRUCTURE OF WOOL FIBRES [1]

7.2.1 Keratins and wool proteins

Proteins are polymers of α- or 2-aminocarboxylic acids. They have an amino group attached to the carbon atom next to the carboxylate carbon atom. Apart from glycine (aminoacetic acid), the 2-carbon atom always has a substituent other than hydrogen. Thus, the four different groups attached to the 2-carbon atom satisfy the requirement for enantiomerism and optical activity. Hydrolysis, or enzyme digestion, of a protein breaks all the amide groups in the polymer and produces the constituent amino acids, which can be isolated and identified.

The four different substituents on the 2-carbon atom in all protein amino acids have the same absolute spatial relationship (configuration) as the substituents in L-glyceraldehyde (2,3-dihydroxypropanal; **1**, in Figure 7.1) and are therefore L-amino acids. This specific configuration of protein amino acids has significant biological consequences. D-2-amino acids (D-serine; **3** in Figure 7.1), whose configurations are the mirror images of those of the L-enantiomers (L-serine; **2** in Figure 7.1), are physiologically inactive. The complexities of the enantiomerism, and the varying proportions of the amino acids constituting proteins are, however, only the beginning of the description of the structure of these complex chemicals.

Wool consists of about 82% of a protein called keratin, but this has various forms. Hard keratins, such as in wool, have a high sulphur content, mainly because of the incorporation of the double amino acid cystine (Table 7.1, Figure 3.5). The remainder consists mainly of other proteins with a lower sulphur content. Wool therefore consists of a number of different polypeptides, with different molecular weights and amino acid compositions. Although the overall amino acid content of wool is known (Table 7.1), the sequences of amino acids along the protein chains are not. The relative amounts of the different amino acids in wool depend upon the part of the fibre analysed, the sheep variety and its diet, and the influence of the combined effects of heat, water and light on exposed fibres (weathering).



1 **2** **3**

Figure 7.1 L-2,3-dihydroxypropanal (**1**); L-serine (**2**); D-serine (**3**)

Because of resonance, the amide or peptide groups in a protein molecule are planar, the carbon–nitrogen bond having some double bond character and restricted rotation. The different 2-amino acid substituents, or side-chains, vary in

Table 7.1 Structure and amount of major amino acids in wool [2]

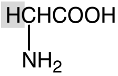
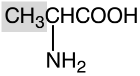
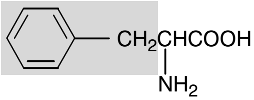
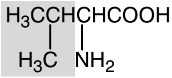
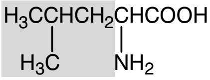
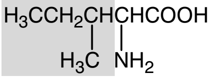
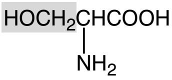
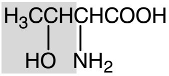
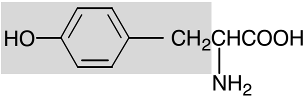
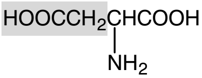
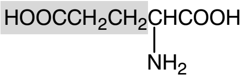
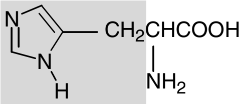
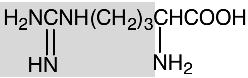
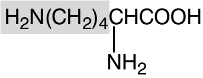
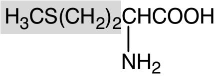
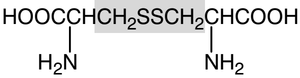
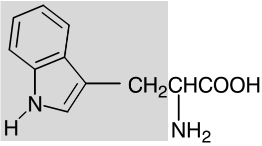
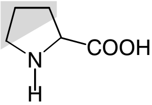
Amino acid	Structure(a)	Mol % (from two sources)		Nature of side-chain
Glycine	 $H\underset{NH_2}{C}HCOOH$	8.6	8.2	Hydrocarbon
Alanine	 $CH_3\underset{NH_2}{C}HCOOH$	5.3	5.4	Hydrocarbon
Phenylalanine		2.9	2.8	Hydrocarbon
Valine	 $H_3C\underset{H_3C}{C}H\underset{NH_2}{C}HCOOH$	5.5	5.7	Hydrocarbon
Leucine	 $H_3C\underset{H_3C}{C}HCH_2\underset{NH_2}{C}HCOOH$	7.7	7.7	Hydrocarbon
Isoleucine	 $H_3CCH_2\underset{H_3C}{C}H\underset{NH_2}{C}HCOOH$	3.1	3.1	Hydrocarbon
Serine	 $HOCH_2\underset{NH_2}{C}HCOOH$	10.3	10.5	Polar
Threonine	 $H_3C\underset{HO}{C}H\underset{NH_2}{C}HCOOH$	6.5	6.3	Polar
Tyrosine		4.0	3.7	Polar
Aspartic acid(b)	 $HOOCCH_2\underset{NH_2}{C}HCOOH$	6.4	6.6	Acidic

Table 7.1 *continued*

Amino acid	Structure(a)	Mol % (from two sources)		Nature of side-chain
Glutamic acid(c)	 $HOOCCH_2CH_2\underset{NH_2}{\underset{\vert}{C}}HCOOH$	11.9	11.9	Acidic
Histidine		0.9	0.8	Basic
Arginine	 $H_2N\underset{HN}{\underset{\Vert}{C}}NH(CH_2)_3\underset{NH_2}{\underset{\vert}{C}}HCOOH$	6.8	6.9	Basic
Lysine	 $H_2N(CH_2)_4\underset{NH_2}{\underset{\vert}{C}}HCOOH$	3.1	2.8	Basic
Methionine	 $H_3CS(CH_2)_2\underset{NH_2}{\underset{\vert}{C}}HCOOH$	0.5	0.4	Sulphur-containing
Cystine(d)	 $HOOC\underset{H_2N}{\underset{\vert}{C}}HCH_2SSCH_2\underset{NH_2}{\underset{\vert}{C}}HCOOH$	10.5(e)	10.0(e)	Sulphur-containing
Tryptophan				Heterocyclic
Proline		5.9	7.2	Heterocyclic

(a) Shading indicates identity of side-chain
(b) Includes asparagine residues
(c) Includes glutamine residues
(d) Includes oxidation by-product, cysteic acid
(e) Values are for half-cystine

size and chemical nature and project outwards from the main polymer chain. There are six main types:

(1) non-reactive hydrocarbon groups, as in alanine;
(2) polar groups such as alcoholic or phenolic groups, as in serine and tyrosine;
(3) basic groups, as in lysine, that influence the maximum amount of acid with which the wool combines and the absorption of anionic acid dyes (Section 1.1.2)
(4) acidic groups, as in glutamic acid;
(5) covalent crosslinking groups, as in cystine, that influence the solubility, swelling and mechanical properties of wool;
(6) heterocyclic groups, as in proline.

The protein chains in wool are held together by hydrogen bonds. These form between the hydrogen atom attached to the nitrogen of an amide group and the oxygen atom in a neighbouring carbonyl group, as in nylon. In addition, the chains are linked by ionic or salt crosslinks, by covalent bond crosslinks, and by weak interactions between non-polar side-groups (Figure 7.2). The latter are often called hydrophobic bonds. They arise because the association of hydrophobic non-polar groups is energetically more favourable when they are in a polar environment. This is analogous to the solubility of benzene in hexane, but not in

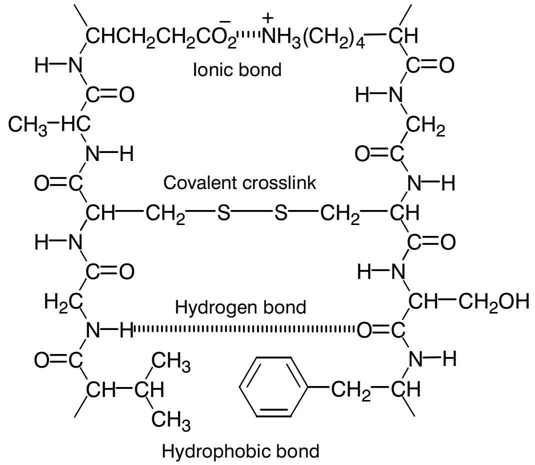
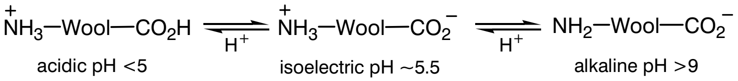


Figure 7.2 Types of inter-chain linkages in wool

water. Exactly the same types of interactions occur between different parts of the same molecule, as between different molecules. These various types of interactions are responsible for stabilising the particular configuration that a protein molecule adopts and for many of its chemical and physical properties.

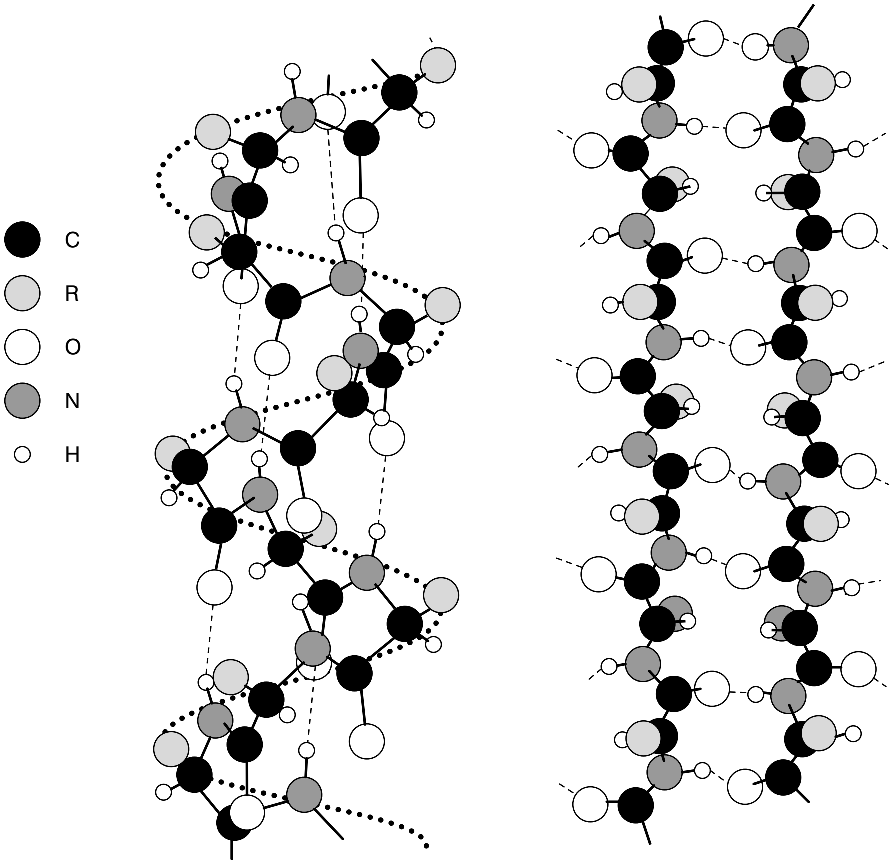
The ionic nature of the acidic and basic side-chains in wool leads to the formation of salt links between the protein chains. Their formation is pH dependent, being at a maximum at the isoelectric point around pH 5.5 (Scheme 7.1). This is the pH value at which the wool fibre has exactly the same number of cationic and anionic groups and is therefore electrically neutral. The work necessary to extend a wool fibre is at a maximum in the pH range from 5 to 9. In this pH range, the ionic salt links help to hold the protein chains together so that they resist elongation. The salt links cannot, however, exist under acidic conditions, when the anionic carboxylate groups are protonated ($pH < 5$), or under alkaline conditions, when the cationic ammonium ion groups are deprotonated ($pH > 9$). Wool contains about 820 mmol kg^{-1} of amino groups and a slightly lower number of carboxylic acid groups. These are responsible for its ability to absorb large amounts of alkalis and acids, and for dyeing processes involving ion exchange.



Scheme 7.1

The disulphide bonds between adjacent protein chains, and between different sections of the same chain, are a consequence of the incorporation of the double amino acid cystine. These covalent crosslinks contribute to the stability of wool fibres and to their mechanical, chemical and physical properties. There are also amide or isopeptide covalent crosslinks, as for example that formed between glutamic acid and lysine residues.

X-ray diffraction of unstretched wool fibres shows a pattern characteristic of α-keratin, in which the individual protein molecules have a helical configuration and wrap around each other in a helix. On stretching the wool fibre, the X-ray diffraction pattern changes to that of β-keratin, in which the chains are fully



α-Keratin (helical)

β-Keratin (extended)

Figure 7.3 Extended and helical molecules of keratin (hydrogen bonds are shown as faint dotted lines)

extended and form sheets of molecules bonded together (Figure 7.3). In this conversion, the intramolecular hydrogen bonds holding the helix together are broken and, once the protein chains are extended, new intermolecular hydrogen bonds form between neighbouring chains. Wool is not, however, very crystalline because the bulky side-groups along the polymer chains prevent the molecules from becoming aligned.

7.2.2 Morphology of wool fibres

Wool is a staple fibre from the fleece of various breeds of sheep. It is a multicellular, protein hair that tapers from the root to a point. Fibre lengths vary from 4 to 40 cm and diameters from 17 to 40 μm ($1\ \mu m = 1 \times 10^{-6}$ m). Wool fibres have complicated structures. The main components are the scaly cuticle, the body of the fibre or cortex, and the cell membrane complex. The latter surrounds the cells of both the cuticle and cortex in a continuous phase. Coarse fibres may also have a medulla or inner core.

Microscopic examination shows the scales on the fibre surface that are characteristic of most animal fibres. The overlapping scales point towards the fibre tip. In a fine wool, they constitute about 10% of the fibre. The friction they generate hinders the movement of the wool fibre in the direction of the tip. This is called the directional friction effect and is partly responsible for the felting and shrinkage of wool articles on washing. The scales consist of several layers and are covered with a hydrophobic outer layer called the epicuticle. It is part of the cell membrane complex and covers all the fibre, except the tip where it has been worn away by weathering.

The cortex is composed of spindle-shaped cells made up of fibrils of keratin, in a matrix of high-sulphur proteins, and surrounded by the cell membrane complex. It comprises about 90% of the wool fibre. In fine wools, the cortex appears as two distinct regions rather like two half-cylinders stuck together along their axes. These two regions are called the ortho- and paracortex. They spiral around each other along the fibre, following the crimp, the orthocortex always being oriented towards the outside of the crimp wave. This structure is similar to that in a bicomponent synthetic fibre. The crimp arises from the unequal rates of hardening of the keratin that begins in the hair follicle, but occurs at different levels on each side of the wool hair. These two cortical regions differ in structure and reactivity. Basic dyes stain the more accessible orthocortex cells but acid dyes show no preference for either cortex.

The cell membrane complex consists mainly of protein and lipid materials and surrounds all types of cells in a continuous network throughout the fibre. It forms a region of poor mechanical strength compared to the rest of the fibre and probably fractures first during fibre abrasion, leading to fibrillation – splitting into the individual cortical cells or even into protein fibrils within the cells. The membrane complex is weakened by extended dyeing at the boil in acidic solution. The medulla, if present, is a central core of cells that may contain coloured pigments. It does not run the entire length of the fibre and there may be hollow spaces.

A model for dyeing based on transfer of the dye from the aqueous solution to the fibre surface, adsorption on the surface and diffusion into the fibre, seems simplistic on considering the complex morphology of the wool fibre. The wool cortex is far from being homogeneous. Different parts of a wool fibre have different degrees of dye absorption due to variations in permeability and chemical composition. Studies on the rate of diffusion of dyes into wool fibres indicate a surface barrier opposing diffusion. This is particularly evident in the early stages of dyeing. Since dyes do not readily penetrate through the exocuticle and the surface scales, they were thought to form the barrier. In fact, dye molecules probably enter the fibre around the scaly, cuticle cells and then diffuse into the fibre along the non-keratinous regions of the cell membrane complex. Hydrophobic lipids in the regions between the cuticle cells, where dye enters the fibre, are partly responsible for the observed dyeing barrier. Dye then transfers from the cell membrane complex into the sulphur-rich proteins of the matrix that surrounds the cortical and cuticle cells, and finally into these cells themselves (Figure 7.4). At the end of dyeing, the keratinous regions are rich in dye and the non-keratinous regions are poor in dye. This is significant because dye in the non-keratinous regions can easily diffuse out of the wool fibres and would result in poor washing fastness.

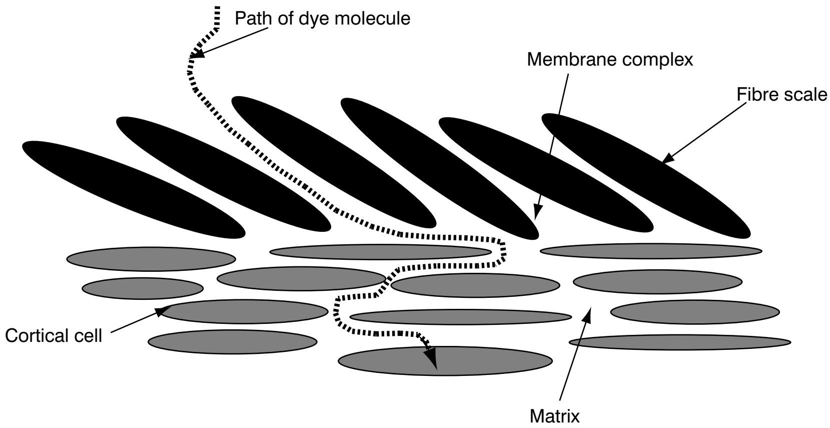


Figure 7.4 Diffusion of dye molecules into the cortex of a wool fibre

7.2.3 Constituents of raw wool

Raw wool contains a variety of different chemicals and dirt that must be removed. These impurities may comprise as much as 60% of raw wool mass. They include wool wax, suint, and a range of vegetable and mineral debris (Table 7.2). Wool wax is a complex mixture of hydrophobic fatty alcohols and fatty acids, whereas suint consists of water-soluble carboxylic acids and their salts from dried animal sweat.

Table 7.2 Approximate composition of raw wool

Component	%
Wool	45
Wool wax	18
Suint	10
Water	12
Debris	15

Raw wool is scoured, usually in a solution of sodium carbonate and a non-ionic detergent, to remove the bulk of these materials [3]. Careful control of the scouring conditions is essential to avoid matting of the fibres and to prevent any damage by hydrolysis of the alkali-sensitive protein. The scouring temperature never exceeds 50 °C and the liquor pH is not greater than 10.5. Mechanical agitation of the mass of fibres must be very gentle to avoid felting. Non-ionic detergents are preferred because wool does not significantly absorb them and they are therefore easily rinsed out. In addition, they have a strong emulsifying action on the wool wax.

The raw wool is washed in a series of baths containing decreasing concentrations of chemicals and with decreasing temperatures. Recovered and purified wool wax is known as lanolin, a component of many cosmetic products. Raw wool is also degreased by treatment with solvents such as solvent naphtha. Solvent extraction is also used to determine the amount of residual wax after scouring.

7.3 PHYSICAL AND CHEMICAL PROPERTIES OF WOOL

7.3.1 Wool quality

Wool fibres vary remarkably in length, crimp, lustre, strength and dye uptake, depending upon which part of the sheep's body they came from and upon the conditions that existed during growth. Merino wool fibres are very fine (17–25 μm diameter) but not very long (60–100 mm), whereas a Lincoln wool is courser (around 40 μm diameter) but much longer (175–250 mm). Wool is graded into various qualities, usually based on the finest yarn that can be spun from it. This depends on the fibre thickness and staple length. The worsted count is the number of hanks containing 560 yards of yarn that can be spun from 1 lb of wool fibre. Thus, 1 lb of a worsted yarn with a 100 count would be 560 × 100 yards long. This is the same as 8.9 tex (g km^{-1}). The length of yarn in a hank for the woollen count varies from place to place, being in the range 100–320 yd. The quality assessment also includes evaluation of the degree of crimp, which is higher for better qualities, and of the lustre and colour. High quality wool is usually free of kemps. These are abnormal fibres with a horny sheath extending into the cortex that resist dye penetration and can give unlevel coloration.

Wool fineness can be assessed by determination of the average fibre diameter using a projected image from a microscope, but requires examination of many fibres. Alternatively, the air flow method used for evaluating the fineness of cotton fibres can be used (see reference 4, chapter 5).

Virgin wool is very expensive, particularly for the better qualities. The chemical treatments that prevent shrinkage and felting on repeated washing of wool fabrics add to the cost. Wool consumption is now only a small fraction of the total for all fibres, and, because of its high price, many articles contain recycled wool.

Wool is used for three major types of fabrics: woollen, worsted and felts. The latter have fibres matted and pressed together with a random arrangement. Woollen and worsted materials are produced using different carding and spinning systems and have quite different appearances and characteristics (Table 7.3).

Table 7.3 Different characteristics of woollen and worsted yarns

Woollen yarn	Worsted yarn
Short fibres	Long fibres
Only carded	Carded and combed
Low twist	High twist
Coarse, soft and voluminous	Fine, smooth and solid
Medium strength	High strength

7.3.2 Wool properties

Wool fibres are hygroscopic and the most hydrophilic of textile fibres. The standard regain is around 16–18% water and clearly significant when wool is sold by weight. The actual regain of purified wool is quite sensitive to traces of residual impurities and to any chemical modification of the protein fibre.

Despite the high regain, wool does not feel damp. Wool is a very warm fibre and is ideal for undergarments in contact with the skin. The absorption of water from perspiration by wool fibres is exothermic and releases heat. On drying, the rate of evaporation from the wool in contact with the body is so slow that there is no cooling effect.

Although wool is hydrophilic, the fibres may be difficult to wet out because of the scaly barrier and thorough wetting usually requires hot water and often a wetting agent. On water absorption, hydrogen bonds with water molecules replace those between amide groups, and salt linkages break as the ionic groups become strongly solvated by water molecules. The fibre therefore becomes weaker. These types of intermolecular force are so predominant in dry or conditioned wool that they can mask the effects of broken peptide and disulphide bonds on the mechanical properties. For this reason, testing of the mechanical properties to evaluate protein damage is often conducted on wet wool.

Wool fibres are elastic and resilient. Wool fabrics therefore do not crease easily, have good crease recovery, and wool garments fit well. Wool fibres are much less rigid than those of cotton. The elastic recovery of wool fibres is 65% for 20% extension and almost 100% for short extensions. The elasticity is related to the reversible deformation of the helical α-keratin molecules, which act rather like springs. The natural crimp of the fibres contributes to the elasticity of wool as the fibres return to their wavy form after deformation. The crimp also stabilises low twist woollen yarns by holding the fibres together. Such yarns trap air, and when used in garments, providing an insulating barrier to loss of body heat.

Like all proteins, wool is a sensitive biopolymer. On extended exposure to light and air, it will gradually deteriorate in quality, often yellowing considerably. For this reason, it is very difficult to maintain the quality white of bleached wool. It is also not very stable to dry heat and yellows readily on over-heating during drying.

7.3.3 Effects of acids and alkalis on wool

Aqueous solutions of acids and alkalis initially influence wool by changing the degree of dissociation of carboxylic acid and ammonium ion groups in the fibre.

For wool, the numbers of amino and carboxylic acid groups are nearly equal, being about 820 and 770 mmol kg^{-1}, respectively. In electrically neutral wool, these are present as ammonium and carboxylate ion groups.

For a protein, the isoelectric point is defined as the pH value where the fibre contains equal numbers of anionic and cationic groups, and has a value of around 5.5 for wool. In acidic solution, the carboxylate ions combine with protons to form neutral carboxylic acid groups and the ammonium ion groups make the fibre cationic. Conversely, in alkaline solution, reaction with hydroxide ions converts ammonium ion to amino groups and the fibre becomes anionic (Table 7.4). Because of the various types of acidic and basic side-groups in wool, these acid–base reactions occur over quite a large pH range, from 1.5 to 4.5 for protonation of carboxylate groups, and from 8 to 13 for deprotonation of ammonium ion groups. There is therefore an extensive region from about pH 5.0 to 7.5 where wool has little bound acid or base. At the isoelectric point, wool has about 770 mmol kg^{-1} of ammonium and carboxylate ion groups and therefore 50 mmol kg^{-1} of free amino groups. The maximum acid binding capacity of wool is determined by back titration of carboxylate groups (770 mmol kg^{-1}) and direct protonation of the free amino groups (50 mmol kg^{-1}). It therefore depends upon the total number of amino groups. Similarly, the total amount of combined alkali depends on the number of ammonium ion groups that are neutralised (770 mmol kg^{-1}) and therefore the number of carboxylic acid groups.

Table 7.4 Numbers of acidic and basic groups in wool under various conditions

Group	Isoelectric point	Acidic (+ 820 mmol kg^{-1} H^+)	Alkaline (+ 770 mmol kg^{-1} HO^-)
Amino, NH_2	50	0	820
Ammonium ion, NH_3^+	770	820	0
Carboxylic acid, CO_2H	0	770	0
Carboxylate ion, CO_2^-	770	0	770

The absorption of acids by wool has considerable significance in dyeing wool with acid dyes. This can initially be considered as a simple process of ion exchange in which the sulphate ion from sulphuric acid initially interacts with an ammonium ion group in the wool but is exchanged for a dye anion during dyeing.

Wool is a sensitive protein. Both acids and alkalis catalyse the hydrolysis of wool proteins and damage to wool can be extensive in hot solutions, particularly under alkaline conditions. In fact, wool rapidly dissolves in boiling 2% aqueous NaOH solution, whereas cotton is totally unaffected by this treatment. Alkaline solutions rapidly loosen the surface scales and penetrate into and attack the cortex. In wool processing, it is essential that the pH of any solution does not exceed a value of 10.0 to 10.5, particularly if the temperature is above 50 °C. Dilute ammonia solution at about pH 10 is a relatively safe choice since wool can withstand treatment under these conditions for 30 min at temperatures up to 90 °C. When using weak alkalis such as ammonia and sodium carbonate in scouring, care is always essential. Wool is even damaged by extended treatment in boiling water. The fibres become weaker, less resilient and yellow.

Wool is considerably less sensitive to hot dilute solutions of acids. Cotton can be completely dissolved by hydrolysis in acid solutions that cause minimal damage to wool. This is used to advantage in the carbonising process in which wool is impregnated with dilute sulphuric acid solution and dried. This converts all cellulosic material into brittle hydrocelluloses that can be removed from the wool by beating. More concentrated acid solutions, or prolonged treatment with hot dilute acid solutions, will, however, cause hydrolysis of the protein. During dyeing, in the presence of acids, there is invariably some degree of damage to the wool fibres, which manifests itself as a loss of strength and abrasion resistance. Alkali damaged wool is even less resistant to acids.

7.3.4 Setting of wool

When damp wool is stretched and dried, as in ironing, the fabric retains the shape it has been given under tension. This dimensional stability arises because hydrogen bonds are broken as the keratin chains are stretched under the influence of water and heat. The intermolecular hydrogen bonds between amide groups are replaced by hydrogen bonds with water. As drying proceeds, new hydrogen bonds then form between the protein molecules in their new positions, which stabilises the new structure. The effect is not permanent and the material may shrink on wetting as the hydrogen bonds are again broken.

The effect is called setting and, in the above case, temporary setting, because of the lack of permanence. The same effect occurs when wet human hair is wound on a curler and allowed to dry. More permanent setting of the dimensions of wool fabrics and articles occurs on treatment with hot water or steam over a more prolonged period. This has a chemical action on the wool. For example, in the decatising process, wool fabric, wound on a roller under tension with a cotton wrapper, is set by passing steam through it. In crabbing, the roll of wool fabric is immersed in boiling or hot water and kept under tension as the water cools. Hydrolysis breaks the disulphide crosslinks and new crosslinks form by reaction of the resulting sulphenic acid groups (Scheme 7.2). The effects of decatising are more permanent than those of crabbing. A decatised wool fabric will retain its shape and have better resistance to shrinking when treated with water provided that the water temperature is below that of the steam used in the decatising process. Reactions such as this must be avoided during extended dyeing at the boil to ensure that permanently set creases do not form.

$$\text{Wool—CH}_2\text{—S—S—CH}_2\text{—Wool} + \text{H}_2\text{O} \longrightarrow \text{Wool—CH}_2\text{—SH} + \text{HOS—CH}_2\text{—Wool}$$

$$\text{Wool—CH}_2\text{—SOH} + \text{NH}_2\text{—Wool} \longrightarrow \text{Wool—CH}_2\text{—S—NH—Wool} + \text{H}_2\text{O}$$

Scheme 7.2

Effective permanent setting of wool fabrics can be carried out by treating the material with reducing agents that break the disulphide crosslinks, promoting increased chain mobility. Thiols, such as salts of thioglycollic acid, and sodium bisulphite are suitable reducing agents. On re-oxidation, new disulphide links form with the chains in their new positions thus providing stability to the new molecular arrangement and the shape of the material (Scheme 7.3). Breaking the disulphide links holding the keratin molecules together causes a significant loss of strength but this returns on re-oxidation.

$$\text{Wool—CH}_2\text{—S—S—CH}_2\text{—Wool} + 2\,\text{SH—CH}_2\text{CO}_2^-$$

$$\downarrow$$

$$2\,\text{Wool—CH}_2\text{—SH} + {}^-\text{O}_2\text{CCH}_2\text{—S—S—CH}_2\text{CO}_2^-$$

$$4\,\text{Wool—CH}_2\text{—SH} + \text{O}_2 \longrightarrow 2\,\text{Wool—CH}_2\text{—S—S—CH}_2\text{—Wool} + 2\,\text{H}_2\text{O}$$

Scheme 7.3

7.3.5 Felting of wool

Washing a textile material releases the stresses applied to the yarns during manufacture and usually causes shrinkage and deformation of the shape of the material. During washing, water absorption softens and lubricates the fibres so that they can return to their original unstrained condition. This effect is called relaxation shrinkage. It is reversible and can be partly rectified by stretching and drying, although shrinkage will occur again on wetting. For some knitted materials, extension rather than shrinkage may occur on washing as the water releases the strain in the yarn loops and they deform more easily.

Washing of woollen articles causes irreversible shrinkage and felting. Mechanical compression and relaxation of the fibres in a woollen fabric during washing cause fibre displacement. This is promoted by the wool fibre's elasticity and the lubricating action of the detergent. The scales on the surface of the wool fibres allow them to move only in the direction of the root, and their friction prevents their return to the original positions. This irreversible process is called felting. It closes up the fabric structure, making it much more compact and of increased rigidity. The separate yarns are frequently much less easily distinguished. Although the mechanism of unidirectional fibre movement is probably an oversimplification, it provides a partial explanation of this important effect. Shrinkage and felting are obviously undesirable in a finished article that is going to be repeatedly washed.

On the other hand, felting is often deliberately carried out during the finishing of many woollen fabrics, either before or after dyeing. The process is called fulling or milling. In a fulling mill, the wet, woollen fabric is pounded and turned around by reciprocating hammers. Rotary milling machines are frequently used. These hold a continuous rope of fabric that passes round and round, driven by a pair of rollers that force the fabric through a compression funnel. The compressed fabric relaxes as it exits the funnel and as it passes round the machine for another cycle. Felting is achieved by repeated compression and relaxation. Rotary milling machines allow combined milling, scouring and desizing before dyeing. Dirty liquor initially squeezed from the material passes into the trough below the rollers and out to the drain. Later, once the oils have been removed, this liquor is retained in the machine.

7.4 WOOL PROCESSING [4]

7.4.1 Scouring wool fabric

Woven and knitted wool materials and yarns must be scoured before dyeing to remove lubricating oils that were added to aid processing. To minimise felting, scouring must be carried out gently, using the lowest temperature, the mildest alkali and mechanical action, and for times as short as 15 min. If milling and scouring are combined, somewhat more vigorous conditions apply. Alternatively, oils can be eliminated by treating the goods in a rotating perforated drum machine using an organic solvent such as perchloroethylene (tetrachloroethene). It is also possible to achieve some felting under these conditions by adding water to the organic solvent. Suitable auxiliary chemicals keep this in fine suspension during the solvent treatment. Whatever process is used, effective elimination of the oil, in a completely uniform manner, is an essential prerequisite to level dyeing.

7.4.2 Means of eliminating wool shrinkage

A variety of methods produce wool fabrics that withstand repeated washing without shrinkage and felting. They are particularly important for knitted woollens and worsted fabrics. Two main principles are used:

(1) modification of the scale structure of the fibre cuticle to decrease the directional friction effect – this can be achieved by chemical treatments that either partially remove the scales or cover them with a smooth film of polymer;
(2) reduction of fibre mobility by adhesion of fibres and yarns at their points of contact and by decreasing fibre elasticity by means of intermolecular crosslinking.

Treatment of wool with chlorine attacks the scales of the cuticle and gives fibres with a smoother surface and a fabric with improved shrink resistance. This is done by treating a scoured wool fabric with dilute HCl solution at room temperature, draining, and then running the goods in water slowly adding sodium hypochlorite solution. The acid retained in the wool reacts with the hypochlorite liberating chlorine (Scheme 7.4). Alternatively, treatment of the moist wool with chlorine gas in a sealed chamber is also effective. After chlorination, treatment with a

$$2\,HCl + NaOCl \longrightarrow Cl_2 + H_2O + NaCl$$

$$Cl_2 + H_2O + NaHSO_3 \longrightarrow NaHSO_4 + 2HCl$$

Scheme 7.4

solution of the reducing agent sodium bisulphite removes residual traces of chlorine (Scheme 7.4). Both chlorination methods, however, require careful control to ensure uniformity of the treatment and to avoid imparting an overly harsh handle to the wool. The reaction of chlorine on the cuticle is very rapid. It is for this reason that the chlorine must be generated or added slowly.

The chlorination process increases the substantivity of acid dyes for the wool and level dyeing becomes more difficult. It will be impossible if the wool has been unevenly chlorinated, since chlorinated wool has a much higher rate of dye absorption. Unfortunately, chlorinated wool also gives much higher rates of dye desorption on washing. Acid dyes with good migration, which might be useful for dyeing unevenly chlorinated wool because of desorption from heavily dyed fibres and re-absorption by paler ones, also have rather poor washing fastness and are almost useless on chlorinated wool that will be washed regularly.

The problem of even chlorination can be partly overcome by use of a compound whose hydrolysis slowly liberates chlorine once it has been uniformly distributed in the wool. The sodium salt of dichloroisocyanuric acid is such a compound (Figure 7.5). Gradually increasing the acidity of the solution at room temperature, or increasing the temperature at a constant pH of about 4.5 to 5.0, controls the rate of chlorine evolution. Continuous processing is possible, but again a bisulphite anti-chlor treatment is needed to remove residual chlorine from the goods.

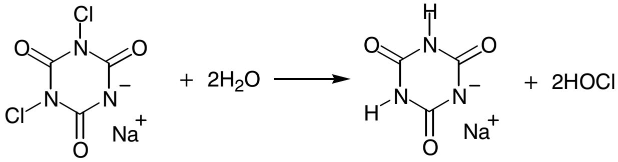


Figure 7.5 Hydrolysis of dichloroisocyanuric acid

The objective of the reaction with chlorine is to modify the scales of the cuticle rather than the cortex. The scales, particularly the tips, are attacked and their mutual friction is reduced thus decreasing the degree of shrinkage on washing. Chlorination also oxidises disulphide crosslinks in the cuticle proteins to sulphonic acid groups (Scheme 7.5). These are strongly solvated by water and the cuticle

$$\text{Wool—CH}_2\text{—S—S—CH}_2\text{—Wool} + 5\text{Cl}_2 + 6\text{H}_2\text{O} \longrightarrow 2\text{Wool—CH}_2\text{—SO}_3\text{H} + 10\text{HCl}$$

Scheme 7.5

therefore swells and becomes softer. Chlorination also generates some water-soluble peptides from the proteins in the cuticle, which also contribute to softening the scales. The anti-shrink effect of chlorination may not be permanent if these proteins are gradually removed from the fibre surface on washing and the scales harden.

A number of other so-called subtractive or destructive wool shrink-resist processes are known. These also modify the scale structure. In particular, the process based on treatment of wool with permonosulphuric acid (H_2SO_5) merits mention. It will be of increasing importance as concern for pollution by organochlorine compounds increases.

The most successful, permanent anti-shrink treatments for wool combine mild chlorination with cationic polymer deposition on the fibre surface. The chlorine-Hercosett method for continuous treatment of wool tops (combed wool sliver) is particularly well known. The process is also applicable to wool garments. Mild pre-chlorination with hypochlorite and acid prepares the wool fibre surface for the cationic polymer. An anti-chlor treatment with sodium bisulphite eliminates residual chlorine and reacts with residual acid to form sulphurous acid. The Hercosett polymer is a polyamide with cationic azetidinium groups introduced by reaction of secondary amino groups with epichlorhydrin (3-chloropropene oxide) (Figure 7.6). The polymer is applied to wool from aqueous solution and is substantive to the anionic wool surface. During drying, the azetidinium groups are able to react with thiol groups in the wool and with free secondary amino groups in other parts of the polyamide chain. This insolubilises and fixes the resin to the fibre.

Hercosett-treated wool has different dyeing properties than wool and chlorinated wool. Under neutral or acidic conditions, the deposited polymer retains a pronounced cationic nature. This arises from residual azetidinium groups and the protonation of the tertiary amino groups from their hydrolysis (2,3-dihydroxypropanamine groups). Anionic acid dyes have higher substantivity for the treated wool and high initial rates of absorption because of their attraction to the cationic polymer coating. Level dyeing requires considerable care. Under washing conditions, these quaternary 2,3-dihydroxypropanamine groups lose their protons, becoming neutral, so that the ionic attraction holding the dye molecules is lost. There is therefore a substantial decrease in the washing fastness of most anionic dyes, except reactive dyes that have covalently bonded to the protein.

A variety of other polymer deposition processes is used for producing shrink-resistant wool. These act by coating the fibre scales and reducing the frictional

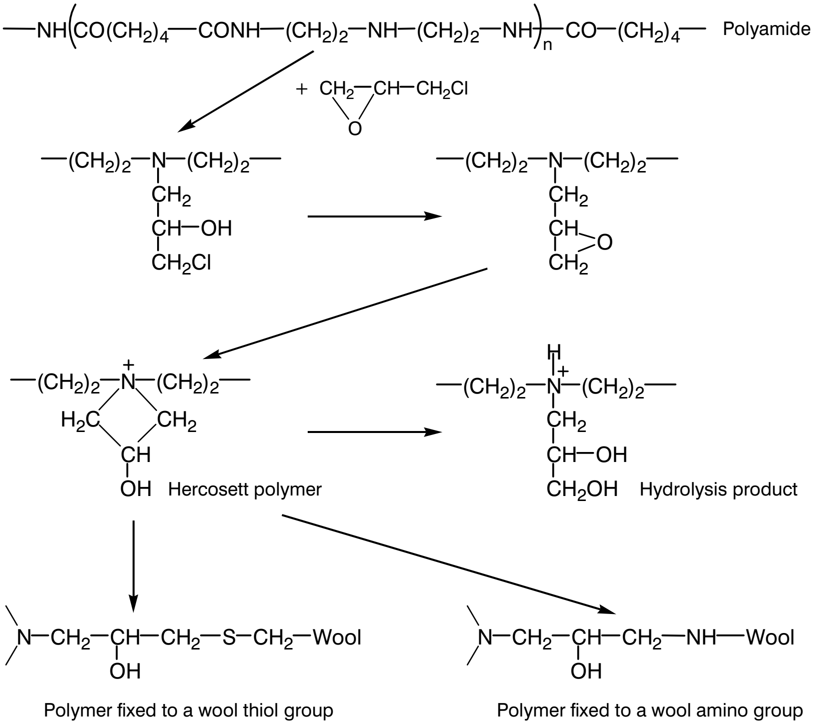


Figure 7.6 Chemistry of the Hercosett process for shrink-proof wool

effect, and by welding fibres together at their contact points. The polymer can be a polyamide produced by interfacial polymerisation, or a silicone or polyurethane coated onto the fibres using an organic solvent. A curing step is usually needed to fix the film of polymer onto the surface scales.

Several different testing procedures are used to evaluate the shrinkage of wool fabrics or articles. These involve evaluation of the relaxation and felting shrinkage in standardised washing and felting procedures. As with other chemical treatments of wool, shrink-resist processes cause some damage to the fibres. This can be assessed by dyeing and wool solubility tests. Damaged wool invariably gives a higher rate of dye absorption and is more readily soluble in dilute NaOH solution, or in solutions of urea and sodium bisulphite. The evaluation of fibre damage is important because damaged wool is less resistant to repeated washing and to abrasion [5].

7.4.3 Bleaching wool

The natural colour of white wool varies from white to pale yellow. The yellow tint is usually a sign that the protein has undergone some reaction on exposure to air and light. To eliminate the yellow tint, or if dyeing bright pastel shades, wool must be bleached. Although bleaching of wool produces a white fibre, the effect is never permanent. On further exposure to air and light, the sensitive protein slowly reacts and again reverts to its more usual yellowish tint.

Wool cannot be bleached with sodium hypochlorite solutions, as for cotton, since it is extensively damaged to the point at which it even dissolves in the solution. The traditional method of bleaching moist wool used sulphur dioxide gas. This simple and cheap process was called stoving but is now obsolete.

Today, the preferred bleaching agent is hydrogen peroxide. Bleaching is usually carried out in weakly alkaline solution containing a stabiliser and a sequestrant, as this gives the best quality white fibres. Even after carefully controlled alkaline bleaching of wool, the goods should not be boiled as the bleached wool is quite sensitive to yellowing. Dyeing of pale shades should be conducted at temperatures not exceeding 80 °C. In some cases, the wool material is simply soaked in hydrogen peroxide solution and dried. If bleaching is used to brighten a dyed fabric, and alkali-sensitive dyes are present, neutral or acidic peroxide bleaching is possible.

7.4.4 Moth-proofing wool

Wool has rather poor resistance to mildew and bacteria that grow when moist wool is stored over an extended period. The larvae of a variety of moths, and some beetles, also eat wool. The adult moth lays its eggs in the wool, the larvae hatch, feed on the wool, and then metamorphose into adult moths, thus continuing the cycle. Considerable damage to the wool usually results.

In the past, it was common practice to store woollen articles with mothballs. These contain chemicals, such as naphthalene or *p*-dichlorobenzene, that are slightly volatile and have a characteristic odour. These chemicals are deterrents but do not really ‘moth-proof’ the fibres. To do this, the wool must be treated with polychlorinated organic compounds developed specifically for wool, or with insecticides generally used in agriculture, or mixtures of the two (Figure 7.7). The major application of these agents is for wool yarn in carpets.

Moth-proofing agents are usually applied during dyeing, some, such as Mitin FF (Figure 7.7), acting rather like colourless acid dyes. They have adequate fastness to washing and light to maintain their moth-proofing effect over the life of the

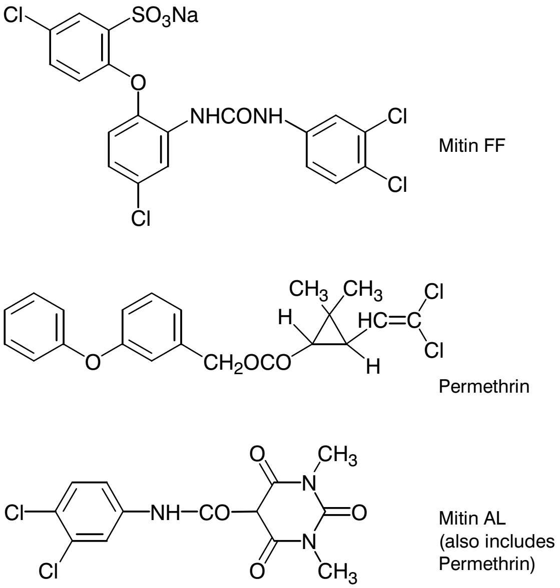


Figure 7.7 Chemicals for mothproofing wool

wool article. Alternatively, the wool may be treated during scouring but the degree of penetration of the agent into the fibres is smaller and the fastness properties are inferior to those obtained by dyebath application.

It is essential that these moth-proofing chemicals are used safely in the mill and that they pose no danger to the consumer. There are increasingly strict requirements on the disposal of organochlorine residues into sewers and natural water systems.

7.5 SPECIALITY ANIMAL FIBRES

A variety of hair fibres such as mohair and cashmere have similar properties to wool, although the fibre morphologies are different. These quality fibres are prized for their fineness and soft handle. Some animal fibres, including wool, may be quite heavily pigmented and have colours ranging from brown to black. All the protein hair fibres possess similar dyeing properties, the differences arising from variations in fibre morphology and the types of protein polymer side-groups.

Despite several attempts, the production of regenerated protein fibres, by extrusion of protein solutions and their coagulation, has not been commercially successful, mainly because of the poor durability of the filaments produced.

Silk filaments are obtained by unwinding the cocoons of the silk worm. The raw fibre consists of twin filaments of a protein called fibroin with a coating of a protein gum called sericin. The silk filaments are degummed using soap solution at or near the boil. Different degrees of degumming are used for different qualities of silk. Silk filaments are often weighted by treatment with tin salts, phosphates and silicates and may therefore contain appreciable amounts of insoluble inorganic material. In all processing, the silk filaments must be protected from breakages by using smooth machinery and placing them in permeable bags.

The amino acid composition of fibroin is quite different from that of keratin. Fibroin has only four major amino acid components – glycine, alanine, serine and tyrosine – containing long sequences of alternating glycine and alanine residues. It has fewer amine and acid side-chains and contains no cystine. Silk only absorbs about 150 mmol kg^{-1} of acid compared to about 820 mmol kg^{-1} for wool. Compared to wool, silk is somewhat less sensitive to alkalis but more sensitive to acids. Treatment with dilute mineral acid solutions causes shrinkage and is used to produce crepe effects. Organic acids harden the fibre surface and increase the scroop, the crunching noise made when the fabric is crumpled. The protein chains in fibroin are fully extended in the β-configuration and silk therefore has lower elasticity than wool. It is, however, sufficiently resilient to give fabrics that retain their shape and resist wrinkling. It is still considered the luxury fibre.

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CHAPTER 8

Water treatment

In textile finishing, water consumption is far greater than the amounts of fibres processed. It is the ubiquitous solvent for the solutions of chemicals used. Rinsing and washing operations alone consume enormous amounts of water. Steam is still the major heat-transfer medium for many processes and the quality of water fed to boilers is often critical.

The volume of aqueous effluent leaving a textile finishing plant is very close to the total input for the many different wet processes. The effluent consists of a relatively dilute solution of a considerable number of chemicals, including acids, alkalis, salts, dyes and other organic chemicals. Any presentation of textile dyeing would be incomplete without some discussion of the quality of water required for textile wet processing, and of the treatment of waste water so that it can be discarded with minimum environmental impact.

8.1 WATER QUALITY FOR THE DYEHOUSE

During the Industrial Revolution, the textile industry invariably grew in regions having an abundant supply of soft water such as in West Yorkshire. Such water is relatively free from calcium and magnesium salts. It does not precipitate soap or other chemicals during washing, or form a scale on the boiler walls when generating steam.

Water for a textile plant may come from various sources. These include surface water from rivers and lakes, and subterranean water from wells. The water may be obtained directly from the source or from the local municipality. Natural and pretreated water may contain a variety of chemical species that can influence textile wet processing in general, and dyeing in particular.

The various salts present in water depend on the geological formations through which the water has flowed. These salts are mainly the carbonates (CO_3^{2-}), hydrogencarbonates (HCO_3^-, more commonly named bicarbonates), sulphates (SO_4^{2-}) and chlorides (Cl^-) of calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+). Although calcium and magnesium carbonates in limestone are relatively insoluble, the action of dissolved carbon dioxide in rain water can leach them out in the form of the more soluble bicarbonates (Scheme 8.1). Hard water contains calcium and magnesium ions and gives an immediate precipitate with soap. Soap is a water-soluble sodium salt of a high molecular weight carboxylic acid, such as stearic acid. Its calcium and magnesium salts are much less soluble and give a gummy precipitate with a soap solution in hard water (Scheme 8.2). When this happens, the cleaning efficiency of the soap decreases dramatically. The dirt in suspension, as well as the precipitated calcium and magnesium soaps, can deposit back onto the material being washed. This gives a dingy fabric with a poor handle that will be difficult to dye in a level shade.

$$\mathrm{CaCO_3(s) + CO_2(aq) + H_2O(l) \longrightarrow Ca(HCO_3)_2(aq)}$$

Scheme 8.1

$$\mathrm{2CH_3(CH_2)_{16}CO_2^-Na^+\ (aq) + Ca^{2+}\ (aq) \longrightarrow \left(CH_3(CH_2)_{16}CO_2^-\right)_2 Ca^{2+}\ (s) + 2Na^+\ (aq)}$$

Scheme 8.2

Besides dissolved salts of natural origin, water may contain a variety of other salts from human or industrial activity. These include nitrates (NO_3^-), phosphates (HPO_4^{2-} and $H_2PO_4^-$) and various metal ions. The ions of certain transition metals, such as those of iron, copper and manganese, can precipitate dyes, or form complexes with them, dulling or even changing their shade. In addition, many of these ions catalyse the decomposition of hydrogen peroxide in bleaching baths. It is not uncommon for a particle of iron rust on the surface of a cotton fabric to generate such rapid peroxide decomposition that the cellulose is totally oxidised and a hole results. These transition metal ions may be present in the natural or municipal water, or, in the case of iron, come from corrosion within pipelines. Both dissolved and colloidal silica in boiler feed water can lead to the formation of a hard resistant scale on the boiler's internal surfaces, considerably decreasing heat transfer efficiency. Organic compounds from the decomposition of vegetable matter in the water, or from sources of pollution, can be very varied. They can have such high concentrations that the water is coloured. Table 8.1 illustrates the quality of water usually considered acceptable for textile processing and steam generation.

Water entering a textile dyeing or finishing plant usually passes through a grill to eliminate floating debris. Small particles in suspension must also be removed.

Table 8.1 Typical dyehouse water quality

Component	Permissible concentrations mg l^{-1}
Hardness	0–25 $CaCO_3$
Iron	0.02–0.1
Manganese	0.02
Silica	0.5–3.0
Alkalinity to pH 4	35–65 $CaCO_3$
Dissolved solids	65–150

The water may pass from the primary source into a settling pond, from which water can be drawn after any small particles have settled to the bottom, or it may be filtered by passage through a bed of fine sand. For particles smaller than about 0.02 mm, a coagulant aids sedimentation and clarification of the water. Addition of small quantities of sodium aluminate ($NaAlO_2$) or aluminium sulphate, and adjustment to around pH 7, give a gelatinous precipitate of aluminium hydroxide that imprisons the small particles and accelerates sedimentation or filtration. Addition of a flocculant, such as a polyacrylic acid–polyacrylamide copolymer, gives better particle adhesion and a higher rate of sedimentation. This type of treatment also improves the colour of the water. Soluble impurities in the water, such as iron, pollutants, and organic matter, are a real problem. Good aeration of the water will usually convert iron into Fe^{3+}, which precipitates as ferric hydroxide unless the water is quite acidic.

8.2 WATER HARDNESS [1]

8.2.1 Consequences of using hard water

The use of hard water in a textile dyeing or finishing mill can have some serious consequences. These include:

(1) precipitation of soaps;
(2) redeposition of dirt and insoluble soaps on the fabric being washed – this can cause yellowing and lead to unlevel dyeing and a poor handle;
(3) precipitation of some dyes as calcium or magnesium salts;
(4) scale formation on equipment and in boilers and pipelines;
(5) reduction of the activity of the enzymes used in desizing;

(6) decreased solubility of sizing agents;
(7) coagulation of some types of print pastes;
(8) incompatibility with chemicals in finishing recipes.

8.2.2 Definitions

Soft water is relatively free of calcium and magnesium ions. It produces a rich foamy lather with soap. This is essential for the soap to be an effective emulsifying agent for oils and dirt. With hard water, the soluble sodium salt of soap reacts with the alkaline earth metal ions and precipitates as the useless and undesirable calcium or magnesium soap (Scheme 8.2). The cleaning ability is lost.

Hardness is defined as the presence of soluble calcium and magnesium salts in the water. If these are present in the form of bicarbonates, the hardness is temporary. Heating hard water containing bicarbonates eliminates dissolved carbon dioxide and the reverse of Scheme 8.1 causes precipitation of calcium carbonate. Magnesium carbonate is slightly soluble in water but heating will cause its hydrolysis into the much less soluble magnesium hydroxide (Scheme 8.3). Simply boiling and filtering the water therefore eliminates temporary hardness. In regions where water has high temporary hardness, and is used directly without treatment, it is not uncommon to see hot water rinsing and washing baths with a generous crust of chalk ($CaCO_3$) on the inner surfaces. This type of precipitation inside a boiler is also undesirable because the scale reduces the efficiency of heat transfer.

$$Mg(HCO_3)_2(aq) \longrightarrow MgCO_3(s) + CO_2(g) + H_2O$$

$$MgCO_3(aq) + H_2O \longrightarrow Mg(OH)_2(s) + CO_2(g)$$

Scheme 8.3

Permanent hardness arises when water contains soluble salts of calcium and magnesium such as chlorides and sulphates. It is unaffected by boiling the water. The total hardness of water is determined by the amount of dissolved calcium and magnesium, but expressed in the form of $CaCO_3$. This is possible because calcium and magnesium carbonates have identical stoichiometry. Therefore, water that contains 1.0 mM calcium and 0.5 mM magnesium ions, has a total concentration of 1.5 mM. Since the molecular weight of $CaCO_3$ is 100 g mol^{-1}, 1.5 mM corresponds to 150 mg l^{-1} of $CaCO_3$, or 150 ppm (parts per million), assuming that 1.0 l of the water has a mass of 1.0 kg. The permanent hardness is that remaining after the water has been boiled and filtered to remove the precipitated calcium and magnesium carbonates and magnesium hydroxide. The temporary hardness is the difference between the total and permanent hardness. Occasionally, hardness due to magnesium alone is of interest, again expressed as the equivalent amount of $CaCO_3$. For the water mentioned above, 0.5 mM of magnesium ions is equivalent to 50 mg l^{-1} or 50 ppm $CaCO_3$.

Understanding water hardness values is often a tedious exercise in manipulation of units. In the past, the hardness of water was given in units called degrees. The definition of one degree of hardness, however, varied from one country to the next (Table 8.2). It is much simpler to express hardness in mg l^{-1} or ppm of $CaCO_3$.

Table 8.2 Various units used for water hardness

Unit of water hardness	ppm $CaCO_3$
1 British degree	14.3
1 American degree	17.2
1 French degree	10.0
1 German degree	17.9
1 mmol l^{-1} $CaCO_3$	100

8.2.3 Determination of water hardness

The hardness of a water sample can be determined by direct titration of a known volume with a standardised solution of a soap such as potassium oleate. Initially, this soap will precipitate, and the calcium and magnesium salts and the water will not produce any foam on shaking. Gradual addition of the potassium oleate solution is continued until the agitation of the solution produces a reasonably permanent foam. From Scheme 8.4, 1.00 ml of 0.02 M potassium oleate solution

$$2R^- K^+ (aq) + Ca^{2+} (aq) \longrightarrow R_2Ca(s) + 2K^+ (aq)$$

$$R^- = CH_3(CH_2)_7{-}CH{=}CH{-}(CH_2)_7CO_2^-$$

Scheme 8.4

is equivalent to 0.01 mmol Ca^{2+}. Thus, if a 100.0 ml sample of water is titrated with 0.02 M potassium oleate solution to just give a permanent foam after addition of V ml of soap, equivalent to V × 0.01 mmol Ca^{2+}, the hardness will be V × 10 ppm $CaCO_3$.

Despite the simplicity of this method, it is not always possible to detect precisely the point at which a layer of foam persists. Hardness is therefore more usually determined by titration with a standardised solution of the disodium salt of ethylenediamine tetra-acetic acid (EDTA). EDTA forms very stable, soluble complexes with calcium and magnesium ions (Figure 8.1). EDTA is a tetraprotic acid and the various acid–base forms are usually abbreviated by H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}, as the degree of dissociation progresses. Scheme 8.5 illustrates complex formation with calcium and magnesium ions. The equilibrium constants are large and ensure quantitative formation of the colourless complexes on addition of EDTA to a solution containing calcium and magnesium ions.

The titration involves gradual addition of standardised EDTA solution (Na_2H_2Y) to the water sample, buffered at pH 10 with an ammonia–ammonium

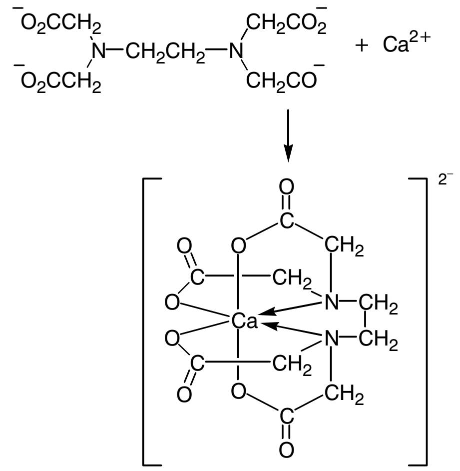


Figure 8.1 Structure of EDTA and its complex with calcium ion

$$Y^{4-} + Ca^{2+} \rightleftharpoons CaY^{2-},\ K = 5.0 \times 10^{10}$$

$$Y^{4-} + Mg^{2+} \rightleftharpoons MgY^{2-},\ K = 4.9 \times 10^{8}$$

Scheme 8.5

chloride solution. The indicator is a dye that changes colour on complexing with calcium or magnesium, such as Eriochrome Black T (CI Mordant Black 11). At the beginning of the titration, the large concentrations of calcium and magnesium ions ensure that all the dye indicator is in the form of the red complexes with these metals ($Ca–Dye^-$, Scheme 8.6). Very close to the equivalence point, the free Ca^{2+} and Mg^{2+} ion concentrations become so low that the added EDTA begins to remove the metals from their red complexes with the dye. This liberates the blue dye ion. The colour of the solution therefore changes from red (dye–metal complex) to blue (free dye anion) at the end-point.

$$\mathrm{Ca^{2+} + H{-}Dye^{2-}\ (blue) \rightleftharpoons Ca{-}Dye^{-}\ (red) + H^{+}}$$

$$\mathrm{Ca{-}Dye^{-}\ (red) + Y^{4-} + H^{+} \rightleftharpoons CaY^{2-} + H{-}Dye^{2-}\ (blue)}$$

Scheme 8.6

In the titration of calcium ions alone at pH 10, the red calcium–dye complex ($Ca–Dye^-$) is not sufficiently stable and the calcium transfers to EDTA liberating the blue dye anion ($H–Dye^{2-}$) slightly before the true equivalence point. For titrations of magnesium ion, the magnesium–dye complex is more stable than that of calcium and the blue colour does not occur until all the Mg^{2+} ions in solution have reacted with the EDTA. Thus, the red-to-blue colour change occurs at the true equivalence point. Towards the end of the titration of hard water, as long as calcium ion is present, it will liberate magnesium ion from the magnesium–EDTA complex because the calcium–EDTA complex is more stable. The liberated magnesium thus ensures that the more stable magnesium–dye complex is always present, until all the calcium has been complexed with EDTA. The last addition of this reagent then removes the magnesium from the red magnesium–dye complex and the solution becomes blue. To ensure that a water sample contains a sufficient quantity of magnesium, it is common to add a little to the EDTA solution before standardisation with a known calcium ion solution.

8.2.4 Water alkalinity

Various dissolved salts in natural water give it an alkaline pH. These are mainly carbonates, bicarbonates and phosphates (Scheme 8.7).

The alkalinity of a water sample can be determined by titration with standardised sulphuric acid solution. With phenolphthalein as the indicator, the equivalence point occurs at about pH 8.3. At this point, all free hydroxide ion is neutralised, carbonate converted into bicarbonate, and phosphate (PO_4^{3-}) into monohydrogen phosphate (HPO_4^{2-}). The alkalinity to pH 8.3 is calculated in ppm $CaCO_3$ based on Scheme 8.8. Therefore, each millimole of sulphuric acid required corresponds to 1.00 mmol $CaCO_3$ in the water sample. If the titration of a 100.0 ml water sample with 0.01 M sulphuric acid consumes V ml of acid, the alkalinity is given by:

$$\begin{aligned}\text{Alkalinity} &= \frac{V(\text{ml}) \times 0.01(\text{mmol H}_2\text{SO}_4\ \text{ml}^{-1}) \times 100(\text{mg CaCO}_3\ \text{mmol}^{-1})}{100(\text{ml H}_2\text{O}) \times 10^{-3}(\text{l ml}^{-1})} \\ &= 10 \times V\ \text{ppm CaCO}_3\end{aligned} \tag{1}$$

At the phenolphthalein end-point of pH 8.3, the water is still slightly alkaline and it is therefore common practice to titrate the sample to a methyl orange end-point, corresponding to about pH 4.5. This ensures that all carbonate is in the from of carbonic acid and all phosphate is present as dihydrogenphosphate ($H_2PO_4^-$). The alkalinity to pH 4.5, often called the total alkalinity, is given by the same equation as above, but, of course, the volume of sulphuric acid solution may be greater.

$$CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + HO^-(aq)$$

$$HCO_3^-(aq) + H_2O \rightleftharpoons H_2CO_3 + HO^-(aq)$$

$$PO_4^{3-}(aq) + H_2O \rightleftharpoons HPO_4^{2-}(aq) + HO^-(aq)$$

$$HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_2PO_4^-(aq) + HO^-(aq)$$

Scheme 8.7

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Scheme 8.8

Table 8.3 relates the total (T) alkalinity and phenolphthalein alkalinity (P) of various types of water to the dissolved salts that are present. In the absence of phosphate ions, there will be some correlation between the alkalinity caused by bicarbonate and the temporary hardness. For example, if the alkalinity to

Table 8.3 Comparison of the phenolphthalein alkalinity (P) with the total alkalinity (T) in ppm $CaCO_3$ and the basic ions present in the water

Analysis result (ppm)	Basic ions present	*Total alkalinity from CO_3^{2-}	*Total alkalinity from HCO_3	*Total alkalinity
P = T	HO^- ion only			T
P = 0, T > 0	HCO_3^- or HPO_4^{2-}		T	
P = 0.5 T	CO_3^{2-} and PO_4^{3-}	T = 2P		
P > 0.5 T	HO^-, CO_3^{2-} and PO_4^{3-}	2(T – P)		2P – T
P < 0.5 T		2P	T–2P	

*In the absence of phosphate ions

phenolphthalein is zero (P = 0), the total alkalinity, assuming no phosphates or weakly acidic pollutants, will be caused by bicarbonate ion and the total alkalinity in ppm $CaCO_3$ will equal the temporary hardness. The alkalinity of water fed to boilers must not be too high because of the risk of corrosion of non-ferrous fittings.

8.3 WATER SOFTENING

Soft water is a desirable prerequisite for all textile wet processes, except for bleaching with solutions of hydrogen peroxide stabilised by sodium silicate. Modern synthetic detergents do not form precipitates in hard water containing calcium and magnesium ions so a certain degree of hardness is tolerable provided that other dyes and chemicals are not seriously affected by this. In general, however, if a mill is in a region where the water is hard, a softening pretreatment is essential for at least part of the water used. The objective of this is simply to reduce the concentration of the alkaline earth metals to a level at which the water has the desired quality. In many cases, the softening process may reduce the calcium and magnesium ion concentrations to zero.

8.3.1 The lime-soda process

The old lime-soda process is now obsolete but was very useful for the treatment of large volumes of hard water. Addition of lime (CaO) and soda (Na_2CO_3) to the hard water precipitates calcium as the carbonate, and magnesium as its hydroxide. The amounts of the two chemicals required are easily calculated from the analysis of the water and stoichiometry of the reactions (Scheme 8.9). Since calcium

$$CaO(s) + H_2O \longrightarrow Ca^{2+}(aq) + 2HO^{-}(aq)$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

$$Mg^{2+}(aq) + 2HO^{-}(aq) \longrightarrow Mg(OH)_2(s)$$

Scheme 8.9

carbonate and magnesium hydroxide are not completely insoluble, the water obtained has a residual hardness of not less than 20 ppm $CaCO_3$. A major problem of this type of process is the disposal of the sludge of precipitated calcium carbonate and magnesium hydroxide.

8.3.2 Ion exchange methods

A zeolite is a naturally occurring insoluble mineral of the sodium aluminosilicate type. When hard water passes through a bed of small particles of such a mineral, an ion exchange reaction takes place (Scheme 8.10). As more and more alkaline earth metal ions are retained by the zeolite, its exchange capacity gradually decreases. Regeneration of the sodium salt of the zeolite involves passing a concentrated solution of NaCl through the zeolite. The calcium and magnesium ions are displaced and leave with the solution (the reverse of Scheme 8.10). After rinsing with water to eliminate the excess salt, the zeolite is ready for another cycle of softening.

$$2(Z^{-}Na^{+})(s) + Ca^{2+}(aq) \rightleftharpoons (2Z^{-}Ca^{2+})(s) + 2Na^{+}(aq)$$

Scheme 8.10

Many zeolites occur in nature but they can also be manufactured. The removal of the alkaline earth metal ions is more effective the greater the surface area of the zeolite particles in contact with the water. For this reason, softening involves percolation of the water down a packed column of the finely ground zeolite, followed by periodic regeneration. Although the calcium and magnesium ions in the water are replaced by sodium ions, these are relatively harmless in textile processing.

The chemical structures of aluminosilicates are based on the structure of silica. This consists of a three dimensional network of SiO_4 units, in which the oxygen atoms have a tetrahedral arrangement around the central silicon atom. These tetrahedra may have common corners or faces. In an aluminosilicate, a number of aluminium atoms replace silicon atoms in the silica structure. The aluminium atoms are bonded to four tetrahedral oxygen atoms but because their atomic number is one less than silicon, each aluminium atom introduced has a negative charge, balanced by incorporation of a cation such as Na^+ or K^+. It is these cations that are available for exchange.

The newer synthetic polymer ion exchangers are much more versatile than the zeolites and are widely used for water softening and demineralisation. They are often called ion exchange resins. Many are based on polystyrene that has been partly crosslinked by incorporation of a small amount of divinylbenzene (2–10%). Suspension polymerisation of the styrene and divinylbenzene produces the crosslinked polymer in the form of small beads. These have the appearance of a fine white sand. Sulphonation of some of the benzene rings, mainly on the bead surfaces, provides anionic sites suitable for cation exchange (Figure 8.2). Since a sulphonic acid is comparable in strength to a mineral acid, these are called strong acid exchangers. They may absorb cations and release hydrogen ions, or, in the form of their sodium salts, exchange sodium ions for other cations in the water (Scheme 8.11).

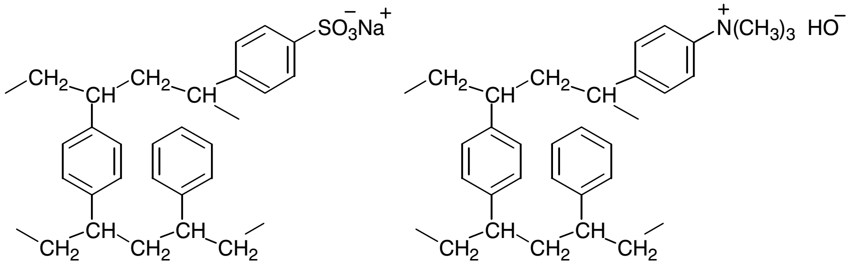


Figure 8.2 Chemical structures of cation and anion exchangers based on cross-linked polystyrene

$$2(\text{Polymer—SO}_3^-\ \text{H}^+)(s) + \text{Ca}^{2+}(aq) \rightleftharpoons (\text{Polymer—SO}_3^-)_2\text{Ca}^{2+}(s) + 2\text{H}^+(aq)$$

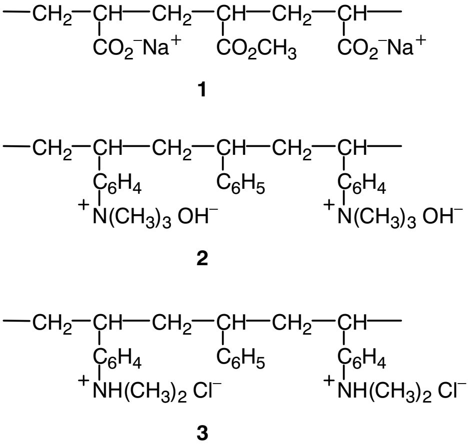
$$2(\text{Polymer—SO}_3^-\ \text{Na}^+)(s) + \text{Ca}^{2+}(aq) \rightleftharpoons (\text{Polymer—SO}_3^-)_2\text{Ca}^{2+}(s) + 2\text{Na}^+(aq)$$

Scheme 8.11

$$2(\text{Polymer—CO}_2^-\ \text{Na}^+)(s) + \text{Ca}^{2+}(aq) \rightleftharpoons (\text{Polymer—CO}_2^-)_2\text{Ca}^{2+}\ (s) + 2\text{Na}^+(aq),\ \text{pH}>5$$

$$\text{Polymer—CO}_2^-\ \text{Na}^+(s) + \text{H}^+(aq) \rightleftharpoons (\text{Polymer—CO}_2^-)_2\text{Ca}^{2+}\ (s) + \text{Na}^+(aq),\ \text{pH}<5$$

Scheme 8.12



$\text{—CH}_2\text{—CH(CO}_2^-\text{Na}^+\text{)—CH}_2\text{—CH(CO}_2\text{CH}_3\text{)—CH}_2\text{—CH(CO}_2^-\text{Na}^+\text{)—}$ (1)

$\text{—CH}_2\text{—CH(C}_6\text{H}_4\text{—}^+\text{N(CH}_3)_3\ \text{OH}^-\text{)—CH}_2\text{—CH(C}_6\text{H}_5\text{)—CH}_2\text{—CH(C}_6\text{H}_4\text{—}^+\text{N(CH}_3)_3\ \text{OH}^-\text{)—}$ (2)

$\text{—CH}_2\text{—CH(C}_6\text{H}_4\text{—}^+\text{NH(CH}_3)_2\ \text{Cl}^-\text{)—CH}_2\text{—CH(C}_6\text{H}_5\text{)—CH}_2\text{—CH(C}_6\text{H}_4\text{—}^+\text{NH(CH}_3)_2\ \text{Cl}^-\text{)—}$ (3)

Figure 8.3 Weak acid cation exchanger, containing acrylic acid (ethenoic acid) units (**1**); strong basic anion exchange resin, containing quaternary ammonium hydroxide groups (**2**); weakly basic anion exchange resin with protonated secondary amino groups (**3**)

The so-called weak acid cation exchangers are usually polymers containing carboxylic acid groups, such as vinyl polymers containing acrylic acid (ethenoic acid) units (**1**, in Figure 8.3). These are used in the form of their sodium salts. They do not exchange hydrogen ions for cations below pH 5 since the free carboxylic acid groups are barely dissociated at low pH values (Scheme 8.12).

Other types of ion exchange resins are available for anion exchange. These may be of the strong basic type, containing quaternary ammonium hydroxide groups (see Figure 8.2, and **2** in Figure 8.3), or weakly basic with protonated secondary amino groups (**3**, in Figure 8.3). Either type will have associated counter anions that exchange with anions in the solution in contact with the resin. The weakly basic types have ammonium ion groups that can lose a proton in contact with an alkaline solution and therefore are ineffective above pH 10 (Scheme 8.13). The ion exchange processes are again reversible so resin regeneration simply involves treatment with a concentrated solution of a salt containing the appropriate anion.

$$\text{Polymer—NR}_3^{+}\text{HO}^{-}\text{(s)} + \text{Cl}^{-}\text{(aq)} \rightleftharpoons \text{Polymer—NR}_3^{+}\text{Cl}^{-}\text{(s)} + \text{HO}^{-}\text{(aq)}$$

$$\text{Polymer—NHR}_2^{+}\text{X}^{-}\text{(s)} + \text{Cl}^{-}\text{(aq)} \rightleftharpoons \text{Polymer—NHR}_2^{+}\text{Cl}^{-}\text{(s)} + \text{X}^{-}\text{(aq), pH<10}$$

$$\text{Polymer—NHR}_2^{+}\text{X}^{-}\text{(s)} + \text{HO}^{-}\text{(aq)} \rightleftharpoons \text{Polymer—NR}_2\text{(s)} + \text{X}^{-}\text{(aq)} + \text{H}_2\text{O, pH>10}$$

Scheme 8.13

Therefore, a strongly basic quaternary ammonium ion resin is regenerated using NaOH solution, and a secondary amine type with NaCl or HCl solution.

The two most important properties of an ion exchanger are its capacity and its selectivity. The capacity is the number of ions that a given mass of resin is capable of binding by exchange, normally expressed in milliequivalents per gram of dry or of wet resin. For example, 1.0 mmol of Na^+ is the same as 1.0 mequiv, but 1.0 mmol of Ca^{2+} is 2.0 mequiv. Therefore, a resin with a capacity of 15.0 mequiv g^{-1} would be capable of binding 15.0 mmol g^{-1} Na^+ or 7.5 mmol g^{-1} Ca^{2+}. The selectivity of the resin determines how strongly it binds a given ion and therefore its ease of exchange. Clearly, for water softening a cation exchange resin should have a higher selectivity for Ca^{2+} and Mg^{2+} than for H^+ or Na^+. Fortunately, the selectivity is often greater for ions of higher ionic charge.

Besides these two properties, the degree of swelling of the resin in contact with the water must be limited. The higher the degree of crosslinking, for example from incorporation of more divinylbenzene in the polystyrene, the lower the extent of swelling. It is also important that the resin particles have a large surface area and that water is able to penetrate into the surface pores.

Water can be totally demineralised by firstly exchanging all cations using a strongly acid form of a cation exchanger. Thus, a solution of salts M^+X^- becomes a solution of acid H^+X^-, the M^+ ions being retained by the resin. Subsequent percolation through a packing of a strongly basic form of an anion exchanger absorbs the X^- ions and liberates HO^- ions into the water. These then neutralise the H^+ ions from the first step. The result is retention of all anions and cations and the neutralisation of H^+ and HO^- to form water (Scheme 8.14). Thus, the

$$2(\text{Polymer—SO}_3^{-}\text{H}^{+})\text{(s)} + \text{Ca}^{2+}\text{(aq)} \rightleftharpoons (\text{Polymer—SO}_3^{-})_2\text{Ca}^{2+}\text{(s)} + 2\text{H}^{+}\text{(aq)}$$

$$2(\text{Polymer—NR}_3^{+}\text{HO}^{-})\text{(s)} + 2\text{Cl}^{-}\text{(aq)} \rightleftharpoons 2(\text{Polymer—NR}_3^{+}\text{Cl}^{-})\text{(s)} + 2\text{HO}^{-}\text{(aq)}$$

$$2\text{H}^{+}\text{(aq)} + 2\text{HO}^{-}\text{(aq)} \rightleftharpoons 2\text{H}_2\text{O}$$

Scheme 8.14

water has been demineralised. It may, however, still contain organic material and dissolved carbon dioxide from the reaction of carbonate and bicarbonate with the acid from the resin. A thorough aeration eliminates the carbon dioxide. Demineralisation is important for water fed to very high pressure boilers.

The use of ion exchange resins for water treatment is relatively simple. The resin is packed into a column containing water and treatment simply involves flowing water up or down the column. The capacity of the resin and the ionic content of the water determine when regeneration will be required. One problem with beds of ion exchangers is the retention in the column of suspended matter and living organisms in the water. Countercurrent rinsing and occasional treatment with a bactericide minimise these problems. For removal of both cations and anions (demineralisation), two columns in series are used, the first for strong acid exchange and the second for strong base exchange. It is even possible to mix anion and cation exchangers in the same bed. If the different types of particles have different densities, they can be separated by sedimentation in a counterflow of water, regenerated separately, and then re-mixed. Figure 8.4 shows a typical series of processes for water softening.

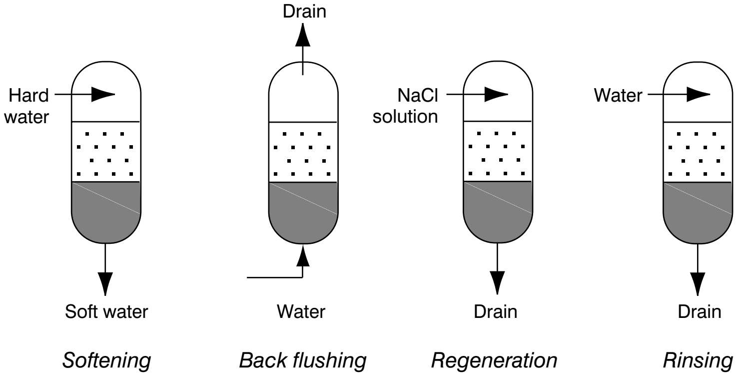


Figure 8.4 Processes for water softening and regeneration using a cation exchanger

8.3.3 Sequestering agents

Transition metal ions in the water supply can pose difficult problems in a dyehouse. Firstly, many of these ions catalyse the decomposition of hydrogen peroxide in bleaching baths. In addition, transition metals often give insoluble salts with dyes, or form complexes that are invariably duller and even different in shade. If the amounts are excessive, the water may be unusable without treatment. On adequate aeration of the water at pH values around 7, iron precipitates as insoluble $Fe(OH)_3$ and can be removed. There is always concern about the possibility of iron from corrosion inside the water pipes in a textile plant.

Addition of a sequestering agent to the water avoids many problems from relatively low concentrations of undesirable metal ions. Sequestering agents react with the metal ions to form very stable complex ions. Examples of such chemicals used in textile processing include EDTA, and related aminocarboxylic acids, as well as polyphosphates such as sodium tetrametaphosphate $Na_4P_4O_{12}$. EDTA is a most effective sequestering agent, particularly in neutral or weakly alkaline solution. It forms such stable complexes with metal ions that it often removes the metal ion from a metal–complex dyestuff molecule, to give the EDTA–metal complex and uncomplexed dye.

Polyphosphates can bind alkaline earth metal ions and thus decrease the effects of water hardness. The product Calgon, sodium hexametaphosphate $Na_6P_6O_{18}$, is widely used for this purpose. Calcium ions replace sodium in the hexametaphosphate, forming a stable complex. The free calcium ion concentration in the water is then so low that calcium soaps do not precipitate. Polyphosphates are frequently present in domestic washing powders for the same reason.

8.4 BOILER WATER

Boilers for steam generation have varying operating pressures and capacities. The use of a high pressure boiler allows a greater generation capacity but to minimise some of the problems discussed below requires a much higher water quality than a low pressure system.

Temporary hardness in boiler feed water gives an accumulation of chalk scum in the boiler and scale on the walls and heating tubes. Deposition on the latter greatly reduces the rate of heat transfer and the boiler becomes increasingly less efficient. At high temperatures and pressures, both calcium and magnesium carbonates and magnesium hydroxide are much less soluble than under ambient conditions and contribute to scaling. Simple phosphates such as Na_2HPO_4, added to boiler feed water, will precipitate insoluble calcium and magnesium phosphate in a form that does not form a crust on the boiler walls and pipes. Polyphosphate sequestrants are less helpful since they tend to hydrolyse rapidly to simple phosphates in boiling water. Treatment with simple phosphates also ensures absorption of colloidal silica. This is significant, since silica scale on pipes and walls is very difficult to remove.

The precipitation of calcium and magnesium in a non-crusting form in the boiler produces suspended material, the rate of accumulation being greater the higher the pressure and the capacity of the boiler. It is quite common to add dispersants such as polyacrylates to the feed water as these keep the precipitates well dispersed to prevent scaling. Discharge of the sludge is necessary from time to time to avoid excessive accumulation and to keep the salinity of the water within reasonable limits. In addition, dispersants and anti-foam chemicals prevent carry-over of sediment and foam with the generated steam.

It is vital that there is minimum corrosion of the boiler and piping. This can be caused by acids, and by dissolved carbon dioxide and oxygen. Iron fittings corrode rapidly if boiler feed water is too acidic, so it is usual to condition the water to about pH 8–9 by addition of NaOH. This also ensures that all carbon dioxide is converted into bicarbonate.

Too high a pH causes caustic embrittlement of non-ferrous metal fittings such as rivets. On the other hand, at pH values below 6, carbon dioxide can attack iron to form ferrous bicarbonate. This can occur in the boiler and in the piping for steam distribution and condensate return. Sometimes, volatile amines, such as ammonia or cyclohexylamine, are added to the water to neutralise any acidity and prevent this.

Dissolved oxygen is a major source of corrosion. Preliminary heating removes most oxygen, since this gas is much less soluble in hot water. Alternatively, it reacts with reducing agents such as sodium sulphite or hydrazine added to the feed water. Sulphite is oxidised to sulphate but hydrazine has the advantage that it does not produce any ionic products (Scheme 8.15).

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

Scheme 8.15

8.5 DYEHOUSE EFFLUENT AND ITS TREATMENT [2]

8.5.1 Contaminants in dyehouse effluents

For many years, the textile dyeing industry was a major source of water pollution. Increasing public awareness of this problem has resulted in much stricter legislation to protect the environment with controls on the types of contaminants and the amounts released. Governments have also become much more aggressive in updating legislation and in enforcing it. Water quality criteria are usually established for drinking water, and for surface and ground waters. The control of the discharge of effluent has become a major preoccupation for industries in Europe and North America. Legislation often sets maximum daily limits and a longer-term average limit for a whole range of contaminants. Controls in developing countries are much less stringent and, in some cases, almost non-existent. This has been a significant factor in the recent re-structuring of the dyestuffs manufacturing and textile finishing industries.

There is little doubt that water quality standards will become increasingly important. Therefore, effluent treatment before discharge will be required, with increasing costs to the textile industry. The impact of textile effluent on aquatic life is an active field of research. There is considerable collaboration through ETAD (the Ecological and Toxicological Association of the Dyes and Organic Pigments Manufacturing Industry [3]) and ADMI (the American Dye Manufacturers Institute). Both have undertaken numerous studies in this area.

Most textile effluent water is discharged into surface waters such as rivers and lakes, either directly or through municipal sewers. The main problem is the wide range of chemicals that it contains and the high level of dilution that usually exists. Table 8.4 lists some of the common pollutants. Of particular concern are those chemicals that are not degraded by water-borne bacteria, and which therefore persist and accumulate in the environment. Many such chemicals, such as polychlorobiphenyls, are extremely toxic and dangerous.

Discharge of effluent to a municipal sewer has the advantage that the sewage treatment is able to remove many, but not all, of the contaminants. Provided the nature and approximate amounts of the contaminants are known, sewage treatment can reduce pollutant levels to the point at which discharge into surface water is then feasible.

Because of the diversity of chemicals in textile effluent, it is usually characterised by a number of general criteria rather than in terms of specific contaminants. These include those described below.

Table 8.4 List of contaminants found in textile finishing effluent

Water pollutants	Examples
Heavy metals	Chromium, copper, zinc
Organochlorine compounds	Moth-proofing agents
Insecticides	Aldrin
Sulphides	Sodium sulphide from dyeing
Colour	Dyes
Surfactants	Detergents, dispersing agents
Oils	Emulsions from scouring
Carbohydrates	Starch sizing
Solvents	Degreasing solvents from scouring
Acids and alkalis	Dyeing assistants

(1) The volume of effluent.

(2) A measure of the amount of oxygen it will consume for oxidation of the organic chemicals it contains. This point is important because depletion of oxygen in water has a negative impact on aquatic life. The biological oxygen demand (BOD) [1] is the amount of oxygen (mg l^{-1} or ppm) consumed in 5 days at 20 °C by growth of bacteria from a culture added to the water. The chemical oxygen demand (COD) [1] is based on a much faster chemical oxidation of organic compounds with hot sodium dichromate solution. The two values are often close but not equivalent. Many organic compounds are readily oxidised by hot dichromate but are resistant to microbial oxidation at ambient temperature. It is typical of textile effluent that the COD is much higher than the BOD. The COD is less affected by the usual effluent treatment processes, and is thus more persistent in the environment. Values range from 200–3000 mg O_2 l^{-1} for BOD and from 500–5000 mg O_2 l^{-1} for COD. The total organic carbon (TOC) in the water serves as an alternative to BOD and COD. All these can be determined by standardised analytical procedures.

(3) Floating insoluble chemicals, mainly insoluble oils and solvents.

(4) Suspended solid materials. These are quite diverse and include short fibres and insoluble dyes or compounds that have precipitated in the effluent because of a change in temperature or pH. Quantities range from 50–500 mg l^{-1}. This can be estimated by filtration or by turbidity measurements.

(5) Colour. This is visible pollution. While it may not be toxic, colour does reduce light transmission into waters and limits photosynthesis. The dyeing industry discharges about 9% of the dyestuffs it consumes. This corresponds

to a considerable degree of colour in a dyehouse effluent. Dyes are not easily biodegraded since, by design, they have good stability towards light and various chemical treatments. Most dyes are not of high toxicity and are eventually removed from water by oxidation or adsorption on sediment, but presence of colour in the water from a dyehouse is undesirable. It is a strong indicator of the presence of much higher quantities of dyeing assistants, almost all of which are present in the effluent. Even a simple chemical such as acetic acid can significantly increase the BOD.

(6) Acidity. The pH may vary from about 4 up to near 12. The acidity of water affects aquatic life and effluent must be neither too acidic nor too alkaline on discharge. This also applies for discharge into a municipal sewer because the micro-organisms used in sewage treatment are equally susceptible.

(7) Toxic chemicals. For the textile industry, the major offenders here are heavy metals such as chromium and copper, organochlorine compounds from insecticides or moth-proofing agents, and sulphides from dyeing with sulphur dyes.

8.5.2 Effluent treatment

Any effluent treatment programme must consider whether the water contaminants are biodegradable, over what time scale, and – if persistent – how they will influence conditions down stream. Even the influence of subsequent water chlorination for drinking purposes on the potential formation of toxic organochlorine compounds must be considered. This a complex subject requiring detailed on-site analysis before arriving at specific recommendations and their implementation.

One very important strategy in reducing water pollution from a textile finishing plant involves minimising waste and optimising process methods so that fewer contaminants are discharged in the effluent. The following list gives some examples of this.

(1) re-use of excess dye solution remaining at the end of a process – this can be incorporated into other dyeing recipes;
(2) mixing acidic and alkaline effluents before discharge to avoid excessive acidity or alkalinity;
(3) replacing starch-based sizing materials with polyvinyl alcohol, which can be recovered by membrane separation techniques and recycled;

(4) process changes and optimisation of the use of problematic chemicals – for example, for the oxidation of leuco vat dyes, hydrogen peroxide or sodium perborate can be substituted for sodium dichromate. Replacement of dyes that require aftertreatment with chromium or copper salts will have a beneficial impact on the immediate water environment. Glucose can replace sodium sulphide as a reducing agent for sulphur dyes. The dye manufacturers now offer 'greener' products and processes such as low salt/high fixation reactive dyes. Many companies are examining the possibilities of recycling water and chemicals, and of recovering heat from hot effluent.

Various types of processes are used in textile effluent treatment. Dyehouse effluent has a composition that is highly time-dependent in terms of both the types and quantities of contaminants. A first stage in treatment is often an equalising lagoon. Equalisation involves holding the combined process effluents for a given period to allow stabilisation of pH and BOD, and time for sedimentation of some solids. This considerably reduces fluctuations in the composition of the water leaving the dyehouse, which can upset down stream processes such as activated sludge treatment.

Biological treatment with organisms may be aerobic (with oxygen) or anaerobic (without oxygen). Many textile mills in urban areas discharge their effluent into municipal sewers. The sewage may be treated in an activated sludge plant. The effluent is mixed with micro-organisms, aerated and then the sludge allowed to settle. The phosphate and nitrogen nutrients needed for bacterial growth are not a problem if the industrial effluent is mixed with regular sewage. Activated sludge treatment considerably reduces the BOD by aerobic oxidation, and adsorption or coagulation of the contaminants. The effects are improved if the sludge is combined with activated carbon. This also protects the micro-organisms from heavy metals. They are sensitive to sudden changes in conditions and industrial effluents in the sewer system should be of relatively constant composition and concentration. The main problem is that of sludge disposal. After suitable treatment, it can be used as fertiliser, or for landfill. In a trickle filter plant, the effluent percolates through a filter bed with the bacteria growing on the surface of the filter medium.

These aerobic microbial oxidation processes reduce the BOD, COD and TOC. The effect on colour from dyes, however, is often only marginal. Some dyes are adsorbed to some extent by the biological treatment. This has only limited effects in removing hydrolysed reactive dyes from the effluent. Because of the high levels of waste, textile auxiliary products should ideally biodegrade rapidly in water, although this is often not the case. Alkyl benzene sulphonate detergents, with a branched alkyl chain, such as that derived from propene tetramer, caused mountains of foam on rivers throughout the industrialised world in the 1960s because of their low rate of biodegradation (Section 9.3.5).

One of the most common effluent treatment methods is that of precipitation. This often involves a combination of precipitation of insoluble salts, coagulation of colloidal material and flocculation. This is similar in principle to the method used for clarifying water described in Section 8.1. Addition of lime (CaO) to the effluent is quite common. This neutralises any excess acidity and precipitates many types of anionic compounds. Treatments with alum or ferric chloride are also popular. The aluminium or ferric hydroxide, along with precipitated aluminium or ferric salts, removes colloidal matter and a number of anionic dyes. This reduces the COD, colour and suspended solids. Sedimentation is assisted by adding a flocculant such as a polyacrylic acid derivative, or a cationic polymer, the latter being able to bind hydrolysed reactive dyes. Again, the disposal of the sediment sludge needs to be considered.

There are a variety of chemical technologies for effluent treatment. Few of these are used in the textile industry because of their cost. This situation may change as environmental protection becomes even more socially and politically acceptable. Chlorination with sodium hypochlorite and acid eliminates much organic material in waste water but may generate even more toxic organochlorine compounds. Oxidation by ozone is much safer but the cost of generating ozone by electrical discharge through oxygen gas is still prohibitive. Other technologies involve reverse osmosis and membrane filtration, adsorption on active carbon, or generation of coagulants by electrochemical techniques. The highest standards of effluent treatment require combinations of different types of treatment. These will probably become more significant, despite the expense, as regulatory controls are increasingly enforced.

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CHAPTER 9

Auxiliary chemicals for wet processing and dyeing

Besides fibres, water and dyes, and specific chemicals for preparation and finishing processes, the textile industry consumes vast quantities of auxiliary chemicals, other than simple acids, bases and salts. These auxiliary products include many kinds of complex organic chemicals used as detergents, wetting agents, dyeing assistants, dispersing and emulsifying agents, dyeing aftertreatment chemicals, lubricants and softeners. They serve to improve the wet processes used in textile finishing. Their consumption in the textile industry exceeds that of dyestuffs and many are used in the manufacture of other types of products such as paper, paints and household detergents.

Unfortunately, like dyestuffs, the brand names and identifying codes of these auxiliary products offer little or no information about their composition. Commercial auxiliary products are frequently mixtures, often containing much water. Any given product sold for a specific purpose can have multiple functions such as wetting, detergent, dispersing and dyeing control capability. For these reasons, the role of auxiliary chemicals in textile wet processing and dyeing is confusing. A chapter on this subject, however, is essential for understanding modern dyeing processes.

Many of these auxiliary chemicals are surfactants; they are chemicals exhibiting surface activity. This means that their molecules tend to accumulate at the surface separating two immiscible materials such as water and a fibre, or water and oil. The concentration of the surfactant at the interface may be more than 500 times greater than in the bulk of the aqueous solution. Surfactant molecules have two key structural features. One part of the molecule is a hydrophobic ‘tail’, such as a long alkyl chain ($C_{15}H_{31}$–); the other part is a hydrophilic polar or ionic group, or ‘head’, such as a carboxylate ion (–CO_2^-). Substances such as $C_{15}H_{31}CO_2^- Na^+$ are slightly soluble in water, strongly adsorbed at phase boundaries, and have a pronounced tendency to aggregate in solution. The aim of this chapter is to introduce these surface-active chemicals and to examine how they function in processes such as scouring and dyeing.

9.1 IMPURITIES IN TEXTILE FIBRES

At any stage during textile manufacture, from loose fibre to grey fabric, fibres may contain a variety of hydrophobic chemicals that interfere with uniform wetting. These impurities may be of natural origin, such as fats and waxes, or synthetic chemicals deliberately applied to the fibres to facilitate processes such as carding, spinning or knitting.

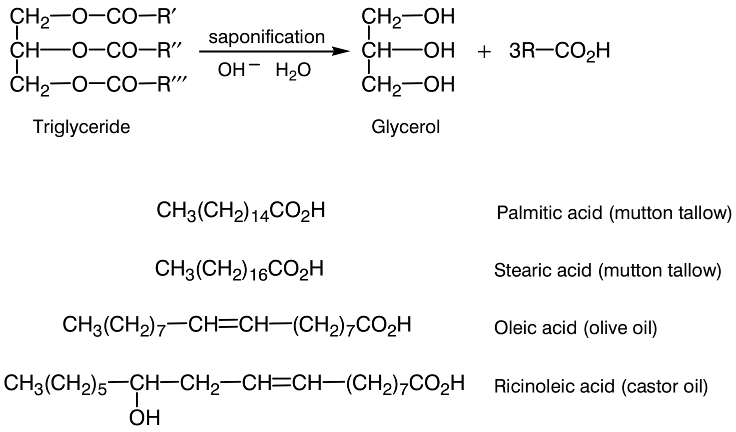
Natural fats and oils are esters of glycerol (1,2,3-propanetriol) and high molecular weight carboxylic acids called fatty acids. Since glycerol has three hydroxyl groups, and each can be esterified, its esters are called triglycerides. The fatty acids usually have an unbranched chain of up to about 20 carbon atoms with a carboxylic acid group on the end carbon atom. In saturated fatty acids the carbon atoms (other than that of the terminal carboxylic acid group) form only single bonds, either to other carbon atoms or to hydrogen atoms, in an unbranched chain. A typical example is stearic acid, $CH_3(CH_2)_{16}CO_2H$ (octadecanoic acid). The triglycerides of saturated fatty acids are usually solids at room temperature.

Unsaturated fatty acids have at least one carbon–carbon double bond along the unbranched carbon chain, as in oleic acid cis-$CH_3(CH_2)_7$–$CH{=}CH$–$(CH_2)_7CO_2H$ (cis-9-octadecenoic acid). Their triglycerides are usually oils at room temperature, but catalytic hydrogenation produces the solid saturated fats (Scheme 9.1). Unsaturated fats rapidly turn rancid on exposure to air. Their reactive carbon–carbon double bonds are sensitive to air oxidation. This causes yellowing and decomposition. Because fibres can absorb the rancid odour, unsaturated oils are not used in textile processing.

$$\underset{\text{Oleic acid}}{CH_3(CH_2)_7{-}CH{=}CH{-}(CH_2)_7CO_2H} + H_2 \longrightarrow \underset{\text{Stearic acid}}{CH_3(CH_2)_7{-}CH_2CH_2{-}(CH_2)_7CO_2H}$$

Scheme 9.1

In natural fats and oils, the glycerol is usually esterified with a mixture of fatty acids. Hydrolysis of fats in hot alkaline solution produces glycerol and a mixture of the alkali salts of the fatty acids. This hydrolysis reaction is called saponification because, when these fatty acid salts have about 12–20 carbon atoms, the alkali metal salts are soaps. Figure 9.1 shows the major products of the saponification of



$$\begin{matrix} CH_2-O-CO-R' \\ | \\ CH-O-CO-R'' \\ | \\ CH_2-O-CO-R''' \end{matrix} \xrightarrow[OH^- \; H_2O]{\text{saponification}} \begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} + 3R-CO_2H$$

$CH_3(CH_2)_{14}CO_2H$ Palmitic acid (mutton tallow)

$CH_3(CH_2)_{16}CO_2H$ Stearic acid (mutton tallow)

$CH_3(CH_2)_7-CH=CH-(CH_2)_7CO_2H$ Oleic acid (olive oil)

$CH_3(CH_2)_5-\underset{OH}{\underset{|}{C}H}-CH_2-CH=CH-(CH_2)_7CO_2H$ Ricinoleic acid (castor oil)

Figure 9.1 Saponification of the triglycerides in castor oil, olive oil and mutton tallow

castor and olive oils, and of mutton tallow. Palmitic acid ($CH_3(CH_2)_{14}CO_2H$, hexadecanoic acid) and stearic acid occur as triglycerides in many animal fats and their sodium salts are often major components of common soap.

Stearic and palmitic acids are saturated acids, whereas ricinoleic and oleic acids have a cis carbon–carbon double bond and are therefore unsaturated. Some unsaturated oils, such as linseed oil, are called drying oils and are used in paints and varnishes. They contain fatty acids such as linoleic and linolenic acids (**1** and **2**, in Figure 9.2), both of which are similar to oleic acid but with two and three non-conjugated carbon–carbon double bonds, respectively. A thin film of this type of oil dries to produce a hard film because of polymerisation induced by oxygen from the air. This type of oil is not used on textiles since any polymerised oil on the fibre is extremely difficult to remove.

$CH_3(CH_2)_4-CH=CH-CH_2-CH=CH-(CH_2)_7-CO_2H$ Linoleic acid

1

$CH_3CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-CO_2H$ Linolenic acid

2

Figure 9.2 Linoleic acid (**1**) and linolenic acid (**2**)

Waxes are often either high molecular weight alcohols (fatty alcohols) or their esters with fatty acids. They are solids with high melting points and very low water solubility. The fatty alcohols do not hydrolyse in alkaline solution and their esters are much more resistant to hydrolysis than triglycerides. Other types of waxes are mixtures of high molecular weight inert alcanes such as paraffin wax.

Both fats and waxes occur as contaminants in textiles, particularly those of natural origin. They are often added to warp size as lubricants. In addition, a material will also usually contain natural or synthetic oils added to lubricate the fibres to assist mechanical processes such as carding or knitting. Fats, oils and waxes are hydrophobic and water-insoluble. Their presence on the surface of a fibre greatly hinders wetting so they must be removed by scouring. This involves treatment of the goods with an aqueous solution of a detergent, sometimes under alkaline conditions, or with an organic solvent. An alkaline solution of a detergent such as soap can remove fats and oils by saponification of glycerides, or by emulsification, whereas a non-polar organic solvent such as perchloroethylene (tetrachloroethene) dissolves these hydrophobic impurities. It is not uncommon to scour with an aqueous solution of detergent containing a small quantity of an appropriate organic solvent in emulsion, in which case saponification, emulsification and dissolution can occur simultaneously. We will now examine exactly how a detergent acts in scouring.

9.2 SURFACE ACTIVITY OF DETERGENTS

Simple soaps are the sodium salts of fatty acids with 12–20 carbon atoms, typified by stearic and palmitic acids. They are obtained by saponification of animal fats using aqueous NaOH and precipitated by addition of NaCl, the glycerol remaining in solution. The potassium salts of fatty acids, obtained by saponification using KOH, are more soluble than sodium soaps. Because they are difficult to separate, they are often available as soft soaps, thick concentrated aqueous solutions still containing glycerol. Natural sodium soaps have limited solubility in cold water. They are more soluble in hot water but redeposit on cooling, forming a gel. Since a soap is the salt of a strong base with a weak acid, it gives a mild alkaline reaction in water (Scheme 9.2).

$$\mathrm{R{-}CO_2^- + H_2O \longrightarrow R{-}CO_2H + HO^-}$$

Scheme 9.2

The major disadvantages of natural soaps are that they precipitate in acidic solution at below pH 5, forming the insoluble free fatty acid, and also in hard water forming the calcium and magnesium salts (Section 8.1). They also readily precipitate in the presence of excess sodium ions. Although modern synthetic surfactants have almost completely replaced natural soaps in textile wet processing, a simple soap solution is a suitable point to begin a discussion of surface activity.

9.2.1 Basic thermodynamics

Before discussing the surface activity and aggregation of soap molecules, a brief introduction to thermodynamics is appropriate. All processes are governed by the laws of thermodynamics. The key thermodynamic equation for predicting whether a process is probable or not is:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT\ \ln(K) \tag{1}$$

In this equation, K is the equilibrium constant for the process, T the absolute temperature, and R the universal gas constant. ΔH^0 is the enthalpy change for the process and corresponds to the quantity of heat absorbed or liberated for a unit amount of change, occurring at constant pressure, under standard conditions, usually at atmospheric pressure and at 25 °C. If ΔH^0 is positive, the process absorbs heat (endothermic), and if negative, it liberates heat (exothermic). The enthalpy change can be considered as the difference between the total bond energies of the final state and those of the initial state of the process. A negative value for the enthalpy change corresponds to a higher value of the equilibrium constant and therefore favours the process. In favourable processes, stronger bonds are formed. The energy released by formation of the new bonds is greater than the energy required to break the initial ones and therefore the process is exothermic.

ΔS^0 is the change in entropy for the process. Entropy is a measure of how molecules are able to disperse the total energy available to them and increases whenever molecules have higher speeds and greater freedom of movement. As a substance passes from solid to liquid to gas, the entropy increases. It also increases with increasing temperature, because the broader distribution of molecule speeds allows better distribution of the total molecular energy. In the above thermodynamic equation, an increase in molecular freedom, corresponding to an increase in entropy (ΔS^0 positive), implies a process with a higher value for the equilibrium constant. Therefore, favourable processes involve increases in molecular freedom.

One of the fundamental principles of thermodynamics is that all favourable processes increase the overall entropy of the system and its surroundings. ΔG^0 is the change in the Gibbs free energy for the process. It is a measure of the total overall change in entropy of the system and surroundings when the process takes place under standard conditions. A negative value corresponds to a large equilibrium constant and a favourable change. This is promoted by an increase in entropy for the process (positive value for ΔS^0) and an exothermic change (negative value for ΔH^0). In fact, the value of ΔH^0 is a measure of the change in entropy of the process surroundings. Any released heat from an exothermic change, increases the temperature of the molecules in the surroundings. The increased molecular speeds correspond to a gain of molecular freedom and thus increased entropy. The overall free energy equation above therefore states that the overall entropy change of the system and surroundings resulting from a given process ($-\Delta G^0/T$) is the sum of the entropy change for the process (ΔS^0) plus that of the process surroundings ($-\Delta H^0/T$).

For the evaporation of 1 mole of liquid water, at 1 atm pressure and 25 °C, $\Delta H^0 = +44$ kJ mol^{-1}. The change is strongly endothermic, indicating that the total bond energy of a mole of water vapour is less than for a mole of the liquid. In the liquid, water molecules are in close proximity, held together in clusters by hydrogen bonds. In the vapour, the molecules are widely separated and have little interaction. The enthalpy of vaporisation is therefore the energy that must be absorbed (endothermic) to break the hydrogen bonds between the water molecules in the liquid so that they can pass into the vapour state. Water vaporisation has $\Delta S^0 = +119$ J mol^{-1} K^{-1}. This is a significant increase in entropy interpreted as the large increase in molecular freedom that is possible when molecules pass from the liquid to the gaseous state. If the above figures are substituted into the free energy equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 44\,000 - 298 \times 119 = +8\,500 \text{ J mol}^{-1} \qquad (2)$$

Thus, water evaporation at 25 °C is not an overly favourable process and the extent of vaporisation at equilibrium is small.

9.2.2 Surface activity and micelle formation

We will first examine how soaps function as detergents and emulsifying agents; the more complex synthetic surfactants act in an identical manner.

When a small amount of a soap, such as sodium stearate, is added to water in a beaker, the first step is dissociation into sodium and stearate ions. The latter then accumulate at the water–air and water–glass boundaries. This is the phenomenon of surface activity, but why does it occur? We know that the molecules have a long, unbranched, hydrophobic alkyl chain that does not interact with water molecules. In fact, the alkyl chain causes the surrounding water molecules to pull back from it and aggregate together by hydrogen bonding, forming a structured cage wall with the alkyl chain of the soap inside, minimising its contact with the water. The soap is soluble because the terminal anionic carboxylate group is hydrophilic and strongly solvated by polar water molecules. At the boundary between water and a more hydrophobic surface such as glass, air or oil, the soap molecules arrange themselves so that the long alkyl chain orients itself into the hydrophobic surface away from the water, with the carboxylate ion remaining in the water. A single layer of such oriented molecules occupies the surface between the two phases.

The available surface between the two phases becomes saturated with soap molecules at quite low soap concentrations and they then begin to accumulate in the bulk of the water. This unfavourable situation, in which the hydrophobic alkyl chains and their surrounding water cages are quite incompatible, is remedied by the soap molecules accumulating together to form molecular aggregates called micelles. The solution is colloidal since the micelles are large enough to scatter a light ray. The hydrophobic alkyl chains come together in the centre of the micelle, excluding any water molecules. In this way, the alkyl chains interact only with each other and avoid contact with water molecules. The carboxylate ion ‘heads’ of each soap molecule are at the outer surface of the micelle oriented into the water, thus keeping it in solution (Figure 9.3). The micelle may incorporate a number of sodium ions, but in smaller numbers than the carboxylate ions so that the micelle is anionic overall.

Surface adsorption and micelle formation are governed by the laws of thermodynamics. The ordering of the soap molecules at a phase boundary, or in a micelle, represents the most stable state of these molecules in the solution. When a soap molecule passes from the aqueous solution into a micelle, the structured cage of hydrogen-bonded water molecules surrounding the alkyl chain collapses. Thus, hydrogen bonds will be broken but the water molecules gain considerable

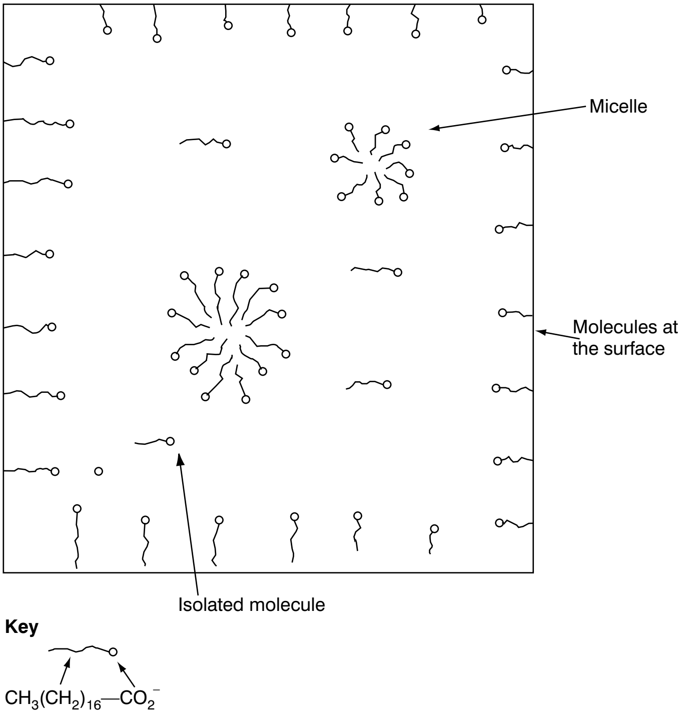


Figure 9.3 Surface activity and micelle formation in an aqueous soap solution

freedom of movement. The alkyl group of the soap molecule, which had no bonding interaction with the water molecules, now forms weak bonds with other alkyl groups in the micelle but the molecule has lost much of its freedom of movement. For micelle formation, $\Delta H^0 = +2$ kJ mol^{-1}, indicating that the bond energy liberated from the hydrophobic interaction of the alkyl chains with each other in the micelle almost offsets that needed to break the hydrogen bonds when the structured water cage around the alkyl groups collapses. Micelle formation is, however, favourable because $\Delta S^0 = +77$ J mol^{-1} K^{-1}, a substantial increase in entropy. The soap molecules give up a considerable degree of freedom on aggregating in the micelle. The entropy increase for the process is, however, dominated by the collapse of the structured cage around each alkyl group of a soap molecule in solution, when it goes into a micelle. Many water molecules that were bonded into the cage wall are therefore free and more mobile. This is the driving force for micelle formation.

The formation of micelles is an important facet of surface activity. It occurs quite suddenly once the phase boundaries are saturated with a monolayer of surfactant molecules and the total concentration in solution increases above a critical value called the critical micelle concentration or CMC. The CMC is a characteristic property of a given surfactant. Its value is often lower than 1.0 g l^{-1}. The formation of micelles depends on:

(1) the preference of the surfactant alkyl groups to interact with each other, in their own hydrophobic environment, rather than remain exposed to the water;

(2) the freeing of water molecules from the hydrogen-bonded cage around the hydrophobic groups when the surfactant molecules aggregate together.

With increasing surfactant concentration above the CMC, the numbers of micelles, and the average number of molecules in a micelle, both increase until eventually precipitation occurs. At the CMC, the change in the arrangement of surfactant molecules in the solution causes abrupt variations in various physical properties of the solution. These include the osmotic pressure, the molar conductivity and the air–solution surface tension, as well as the detergent power of the solution (Figure 9.4).

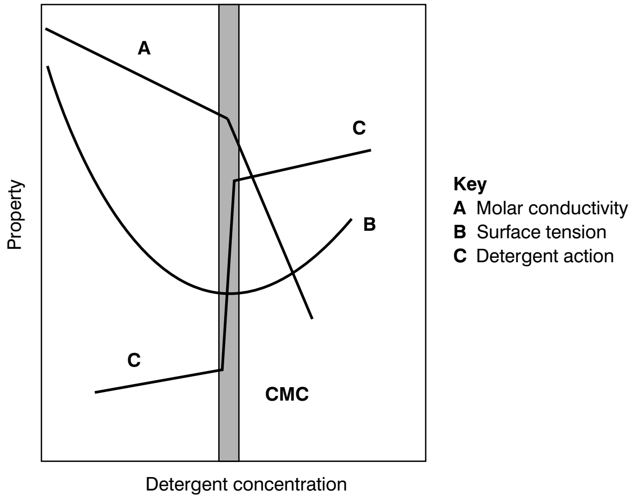


Figure 9.4 Variation of some physical properties of detergent solutions close to the CMC (critical micelle concentration)

In the interior of liquid water, each molecule is surrounded uniformly and equally attracted by neighbouring molecules in all directions. The surface tension originates from the unbalanced attraction of water molecules at the air–liquid interface towards neighbouring molecules in the bulk of the water pulling them inwards away from the air. These intermolecular attractions are mainly hydrogen bonds. If a liquid such as water has little attraction for molecules in the interface with which it is in contact, such as air, the surface tension will act to reduce the liquid surface area in contact with that interface. This is why water droplets in air, or on a wax surface, are approximately spherical. It is exactly the same phenomenon that causes water molecules to become more structured around the hydrophobic alkyl chain of a soap molecule. The air–water surface tension of a surfactant solution decreases rapidly as the concentration increases because surfactant molecules replace water molecules at the interface, with their alkyl chains and carboxylate groups oriented away from and towards the water, respectively. The surface tension increases somewhat, however, once the CMC has been exceeded (Figure 9.4).

Surface activity and micelle formation are dynamic effects and surfactant molecules are undergoing constant interchange between the interfacial monolayers, micelles and solution. Micelles may have different shapes and sizes depending on the surfactant, its concentration and the temperature. The effectiveness of a surfactant in emulsifying oils and fats depends very much on the micellar composition of the solution and therefore on the detergent concentration and temperature. Once the CMC has been reached, the detergent action increases only slowly and the use of a large excess of surfactant is wasteful (Figure 9.4).

It is not uncommon for a combination of two different surfactants to produce an effect that is greater than the combined individual effects of the two components. This is called a synergistic effect. It probably comes about from the formation of mixed micelles, containing molecules of both surfactants, that are more effective than micelles of the individual surfactants. These are complex chemical systems. Many products have special formulations for a particular purpose and the best combinations and concentrations for a particular process are often determined by trial and error.

9.2.3 Emulsification, detergency and wetting

How then does the surface activity of a surfactant influence removal of dirt from a fabric and its emulsification in solution? The emulsification of oil droplets in water using a surfactant is an appropriate starting point. As the two immiscible liquids are vigorously stirred, the oil breaks up into small droplets dispersed in the water. The oil–water interface has a high surface tension. The molecules in the bulk of the hydrophobic oil pull in those at the surface in contact with the water. This minimises the surface and the interaction with the surrounding water and the oil droplets become spherical. If stirring is halted, the small oil drops will coalesce and the liquids will separate into two layers, with the oil floating on top of the water. In the presence of an anionic surfactant, such as sodium stearate, at its critical micelle concentration, each tiny oil droplet becomes surrounded by surfactant molecules, with their alkyl chains oriented into the oil surface and the anionic 'heads' extending into the water. The tiny droplet is like a giant micelle with an oily centre. Once agitation stops, the tiny oil droplets cannot now coalesce as the negatively charged monolayer of surfactant molecules at the oil–water interface causes mutual repulsion of the drops. The oil remains emulsified. The droplets are very small and they scatter light effectively, giving the emulsion a milky appearance.

The ability of surfactant molecules to adsorb on surfaces and orient themselves so that the ionic group is in contact with the water, and the alkyl chain is oriented away from it, is crucial in the wetting of fibres. This involves the spreading of water all over their surfaces. There must be strong molecular interaction between the water and the fibre to be wetted. This is aided by the accumulation and orientation of surfactant molecules at the water–air and water–fibre interfaces. These effects are usually illustrated by means of the contact angle at the fibre–water–air interface (Figure 9.5). The surfactant in the water decreases the water–air and water–fibre surface tensions, but the unchanged fibre–air surface tension

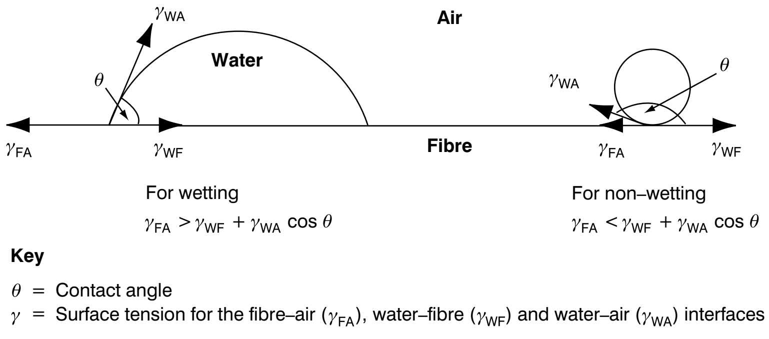


Figure 9.5 Contact angles at the fibre surface for wetting and non-wetting

causes extension of the droplet with a decrease in the contact angle. The water drop therefore spreads out over the surface.

Complete wetting of fibre surfaces is crucial in all wet processes for textiles, particularly for dyeing. Uneven fibre wetting in dyeing invariably leads to uneven dye absorption. Wetting agents are widely used in dyeing processes to ensure good penetration of the dye liquor into the fibre mass. The chemicals used must be compatible with the dyeing conditions and be effective wetting agents over a range of temperatures, at various pH values and in the presence of salts.

The action of a detergent involves similar principles. Many types of dirt on a textile surface are hydrophobic in character. During washing, the surface of the dirt on the fabric becomes surrounded by surfactant molecules, with their hydrophobic 'tails' oriented into the dirt. The surfactant molecules also saturate the fibre–water interface in a similar fashion. This decreases the fibre–water and oil–water surface tensions. The unchanged oil–fibre surface tension, and the repulsion between the negative charges of the fibre–water and dirt–water interfaces, cause the dirt to reduce its surface area by rolling up. The effect of the surfactant in the washing solution is to decrease the contact angle, the reverse effect of that in wetting (Figure 9.6). The contact angle must be greater than 90° to remove oil from a fibre. Eventually, the dirt begins to lift from the fibre and is removed into the solution. It is held in suspension by electrostatic repulsion, as in the case of emulsified oil droplets. Emulsified dirt is not likely to be redeposited on the fibre surface because of mutual repulsion of the negatively charged layers of adsorbed surfactant molecules on the dirt–water and fibre–water interfaces.

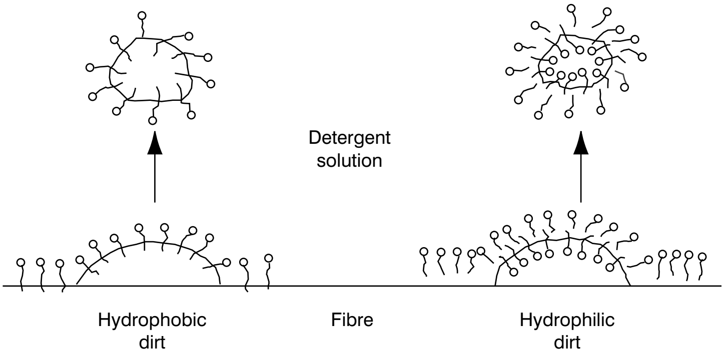


Figure 9.6 Surfactants removing hydrophobic and hydrophilic dirt from a fibre surface

A similar mechanism applies for eliminating insoluble hydrophilic polar dirt. Firstly, surfactant molecules adsorb onto the surface of the hydrophilic dirt, but, in this case, the anionic 'heads' orient into the surface of the polar dirt. To avoid contact of the hydrophobic 'tails' with the water, a second layer of surfactant molecules forms with their hydrocarbon tails interacting with those extending outwards from the first layer. This second layer of molecules has its anionic groups exposed towards the water. Such dirt therefore rolls up and lifts from the surface and is held in suspension, as before (Figure 9.6).

Although many surface-active chemicals can act as both wetting agents and detergents, this is not always true. Wetting depends mainly on reducing the surface tension of the wetting liquid, whereas detergency depends on micelle formation and the ability of the surfactant to keep dirt in suspension. The surfactant alkyl chain must be at least six carbon atoms long for surface activity to occur but at least twelve for even minimal detergent action.

Having established the principles of surface activity and micelle formation, and their role in wetting, emulsification and detergency by means of simple soap molecules, we will now examine the chemical nature of the many types of synthetic surfactant.

9.3 SYNTHETIC SURFACTANTS

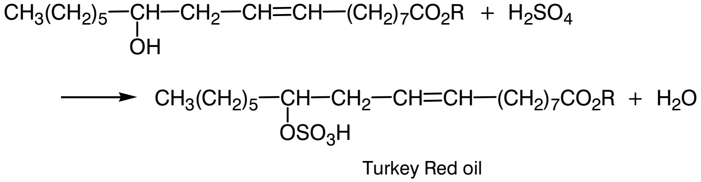
In textile wet processing, a variety of synthetic surfactants have replaced the natural soaps because of the ease of precipitation of the latter in acid solution or in hard water. Most synthetic products do not have these disadvantages and are widely used as detergents, wetting, dispersing and emulsifying agents, as well as dyeing assistants. They are manufactured from both natural starting materials, such as stearic or oleic acid, and from fully synthetic petrochemicals. Surfactants are usually classified according to their ionic character:

(1) anionic surfactants, usually organic sulphates and sulphonates;
(2) cationic surfactants, typically quaternary ammonium or pyridinium salts;
(3) non-ionic surfactants containing polar polyethylene oxide chains;
(4) amphoteric surfactants, whose molecules have both anionic and cationic sites.

9.3.1 Anionic surfactants

This is the major group comprising almost 70% of commercial surfactants. Anionic surfactants are invariably the sodium salts of either aliphatic or aromatic sulphonic acids (R–SO_3Na, sulphonates), or of the sulphuric or phosphoric acid esters of alcohols (R–O–SO_3Na, sulphates; R–O–PO_3Na, phosphates). They are derived from both natural and synthetic chemicals.

Turkey Red oil, named after its use in the dyeing of the famous Turkey Red (Section 1.2.2), is the sulphate ester of castor oil. This consists mainly of the triglyceride of ricinoleic acid. Although the chemical structure of Turkey Red oil is usually as shown in Scheme 9.3, it is probably a mixture of various species depending upon the particular sulphation reaction and isolation conditions. The sulphuric acid not only esterifies the hydroxyl group, but can also add to the carbon–carbon double bond and catalyse hydrolysis of the triglyceride, giving some free carboxylic acid groups.

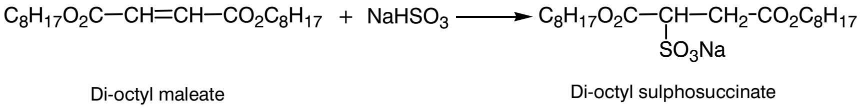


$$CH_3(CH_2)_5-\underset{OH}{CH}-CH_2-CH{=}CH-(CH_2)_7CO_2R + H_2SO_4$$

$$\longrightarrow CH_3(CH_2)_5-\underset{OSO_3H}{CH}-CH_2-CH{=}CH-(CH_2)_7CO_2R + H_2O$$

Scheme 9.3

A variety of other sulphated oils come from addition of sulphuric acid to the carbon–carbon double bond of olive oil (triglyceride), simpler oleate esters, or other unsaturated oils. Turkey Red oil, sulphated olive oil, and the sulphonated succinate ester derivatives (Scheme 9.4), are all effective wetting and emulsifying agents, but not particularly good detergents. The placement of the anionic group approximately halfway along the carbon chain, so that the alkyl groups on either side have only 6–10 carbons atoms, is responsible for the poor detergent properties. On the other hand, alkylated benzene sulphonates (**3**, in Figure 9.7) are excellent detergents. They have an anionic sulphonate group at the very end of an extended hydrophobic chain of carbon atoms. Surfactants with long hydrophobic 'tails' terminating with an anionic group, are invariably good detergents, whereas those with shorter hydrophobic chains or sections are poor detergents but often good wetting agents.



$$C_8H_{17}O_2C-CH{=}CH-CO_2C_8H_{17} + NaHSO_3 \longrightarrow C_8H_{17}O_2C-\underset{SO_3Na}{CH}-CH_2\text{-}CO_2C_8H_{17}$$

Scheme 9.4

Other important types of anionic surfactants include sulphuric and phosphoric acid esters of the products of partial polymerisation of ethylene oxide onto the hydroxyl groups of alkylphenols or alcohols (4, in Figure 9.7). Since phosphoric acid is a triprotic acid, its esters may have one, two or three alkyl groups (5, in Figure 9.7). The products are invariably complex mixtures. Many of the sulphate and sulphonate surfactants are sodium salts but some are salts with amines such as triethanolamine. The latter are oil-soluble and excellent emulsifiers.

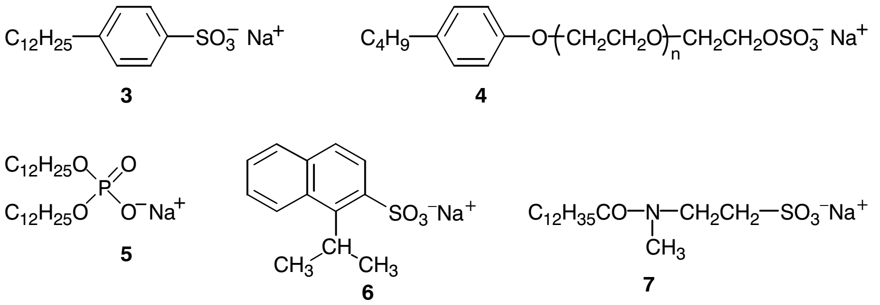


Figure 9.7 Structures of some typical anionic surfactants

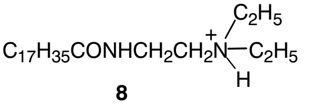
The synthetic sulphate and sulphonate surfactants have more soluble calcium and magnesium salts, so, unlike soap, they do not precipitate easily in hard water. Since sulphuric and sulphonic acids are strong acids in water, anionic surfactants containing these groups do not precipitate when their solutions are acidified, as do surfactants based on carboxylic acids. One of the major problems with anionic surfactants is their propensity to form large amounts of foam. This can cause environmental problems. Even low concentrations carried over into a dyebath after scouring can produce sufficient foam to interfere with uniform transfer of the dye from the solution to the fibres.

In any particular application, it is essential that the surfactant used is stable at the operating temperature and pH. Problems of surfactant instability in acidic and alkaline solutions are common. Some anionic surfactants, such as simple alkylnaphthalene sulphonates (6, in Figure 9.7) are not effective detergents but they can be used as wetting agents during the carbonising of wool as they remain active in acidic solution (Section 7.3.3). Typical anionic sulphate ester wetting agents (Turkey Red oil, Scheme 9.3) are often not stable in the strongly alkaline NaOH solution used for mercerisation of cotton (Section 5.4.6). They may be hydrolysed or salted out of solution. Surfactants based on tertiary amides from fatty acids and *N*-methyltaurine (2-*N*-methylaminoethane sulphonic acid) are good detergents with better stability in alkaline solution (**7**, in Figure 9.7). Provided that added salts do not precipitate the surfactant by the common ion effect, they often increase the efficiency of anionic detergents. The incorporation of cations into the detergent micelles influences the overall charge on the micelles, the degree to which they repel each other and therefore their emulsifying action.

9.3.2 Cationic surfactants

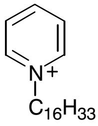
These comprise a small group of surfactants that are mainly quaternary ammonium or pyridinium salts (for example, **8** and **9**, in Figure 9.8). As for anionic surfactants, these may be derived from natural fatty acids or from synthetic chemicals. They are used mainly as softening or dyeing aftertreatment and retarding agents. The long hydrophobic 'tails' of cationic agents, deposited as a film on the fibre surface, lubricate it and provide a much smoother and softer handle.

Many fibres in water develop a negative surface potential relative to the solution and therefore attract cationic chemicals. Rinsing does not easily remove them and they are not used as detergents and wetting agents. There is a risk that suspended dirt, with its surrounding layer of cationic surfactant molecules, will redeposit back onto the negatively charged fibre surface.



$C_{17}H_{35}CONHCH_2CH_2\overset{+}{N}H(C_2H_5)_2$

8



9

Figure 9.8 Structures of some typical cationic surfactants

Cationic auxiliaries are not usually compatible with anionic products and they are rarely used together. The two types interact with each other to form an insoluble organic salt. This is often rather gummy and difficult to remove if deposited on the fibre surface. Emulsification with excess surfactant or a non-ionic dispersing agent avoids this precipitation. Cationic agents are often used to aftertreat dyeings where anionic dyes of poor washing fastness have been used.

The cationic product interacts with the anionic dye in the fibres, forming a high molecular weight organic salt of decreased water solubility and much reduced diffusion rate. The washing fastness is therefore improved. Unfortunately, many of these products decrease the light fastness of the aftertreated dyeing.

9.3.3 Non-ionic surfactants

This is the second most important group of surfactants. They are mainly chemicals whose molecules have the usual hydrophobic 'tail' connected to a short polyethylene oxide chain. This will usually have about five to twenty $–CH_2CH_2O^–$ units linked together and forms the polar hydrophilic 'head' to whose oxygen atoms water molecules can hydrogen-bond. A wide range of products is available with different types of hydrophobic groups and varying degrees of polymerisation of the polyethylene oxide chain. Some have polypropylene oxide 'heads', usually promoting oil solubility. The non-ionic surfactants are produced from natural or synthetic carboxylic acids, alcohols, phenols, amines and amides, and ethylene oxide (for example, **10**, **11** and **12,** in Figure 9.9). Polyethylene oxide derivatives obtained by polyethoxylation of thiols give good detergents with high biodegradability, a factor that is becoming of increasing importance. All the precursors, such as alcohols, phenols and thiols, have a reactive hydrogen atom capable of adding ethylene oxide and initiating its partial polymerisation. The products are mixtures with molecules having polyethylene oxide chains of varying lengths.

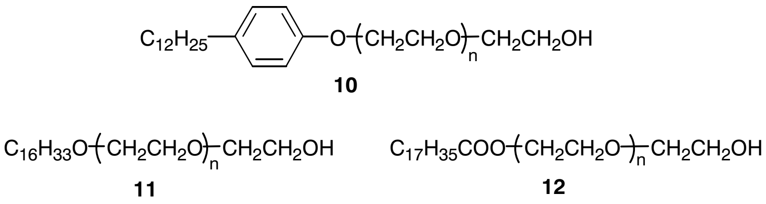
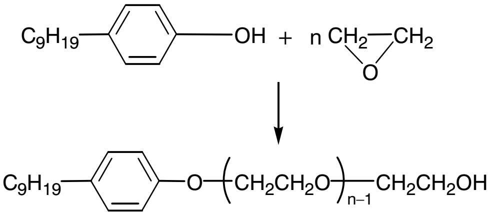


Figure 9.9 Structures of some typical non-ionic surfactants

Alkyl polyethylene oxides such as those derived from stearyl alcohol (1-octadecanol) usually have about 10–20 ether units in the chain, whereas alkyl–aryl types (Scheme 9.5) have a shorter chain with about 5–10 ether units. As for all surfactants, the hydrophilic/lipophilic (water-loving/fat-loving) balance between the polyethylene oxide 'head' and the hydrophobic 'tail' determines the performance in a given application. Typically, about 65–70% of the molecular mass of a non-ionic surfactant is polyethylene oxide, to achieve the appropriate balance between the 'head' and 'tail'.

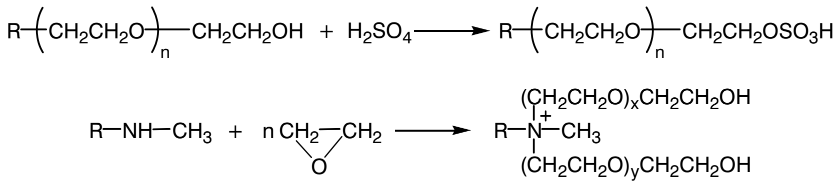


Scheme 9.5

The oxygen atoms in the polyethylene oxide chain are solvated by hydrogen bonding with water molecules and constitute the hydrophilic group of this type of surfactant, which is responsible for its water solubility. Non-ionic surfactants form micelles in the same way as ionic surfactants but with the polyethylene oxide chain oriented towards the water. On heating their micellar solutions, the degree of hydrogen bonding between the water and the polyethylene oxide chain decreases, thus decreasing the solubility. Many solutions of non-ionic surfactants have characteristic cloud points. This is the temperature at which the solution suddenly becomes cloudy on heating as two different phases separate from the solution, one rich in surfactant and the other depleted. The CMC decreases with increasing temperature and is at a minimum just below the cloud point. This is often the optimum temperature for effective detergency. The cloud point increases with the length of the polyethylene oxide chain but decreases in the presence of salts. It is usually around room temperature for 4–5 polyethylene oxide units but over 90 °C for 12–14 units. Solutions of long chain polyethylene oxides ($n = 20$–25) do not cloud below 100 °C.

Since polyethylene oxide chains have a terminal hydroxyl group, this may be esterified with sulphuric acid. In this way, anionic sulphate surfactants with a polyethylene oxide chain can be made. Similarly, reaction of ethylene oxide with secondary and tertiary amines generates weakly cationic surfactants with polyethylene oxide chains (Scheme 9.6).

Non-ionic surfactants are usually excellent wetting agents and detergents. Those based on polyethylene oxide are usually water-soluble while those from polypropylene oxide are oil-soluble. Their major disadvantages are considerable



Scheme 9.6

foaming, and clouding at higher temperatures and salt concentrations. To some extent, a low cloud point can be overcome by blending the non-ionic surfactant with an anionic product that serves as an emulsifiant.

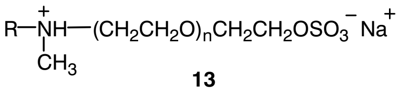
The other major types of non-ionic surfactant are the fatty acid alkanolamides prepared from fatty acids or their esters and ethanolamines (Scheme 9.7). These products are excellent anti-redeposition agents in soaping-off. They are also excellent lubricants and are often components of anti-crease agents when dyeing fabric in rope form.

$$R{-}CO_2H \;+\; NH(CH_2CH_2OH)_2 \longrightarrow R{-}CON(CH_2CH_2OH)_2 \;+\; H_2O$$

Scheme 9.7

9.3.4 Amphoteric surfactants

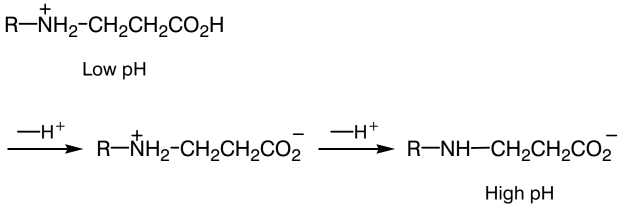
These form a minor group of amphoteric agents, used mainly as lubricants, dyeing retarders and softeners. They may have both cationic and anionic sites in the same molecule, depending upon the pH of the solution (**13**, in Figure 9.10). In acidic solution, some of these products will be cationic, but become anionic at higher pH (Scheme 9.8). At pH values close to their isoelectric point, they exist as zwitterions but are least effective as surfactants under these conditions. These chemicals have excellent stability in acidic and alkaline solutions and little sensitivity to salts. Amphoteric agents such as a polyethoxylated amine with a sulphated terminal hydroxyl group are useful for increasing the rate of dye uptake of tippy wool, i.e. wool whose fibre ends have been damaged by exposure. Some of these products have anti-bacterial and anti-static effects.



$$R{-}\underset{\substack{|\\ CH_3}}{\overset{+}{N}}H{-}(CH_2CH_2O)_nCH_2CH_2OSO_3^{-}\,Na^{+}$$

13

Figure 9.10 Structure of an amphoteric surfactant – both cationic and anionic sites in the same molecule



$$R\text{—}\overset{+}{N}H_2\text{-}CH_2CH_2CO_2H \xrightarrow{-H^+} R\text{—}\overset{+}{N}H_2\text{-}CH_2CH_2CO_2^- \xrightarrow{-H^+} R\text{—}NH\text{—}CH_2CH_2CO_2^-$$

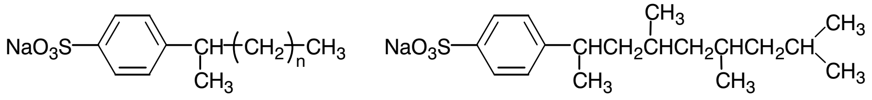
Scheme 9.8

9.3.5 Advantages and disadvantages of synthetic surfactants

What are the advantages of synthetic surfactants over the natural soaps? We have already noted that the sodium salts of fatty acids are effective surfactants but precipitate as insoluble calcium and magnesium salts in hard water, and as the free fatty acid in solution of pH below about 5. Both precipitation reactions tend to form gummy deposits on fabrics, which are often quite difficult to remove. Calcium and magnesium soaps possess no detergent action and hard water requires the use of much more soap for effective cleaning. The problem of hardness can be partly overcome by use of a water-softening sequestering agent, such as a polyphosphate (Section 8.3.3), along with the soap. In addition, pure soap solutions are weakly alkaline and soft soaps, which have residual glycerol and possibly alkali from the saponification reaction, may be even more so.

The synthetic surfactants do not suffer from these problems but have their own particular disadvantages. Firstly, anionic surfactants should not come into contact with those of a cationic nature. The two types are quite incompatible and produce a gummy precipitate of an organic salt. In any application, where this might be a possibility, either one of the ionic surfactants must be replaced by a non-ionic one, or a non-ionic surfactant must be used to keep the precipitated organic anion–cation salt in suspension. Secondly, many of the fully synthetic surfactants, particularly those with branched alkyl chains, have low biodegradability. They tend to persist in natural waters after discharge in the effluent. If the water is turbulent, this often leads to the formation and accumulation of persistent foam from the surface active agents. Detergents in which the alkyl chain is unbranched and more readily oxidised by bacteria in the water (**14**) have replaced the non-biodegradable types (**15**, in Figure 9.11).

Surfactants must always be evaluated under the conditions that prevail during their use, particularly to establish that they are stable. This is essential for processes in which the solution is strongly acidic or alkaline, or if high concentrations of salts are present. It is also important, in many applications, that



14

Biodegradable

15

Non-biodegradable

Figure 9.11 Structures of biodegradable and non-biodegradable alkylbenzene sulphonate detergents

rinsing removes surfactant residues from a fabric. This is essential before application of water-repellent finish to a fabric.

Almost all commercial surfactant preparations are mixtures of chemicals arising either from the raw materials and the reactions used in their manufacture, or from deliberate mixing of different surfactants to achieve a particular effect. Many are sold as concentrated aqueous solutions and therefore their cost effectiveness must always be evaluated.

9.4 OTHER APPLICATIONS OF SURFACTANTS

Although surfactants in the textile wet processing industry are used mainly as wetting agents, detergents or emulsifying and dispersing agents, certain types of surfactants are used as softeners, lubricants, and anti-static and anti-bacterial agents. Their use for controlling the rate of dye uptake, and thus the levelness of the dyeing, has increased considerably, in direct relation to the demands for improved fastness to washing that require the use of dyes of poor migration. Cationic auxiliaries are also used to aftertreat dyeings with anionic dyes.

In most applications, and particularly in dyeing, the role of auxiliary products is not well understood for a number of reasons:

(1) it is difficult to evaluate their concentration in a given product;
(2) commercial products invariably have unknown formulations and the number and nature of the chemical constituents is rarely clear;
(3) there has been little fundamental work on the mode of action of various auxiliary products.

9.4.1 Dyeing levelling agents

Levelling agents for dyeing are often surfactants that are said to be either fibre substantive or dye substantive. Anionic surfactants, such as sulphates or sulphonates, are often used to control the rate of dyeing of wool and nylon in weakly acidic solution. Their small molecular size allows rapid penetration into these fibres and interaction with the ammonium ion groups therein. This slows down dye absorption by ion exchange, but eventually the more substantive dye molecules will displace the anionic surfactant by ion exchange (Section 1.1.2, Scheme 1.4). When acting in this manner, these auxiliary chemicals are often called blocking agents. Another important example is in the dyeing of acrylic fibres with cationic dyes. This involves ion exchange at the anionic sites in the fibre. Cationic dyes often have a very high initial rate of adsorption on the fibre surface above a critical temperature, which can lead to unlevel dyeing. Cationic surfactants of low substantivity initially block a considerable number of the anionic sites in the fibre and allow a more gradual uptake of dye, leading to a uniform dyeing (Scheme 9.9).

$$\text{Acrylic—}SO_3^-\,Na^+ + R_4N^+ \longrightarrow \text{Acrylic—}SO_3^-\,R_4N^+ + Na^+$$

$$\text{Acrylic—}SO_3^-\,R_4N^+ + \text{Dye}^+ \longrightarrow \text{Acrylic—}SO_3^-\,\text{Dye}^+ + R_4N^+$$

Scheme 9.9

Dye-substantive levelling agents prevent dye absorption by the fibre by complex formation with the dye in the dyebath. This complex is of such a molecular size that it cannot penetrate into the fibre. As the dyeing temperature gradually increases, the complex becomes less and less stable and the dye is gradually liberated and free to enter the fibres. Cationic agents can function in this way interacting with anionic dyes. Polyethoxylated amines are non-ionic/cationic products in weakly acidic solution that complex with anionic dyes and retard dyeing. They may have quite long polyethylene oxide chains (n = 90–120). The cationic site interacts with the anionic dye, but the long polyethylene oxide chain keeps the organic salt in dispersion. The mechanisms of dye–surfactant interaction have not been extensively studied and there are very few publications providing any insight into this important type of behaviour.

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CHAPTER 10

An introduction to dyes and dyeing

10.1 DYES

10.1.1 The molecular structures of dyes

The structures of dye molecules are complex in comparison with those of most common organic compounds. Compare the molecular formula of acetic acid, $C_2H_4O_2$, with that of even a simple dye such as Orange II, $C_{16}H_{11}N_2SO_4Na$ (Figure 1.2). Despite their complexity, dye structures have a number of common features. Most dye molecules contain a number of aromatic rings, such as those of benzene or naphthalene, linked in a fully conjugated system. This means that there is a long sequence of alternating single and double bonds between the carbon and other atoms throughout most of the formal written structure. This type of arrangement is often called the chromophore or colour-donating unit. The conjugated system allows extensive delocalisation of the π electrons from the double bonds and results in smaller differences in energy between the occupied and unoccupied molecular orbitals for these electrons. At least five or six conjugated double bonds are required in the molecular structure for a compound to be coloured. The wavelength of the absorbed light able to excite an electron from an occupied orbital to the first unoccupied molecular orbital then corresponds to visible light. The smaller the energy difference, the longer the wavelength of the light absorbed, according to the Planck equation:

$$\Delta E = h\nu = \frac{hc}{\lambda} \qquad (1)$$

In this equation, ΔE is the energy difference between the implicated molecular orbitals, h is Planck's constant, ν is the frequency and c is the speed of the absorbed light, and λ is its wavelength. Conjugation results in a framework with all the atoms lying in the same plane. Figure 10.1 shows some typical examples of dye structures with different chromophores.

Dyes with good water solubility usually have an ionic centre in their molecules. This may be relatively localised, as in a sulphonate group attached to a benzene

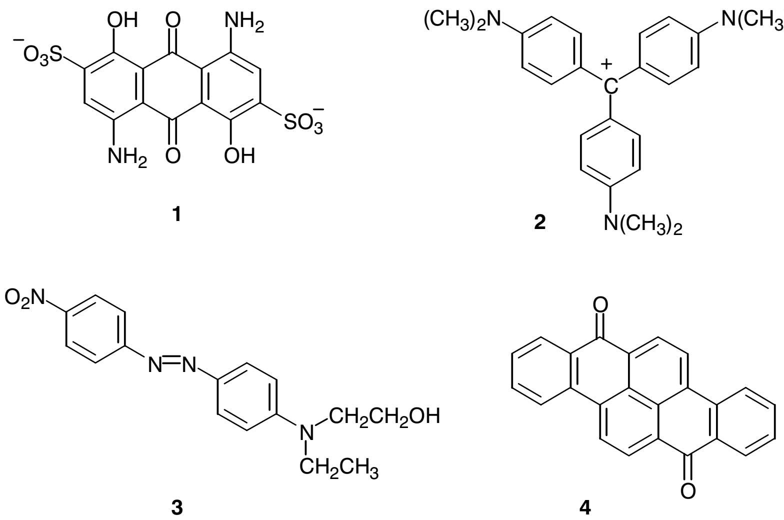


Figure 10.1 Chemical constitutions of typical dyes

ring (**1**, in Figure 10.1, CI Acid Blue 45). If the atom bearing the ionic charge is part of a conjugated chain, a delocalised charge results, as in a cationic triphenylmethane dye (**2**, CI Basic Violet 3). In the case of the non-ionic disperse dyes (**3**, CI Disperse Red 1), the presence of polar substituents, such as a hydroxyl group, promotes slight solubility in water. Vat dyes (**4**, CI Vat Yellow 4), which are water-insoluble pigments, have no ionic groups in their molecules. Their key structural characteristic is a pair of conjugated carbonyl groups. On reduction, the carbonyl groups become anionic phenolate groups so that the leuco compound is water-soluble and able to dye cotton (see also Indigo in Figure 1.4).

10.1.2 Composition of commercial dyes

Some commercial dyes are fine powders; others may be granular to eliminate dusting problems. Powdered dyes that easily dust during handling can quickly contaminate a large area, including the workers. Those dyes that are initially pigments, such as vat and disperse dyes, are also available as aqueous pastes. These obviously contain less actual colorant, because of the high water content, but often also have less dispersing agent than solid forms because they are easier to re-disperse in water. Dyes are also available as liquid solutions or dispersions. These are ideal for continuous dyeing, where simple dilution of the liquid dye allows the rapid preparation of large volumes of dye solutions. Liquid dyes should be stable to heating and cooling, resistant to sedimentation and stratification, and not contain unsafe co-solvents or additives.

Commercial dye powders also contain various other chemicals besides the principal dyestuff. These include diluents such as salts or starch, wetting agents, dispersants, impurities from manufacture such as residual intermediate chemicals, anti-dusting agents (oils), buffers (sodium carbonate or phosphates), stabilisers, and shading dyes. In the manufacture of successive batches of a given dye, it is almost impossible to obtain identical products because of slight process variations. Addition of NaCl to solutions of water-soluble sulphonated dyes precipitates the sodium salt of the dye but the amount of salt solution adhering to the filtered precipitate varies from batch to batch. This solution evaporates during drying and the salt remains in the product. Batch to batch variations in the colour yield (the depth of colour attainable with a given amount of dye) and in hue, although slight, are the norm. Because of this, each batch of dye must not only have the correct physical form, with the appropriate additives, but also be standardised so that it will give dyeings of the same hue and colour yield as previous batches. This is the major reason for the presence of inert diluents and small amounts of shading dyes. The latter, of course, must have similar dyeing properties to the parent dye. Some dyes may even be available in more than one strength, such as the acid dye Sandolan Rhodamine E-B 300% (CI Acid Red 52). This dye will produce a dyeing with a given depth of colour using a third of the weight of the standard product, which is rated at 100% strength.

Frequently a dye powder does not consist of a single principal coloured chemical. Some products are mixtures of different isomeric colorants, or contain substantial amounts of other coloured by-products from the dye-forming reaction. Others are deliberate mixtures of different pre-made dyes, while some dyes are prepared from mixtures of intermediates. In some cases, as for the sulphur dyes, the manufactured product may be of unknown chemical constitution and may be a complex mixture of coloured chemicals.

Commercial products are used directly for dyeing, but occasionally in dyeing research there is a need for purified dyes. Dye purification is not easy. Washing of water-insoluble dyes with hot water removes some additives. The product can then be dried and recrystallised from an appropriate solvent. Usually, the product obtained must then be finely ground with a dispersing agent so that it will readily disperse in water. The purification of water-soluble dyes is much more difficult. Sulphonated dyes may be salted out several times with sodium acetate, which can finally be removed after drying by extraction with ethanol, if the dye itself is not too soluble. Ion exchange methods are sometimes useful, as are chromatographic methods (see Chapter 24). The yield of purified dye is always very low and it is often difficult to ascertain if the dye is in fact pure and free from contaminants [1].

10.1.3 Dye selection

There are numerous factors involved in the selection of dyes for colouring a fabric in a particular shade. Some of these are:

(1) the types of fibres present;
(2) the form of the textile material and the degree of levelness required – level dyeing is less critical for loose fibres, which are subsequently blended, than it is for fabric;
(3) the fastness properties required for any subsequent manufacturing processes and for the particular end-use;
(4) the dyeing method to be used, the overall cost, and the machinery available;
(5) the actual colour requested by the customer.

The last point is not trivial. Although many types of dyes are available, in a wide range of colours, customers have definite ideas about exactly what colour their goods should be and will often provide a sample. The dyer will usually only be able to match this colour by dyeing the goods with a mixture of two to four dyes. The basic principles are much like those used in painting, many colours being obtained by mixing suitable amounts of red, yellow and blue colorants.

Obviously, the dyes selected to colour a high quality cotton material for shirts must be quite different from those for a cellulose acetate fabric for coat linings. For the former, high washing fastness and moderate light fastness are essential, but are insignificant for the latter. The dye manufacturers can assist in making a successful choice of dyes but there is no substitute for experience.

10.2 DYEING METHODS

The objective of dyeing is the uniform coloration of the mass of fibres constituting the material, usually to match a pre-specified colour. Any significant difference in colour from that requested by the customer, and any unlevelness of the colour of a fabric, will be immediately apparent. Many factors can influence the final colour appearance. These include fibre characteristics such as the lustre, denier, staple length, texture, and cross-section, as well as the cloth construction. Since a client's coloured sample is rarely of the same material as that to be dyed, dyehouse laboratories devote considerable time to dyeing trials aimed at developing recipes to reproduce the desired colour on the given goods.

Coloration of a textile material is achieved in a number of different ways:

(1) direct dyeing, in which the dye in the aqueous solution in contact with the material is gradually absorbed into the fibres because of its inherent substantivity;
(2) dyeing with a soluble precursor of the dye, which forms an insoluble pigment deep within the fibres on treatment after dyeing;
(3) direct dyeing followed by chemical reaction of the dye with appropriate groups in the fibre;
(4) adhesion of the dye or pigment to the surface of the fibres using an appropriate binder.

All of these methods but the last require that the fibres, at some stage, absorb the dye, or an appropriate precursor, from an aqueous solution. This process is essentially reversible. Note, however, that precipitation of a pigment and reaction with the fibre are irreversible chemical processes.

Dyeing is either a batch exhaustion process, or a continuous impregnation and fixation process. In the exhaust technique, all the textile is in repeated contact with all the dye liquor during dyeing and the fibres gradually absorb the dyes. Careful control of the dyeing temperature, pH and auxiliary chemical concentrations is often necessary to obtain level, well-penetrated dyeings. This is essential if the initially absorbed dye is unable to migrate from heavily dyed to poorly dyed areas during the process. In continuous impregnation methods, the fabric passes through a small bath containing the dye solution and then two rubber-covered rollers squeeze out the excess solution. This process is called padding. There is no migration of the dye from the point of impregnation except into the fibres, which is assisted by the pressure rollers. Each small segment of fabric encounters the dye liquor only once so padding must be uniform across the fabric width and along its entire length. After padding, the dyes must diffuse into the fibres. This step is called fixation. It may be as simple as rolling up the fabric and batching it for several hours, or as complex as a rapid thermal treatment in a steamer or hot air oven.

Other operations often precede or follow the actual process of dyeing. Pretreatments include scouring and bleaching, sometimes as separate continuous operations, or as batch processes in the dyeing machine. These remove natural and synthetic impurities from the goods and should result in uniform water absorbency. After dyeing, the material is rinsed to remove adhering solution but it may need additional treatment while still in the dyeing machine. These aftertreatments may include:

(1) washing in detergent, at or near the boil, to remove any unfixed dye or loosely adhering pigment from the fibre surfaces – this process is called soaping;
(2) treatment with chemicals to improve the fastness properties of the dyeing – this often causes a change in shade and complicates colour matching;
(3) application of simple finishing chemicals such as softeners.

10.3 DYEBATH AND FABRIC PREPARATION

A number of preparatory steps are essential before dyeing. Once the goods are in the dyeing machine, they must be thoroughly wetted out to remove trapped air. This is to ensure that the dye solution will have equal access to all fibre surfaces. Wetting-out may involve running the material in the dyeing machine in warm or hot water, in the presence of a wetting agent if wetting is likely to be difficult. Fabric that has been scoured or bleached in the dyeing machine must be rinsed to remove residual chemicals. It will already be completely wet but must be run in water and the pH value checked, and adjusted if necessary, before the dyes are added.

Dyeing is often one of the final processes in production. Many types of dyeing faults, such as colour blotches and spots, colour shading from side-to-side, end-to-end or face-to-face of the material, water marks, and crack or crease marks, are often a consequence of poor preparation, or dye selection, or dyeing technique. For uniform dyeing, the fabric's absorbency must be uniform. While preparation may not totally remove all the natural and synthetic chemicals present in the grey material, the residues should be minimal and uniformly distributed.

Even the preparation of the solution or dispersion of the dyes is not necessarily as simple as it might seem. Water-soluble dyes must be completely in solution, otherwise undissolved particles may cause deeply coloured spots where they contact the cloth surface. Dye powders are normally pasted with warm water. A wetting agent, or some alcohol, often helps in wetting of the powder. Cold, warm or even boiling water is then poured onto the paste and the mixture stirred well. Granular forms can often be simply dispersed in water and dissolved by stirring. Boiling will usually dissolve all the dyes if the concentration is high or if they are of limited solubility. The concentrated dye stock solution is added to the bath through a fine sieve to ensure removal of any undissolved particles. The same techniques are also used to prepare dispersions of insoluble dyes such as vat and disperse dyes. The particles of such dyes are so fine that they pass through a sieve as they are added to the dyebath. In some cases, very soluble dyes may be placed directly into the water already in the dyebath before the goods are present. The water is then heated by steam injection and more cold water added. Most dyes are usually easy to dissolve, but the less soluble types require care.

The usual sequence of steps before batch dyeing is to fill the machine with water, enter the fabric and ensure it is thoroughly wetted. Any initially needed chemicals are then added. Once the initial dyeing temperature is established, the dyes are added, either all at once, in several portions, or continuously from a reservoir, depending on the particular dyeing machine.

10.4 TERMS USED IN DIRECT EXHAUST DYEING

10.4.1 Exhaustion

In exhaust dyeing, all the material contacts all the dye liquor and the fibres absorb the dyes. The dye concentration in the bath therefore gradually decreases. The degree of dyebath exhaustion as a function of time describes the rate and extent of the dyeing process. For a single dye, the exhaustion is defined as the mass of dye taken up by the material divided by the total initial mass of dye in the bath, but for a bath of constant volume:

$$\%\ \text{Exhaustion} = \frac{C_0 - C_s}{C_0} \times 100 \qquad (2)$$

where C_0 and C_s are the concentrations of dye in the dyebath initially and at some time during the process, respectively.

Exhaustion curves such as that shown in Figure 10.2 may be determined at a constant dyeing temperature, or under conditions where the temperature and other dyeing variables are changing. For many dyeings, a gradual increase of the dyeing temperature controls the rate of exhaustion, aided possibly by the addition of chemicals such as acids or salts. In cases where the dyes in the deeply dyed fibres are not able to desorb into the bath and then be redistributed onto paler

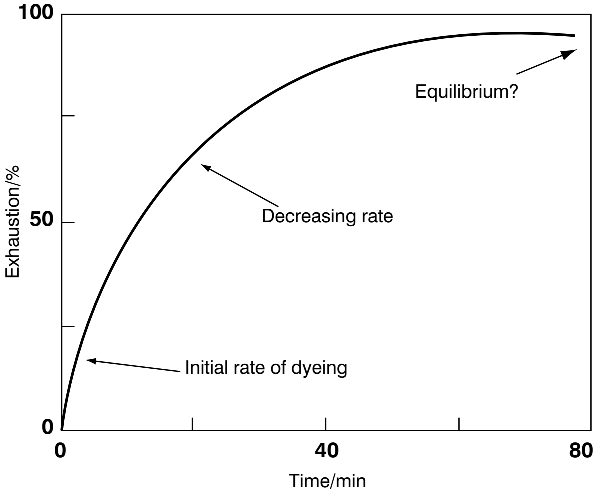


Figure 10.2 Dyebath exhaustion as a function of time

fibres, such control is essential to ensure that the final colour is as uniform as possible. Such redistribution of dyes is called migration.

The slope of a dyeing exhaustion curve (Figure 10.2) defines the rate of dyeing at any instant during the process. The rate of dyeing gradually decreases until, if dyeing is continued long enough, an equilibrium is reached where no more dye is taken up by the fibres. There is now a balance between the rates of dye absorption and desorption. The equilibrium exhaustion is the maximum possible under the given conditions. The lack of any further increase in exhaustion does not necessarily mean, however, that a true equilibrium exists. It is possible for the dye in solution to be in equilibrium with dye located on the outer surfaces of the fibres. True equilibrium only exists when the dye in solution is in equilibrium with dye that has fully penetrated into the centre of the fibres. Dyeings rarely continue to this point since it may take a relatively long time to attain. In fact, many commercial dyeings barely reach the point of constant exhaustion.

The degree of exhaustion of a dye at equilibrium is higher the greater the substantivity of the dye for the fibre being dyed. Often, a very substantive dye will give a high initial rate of absorption, or strike. Substantivity is the ‘attraction’ between dye and fibre whereby the dye is selectively absorbed by the fibre and the bath becomes less concentrated. Both the initial strike and the rate of exhaustion vary with the dyeing conditions. Rapid strike of a dye invariably results in initial unlevelness of the colour and must be controlled if the dye cannot subsequently migrate from strongly to weakly dyed areas.

The dyer must consider the initial strike, the overall rate of dyeing and the depth of colour that can be obtained in a given dyeing time, even if equilibrium has not been reached. In order that dyes are economically used, and as little as possible is wasted in the dyehouse effluent, the dyer prefers a high degree of exhaustion in a relatively short dyeing time. Dyeing, however, must not be so rapid that it is difficult to produce a level dyeing.

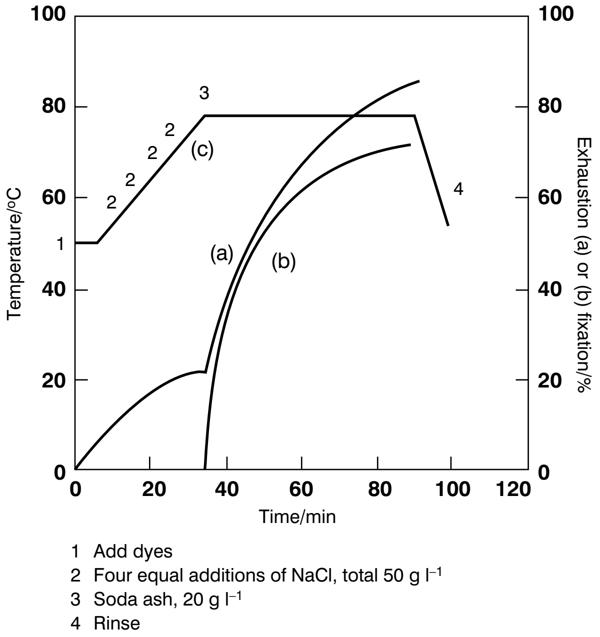


Figure 10.3 Diagram showing variations in dye exhaustion (a), reaction with the fibre (b), temperature (c) and chemical additions, for dyeing cotton with a reactive dye of low substantivity and reactivity

Diagrams showing the temperature variation, and the times of chemical additions, also summarise the dyeing process. Figure 10.3 shows the more complicated situation of dyeing cotton with a fibre-reactive dye where the degree of exhaustion of the dye and its subsequent reaction with the cotton are controlled by variation of the dyebath temperature and by the addition of salt and later of sodium carbonate. In this case, once the dye has reacted with the cotton, migration is impossible. In the early stages of the process, the dyeing conditions do not promote reaction between the dyes and fibre and the dyes are allowed to migrate from fibre to fibre. The reaction of the dye with the cotton starts as soon as the pH of the dyebath is increased by addition of sodium carbonate.

10.4.2 Amounts of dye and colour yield

The amounts of dyes used to produce the colour desired are usually expressed as a percentage of the weight of the dry material, and abbreviated as % owf, or % dye on the weight of fibre. Thus, 1.00 kg of dye used to colour 100 kg of cloth corresponds to a 1.00% dyeing. Colour reproducibility depends upon accurate weighing of both the goods and the dyes. This may be difficult when hydrophilic fibres such as cotton, viscose or wool are present. These absorb varying amounts of water from the air depending upon the relative humidity and temperature. In such cases, the regain of the material must be known and the amount of dye calculated on the basis of the dry goods.

With increasing amounts of absorbed dyes, the colour of the goods obviously becomes deeper, but also usually duller, and often with a slight change in hue. Deep shades frequently have lower fastness to wet treatments and rubbing than pale shades produced with the same dyes. On the other hand, deeper dyeings have higher light fastness. The colour yield is the depth of colour of a dyeing per unit amount of dye in the material. Quantitative assessment is possible from measurement of the reflection spectrum of a sample of the dyeing and the percentage of the dye (Chapter 24). Dyehouse laboratories often determine the relative colour yields of comparable dyes to evaluate their cost effectiveness.

10.4.3 Liquor-to-goods ratio

The liquor-to-goods ratio, or simply the liquor ratio, gives the weight of the bath solution relative to the weight of the dry material being dyed. Since the density of the solution is usually very close to 1.00 kg l^{-1}, the liquor-to-goods ratio is usually given in l kg^{-1}. Many newer dyeing machines operate with lower liquor ratios in order to minimise the consumption of energy for heating the water. An increase in the liquor ratio causes a decrease in the degree of exhaustion, under the given conditions, and therefore a decrease in the depth of colour of the dyeing. If dyeing is described by a simple equilibrium constant K in the form of the ratio of the concentration of dye in the fibre (C_f g dye kg^{-1} fibre) and the concentration in the bath (C_s g dye kg^{-1} solution), *K* will be given by:

$$K = \frac{C_f}{C_s} = \frac{(C_0 - C_s) \times L}{C_s} = \frac{(C_0 - C_s)}{C_0} \times \frac{C_0}{C_s} \times L = \frac{(E \times L)}{(1 - E)} \qquad (3)$$

where *E* is the fractional exhaustion and *L* is the liquor ratio. Rearrangement of this equation gives:

$$E = \frac{K}{(K + L)} \qquad (4)$$

Because *K* is a constant, under given conditions, an increase in the liquor ratio *L* is accompanied by a corresponding decrease in the equilibrium exhaustion *E*.

High liquor ratios also increase the consumption of chemicals added during dyeing if these are required at a specific concentration. For example, a concentration of 20 g l^{-1} of NaCl in the dyeing of 50 kg of cotton at a 20:1 liquor ratio requires 20 kg of NaCl, but only 5 kg at a 5:1 ratio. Accurately establishing the liquor-to-goods ratio is necessary for reproducible dyeing.

10.4.4 Rate of dyeing and strike

Dyeing rates are of greater practical significance than the exhaustion at equilibrium. This is because continuation of dyeing to equilibrium is uneconomic. Dyeing should be neither too slow nor too fast. Slow dyeing involves long dyeing times with increased risk of fibre damage and dye decomposition, particularly at higher dyeing temperatures. It is too costly. On the other hand, very rapid dyeing will usually result in the colour being unlevel.

The slope of the exhaustion curve gives information on the rate of dyeing. Determination of these curves, however, requires much work and they are dependent on the dyeing conditions and the nature of the goods. The dyeing rate is influenced by the temperature and by chemicals such as salts and acids, all of which also influence the final exhaustion. A clear distinction of the effects of process variables on the dyeing rate and on the final exhaustion at equilibrium is essential.

The rate of dyeing depends, in some cases, on the rate of liquor circulation in the dyeing machine. Dyeing consists of three steps:

(1) transfer of dye from the bulk of the solution to the fibre surface;
(2) adsorption of dye onto the fibre surface;
(3) diffusion of adsorbed dye into the fibre interior.

The adsorption equilibrium is usually rapid, and the overall rate of dyeing depends on the rate of diffusion of the dye into the fibres. This implies that the rate at which dye liquor arrives at the surface of the fibres does not control the dyeing rate. This may not always be so in machines where there is inadequate relative movement of the goods and dye liquor, or in situations where diffusion is rapid or the bath concentration is low.

Materials composed of finer fibres have a much larger specific surface ($\mathrm{m^2\ kg^{-1}}$) and a higher dyeing rate, even though the equilibrium exhaustion may not be significantly different from that of a material made of courser fibres of the same polymer. If the dyeing rate is proportional to the fibre surface area per unit mass, it will be inversely proportional to the fibre radius, *r*, and thus inversely proportional to the square root of the fibre tex.

$$\begin{aligned} \text{Dyeing rate} &\propto \frac{\text{area}}{\text{mass}} \propto \frac{2\pi\ r}{\pi\ r^2} \propto \frac{1}{r} \\ \text{Fibre tex} &\propto \pi r^2 \\ \text{Dyeing rate} &\propto \frac{1}{\sqrt{tex}} \end{aligned} \qquad (5)$$

Dyeings on filaments that are finer also appear paler. These two effects have considerable impact on the dyeing of the newer synthetic microfibres.

The initial rate of dyeing (the initial slope of exhaustion versus time) is called the strike. Rapid strike by a dye often results in initial unlevelness and must be avoided for those dyes that cannot subsequently migrate from heavily to lightly dyed areas of the fabric. For dyes of rapid strike, the dyeing conditions must limit the initial rate of exhaustion, and therefore improve the levelness of the dyeing. The strike depends on the dyeing temperature, the dyeing pH, and the addition of chemicals. Even for dyes of moderate and low strike, the objective of uniform dyeing of the fibre mass is rarely achieved during the initial stages of the operation. This is because of irregularities in the material's construction, in the fibre packing, and in the distribution of residual impurities, as well as differences in temperature and flow rate of the solution in contact with the fibres.

The strike of a dye is evaluated by a simple test. After a few minutes of dyeing a sample of fabric, a second undyed sample is added and the two samples are then dyed together for several minutes, removed and rinsed. For dyes of high strike, the first sample is much deeper in colour than the second. Dyeing of the two samples may be continued to establish how long it takes for them to have the same final colour. Alternatively, a series of samples may be dyed in succession for a constant short period in the same bath. As each dyed sample is removed, it is replaced by an undyed one, and so on. After the test, the coloured samples are placed side by side in the order they were dyed. Rapid dyeing dyes give a short series of heavily dyed samples, the later samples being much paler. For slow dyeing dyes, the colour is less deep but the depth is much more uniform over the entire range of samples. This type of test may be carried out with a constant or variable bath temperature.

10.4.5 Migration and levelling

Unlevel dyeings can arise for a number of different reasons, some of which are beyond the control of the dyer. Types of unlevel dyeing include stripiness in either material direction or at random, end or edge differences, light and dark patches, and skitteriness (closely spaced light and dark regions). Unlevel dyeing can usually be traced to poor preparation, to other faults in the goods, or to problems in the operation of the machine or in the dyeing procedure. Specific dyeing machines give certain types of faults, such as crease marks in winch dyeing (Section 12.4.1), or non-uniform dyeing from uneven liquor flow in a package machine (Section 12.3.2). Material faults that cause unlevelness include uneven distribution of residual chemicals, variations of the fibres, and uneven treatment with chemicals or by mechanical or thermal processes. Inadequate control of the rate of dye absorption will obviously give unlevel dyeings unless the dye can subsequently migrate from deeply dyed to lightly dyed regions of the goods.

The ability of a dye to migrate and produce a level colour, under the given dyeing conditions, is obviously an important characteristic. It can overcome any initial unlevelness resulting from a rapid strike. Migration of the dye demonstrates that the dye can be desorbed from more heavily dyed fibres and re-absorbed on more lightly dyed ones. This is important in package dyeing where uniform colour of the yarn throughout the bobbin is essential. While migration is important for level dyeing, it has two major drawbacks. Firstly, the dye's ability to desorb from dyed fibres during migration usually means that the dyeings have lower fastness to washing. Dyes of very high washing fastness are essentially non-migrating dyes for which level dyeing depends upon very careful control of the rate of dye uptake by the material. The second problem with migrating dyes is that good migration may result in lower exhaustion, again because of their ability to desorb from the fibres.

Migration tests characterise a dye's levelling behaviour. Undyed fabric is treated with an identical dyed sample in a blank dyebath, with all the required dyeing chemicals but no added dye, under the same conditions as in dyeing. After a given time, the degree of transfer of colour from the original dyed to the undyed sample is evaluated. Alternatively, small samples of the originally undyed and dyed fabric may be taken at intervals during the test and their colour examined. As Figure 10.4 shows, a dye capable of migration easily transfers to the undyed fabric and after a short time both samples will have the same amount of dye and the same colour depth. There will also usually be some dye in the solution. Exactly the opposite is found for non-migrating dyes. Little dye transfers from the dyed to the undyed fabric.

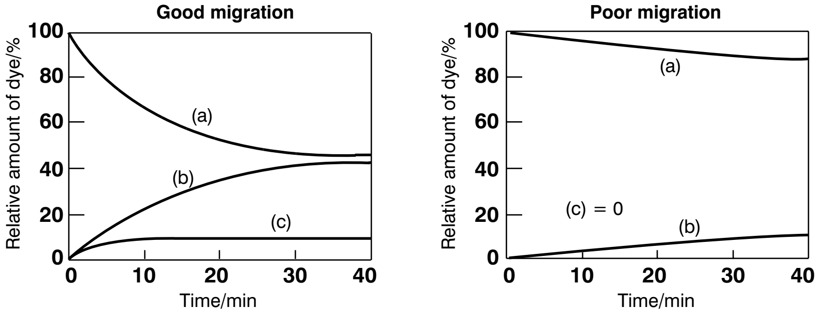


Figure 10.4 Typical quantitative results of migration tests for dyes of good and poor migration ((a), original dyed sample; (b), original undyed sample; (c), bath solution)

10.4.6 Effect of temperature on exhaustion and dyeing rate

The rate of dyeing increases with an increase in temperature but the final exhaustion may increase or decrease depending upon the particular dyeing system. Figure 10.5 illustrates that increasing the temperature increases the initial rate of dyeing. This is the usual effect of temperature on the rate of a process. In the case shown, however, the equilibrium exhaustion is lower at the higher dyeing temperature. Le Chatelier's principle predicts this effect of temperature for an exothermic dyeing process. This principle states that a system at equilibrium reacts to an applied constraint in a manner that minimises its effect. Dyeing is usually an exothermic process (heat releasing); the interaction between the dye and fibre molecules is stronger than between the dye and water molecules in solution. The dyeing equilibrium reacts to an increase in temperature by absorbing more heat energy. It therefore shifts in the endothermic direction (heat absorbing), dye desorbing from the fibres so that the final exhaustion is less at the higher temperature.

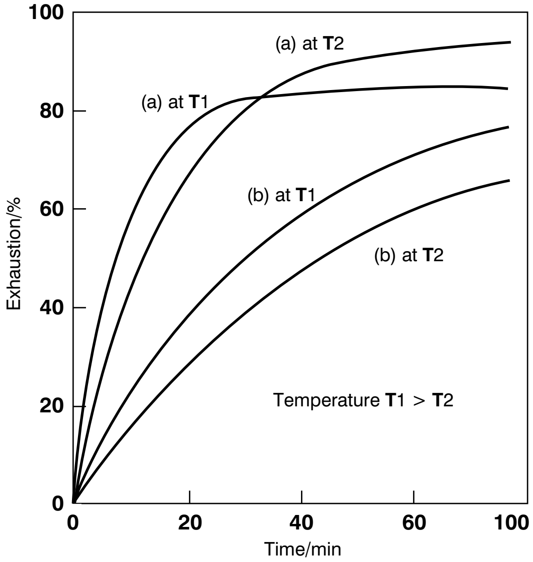


Figure 10.5 Dyebath exhaustion as a function of time for slowly (b) and rapidly (a) dyeing dyes at two temperatures, where T1 > T2

In some cases, as for some direct dyes on cotton, the final exhaustion increases as the temperature of dyeing increases. This is because of the effect of temperature on the aggregation of the dye in solution. A dilute solution of a dye does not necessarily consist of a collection of individual dye molecules surrounded by water molecules. Many dyes, in solutions at lower temperatures or at high salt concentrations, exist as micelles or aggregates containing many molecules. Their behaviour is identical to that of surfactant molecules. Only individual dye molecules, however, are able to diffuse into the fibres. A rapid equilibrium exists between single molecules and aggregates in solution. Aggregation is slightly exothermic. As the dyeing temperature increases, the aggregates gradually break up (heat absorbing) so that more individual molecules are available for penetration into the fibres. The exhaustion thus increases with increasing temperature. Eventually, if the dyeing temperature increases further, and aggregation is no longer significant, the final exhaustion will begin to decrease with increasing temperature. In the dyeing of synthetic fibres with disperse dyes, the dyebath exhaustion often apparently increases with increasing temperature at temperatures around the dyeing transition temperature. This is more of a kinetic effect related to the rate of dye diffusion, controlled by polymer chain segment mobility.

Practical dyeing rarely reaches equilibrium. A rapidly dyeing dye may soon reach equilibrium and dyeing may only require a relatively short time ((a), in Figure 10.5). For such a dye, dyeing at lower temperatures gives the best exhaustion ((a), at temperature T2), assuming that dyeing is still reasonably rapid. For a slowly dyeing dye ((b) in Figure 10.5), the best exhaustion normally occurs at higher dyeing temperatures ((b), at temperature T1) because dyeing is far from equilibrium and the exhaustion depends on the rate of dyeing and the time.

10.4.7 Dye compatibility

Exhaustion curves characterise the dyeing properties of a dye and are useful for selecting compatible dyes. One of the dyer's major objectives is to produce goods having the exact shade desired by the client. This usually requires the use of a mixture of dyes, often a mixture of red, blue and yellow. These should all be dyes with about the same rate of dyeing. They should have very similar rates of exhaustion when used in mixtures under the given dyeing conditions. During dyeing, the colour of the goods will then gradually become deeper, but, since the dyes are absorbed in the same proportions throughout the process, the hue does not change and the goods will always be on shade. The dyer can then stop the process as soon as the colour is deep enough. If the dyes do not have approximately equal dyeing rates, the hue will be constantly changing from that of the more rapidly absorbed dyes towards that of the more slowly absorbed ones that remain in the dyebath longer. The dyer then has to contend with both the gradual increase in depth of shade and the shifting hue. It will be lucky indeed if the dyeing has the correct colour depth at the moment when it has the correct hue. Mixtures of dyes that build up on shade, with no change in hue, are said to be compatible. Dye manufacturers go to considerable lengths to select combinations of compatible dyes.

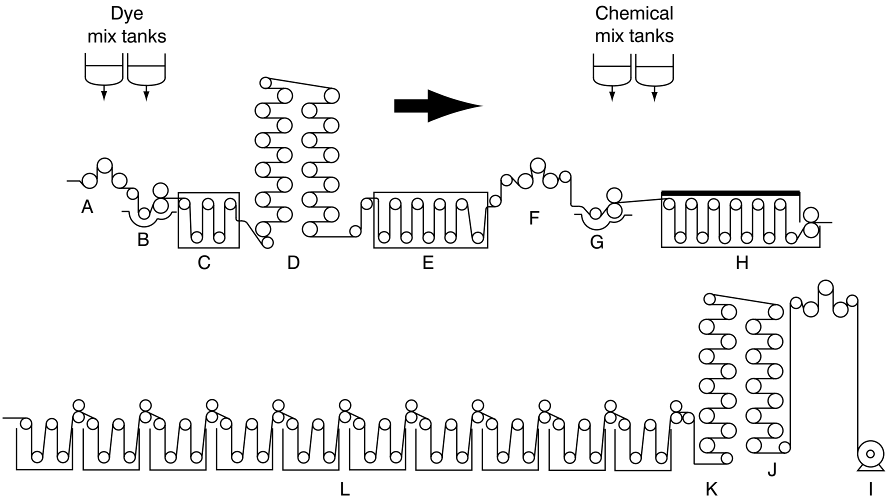
One useful way of testing for the compatibility of dyes in mixtures is to carry out a large number of dyeings, but after different dyeing times, a sample of the dyed fabric is removed from a given container and replaced with an identical piece of undyed material. Each dyeing is then continued for the same total time. The series of samples removed from the dyebath, arranged in order of the sampling time, will have decreasing colour depths. The series of replacement samples, in order of their introduction time, will have increasing colour depths. For compatible dyes, all the dyed samples will have the same hue, with colour depths in relation to the actual amount of time spent in the dyebath. Otherwise, the two series of dyeings show irregular differences in both hue and in depth.

10.5 CONTINUOUS DYEING

10.5.1 Introduction

Continuous dyeing is most economic for production of very large lots of a single colour. This presents particular problems of process control to ensure constancy of the shade over lengths of material that may exceed 50 000 m running for over 8 hours. Today, there is more demand for smaller lots in diverse colours. This often makes continuous processing uneconomical unless rapid colour change-over is possible. A typical continuous dyeing range may contain up to 400 m of fabric and the customer may only want as little as 8000 m. Rapid establishment of steady-state dyeing conditions and of shade consistency are essential when running at speeds of up to 100 m min^{-1}. Continuous dyeing of woven fabrics of cotton and polyester, and their blends, is predominant. Knitted fabrics are rarely dyed continuously because they undergo considerable elongation when under tension. Continuous dyeing of carpets is also quite popular, particularly in the USA.

A continuous dyeing range may have as many as 4–12 pieces of equipment in line (Figure 10.6). Some of these may be omitted, or passed over, for particular dyeing processes. Section 12.6 gives specifics about various types of equipment. A leader cloth will already be threaded through the various units. This is the end cloth remaining from the last lot of material that was dyed. The start of the fabric to be dyed is stitched to this leader and fed into the range from a large roller mounted on a sturdy frame. The end of this piece will be stitched to the start of the next roll and so on, without stopping production, if possible. This necessitates use of a fabric accumulator where the remainder of a roll of fabric can be quickly



Key

A	Moisture cans	H	Steamer
B	Dye pad	I	Fabric winder
C	Pre–dryer	J	Cooling cans
D	Initial dry cans	K	Dry cans
E	Thermosol oven	L	Washing units for rinsing, oxidising and soaping
F	Cooling cans		
G	Chemical pad		

Figure 10.6 A pad–thermosol–pad–steam continuous dyeing range for cotton/polyester fabrics

piled up and its end isolated. The final roll will also have an end cloth stitched onto it that will stay in the machine and introduce the next lot.

Most continuous dyeing processes can be divided into four stages:

(1) dye application by padding;
(2) dye fixation, usually in hot air or steam;
(3) washing-off of unfixed dye and auxiliary chemicals;
(4) drying, usually on steam-heated cylinders.

Besides fully continuous dyeing, there are a considerable number of semi-continuous processes in which fabric is continuously impregnated with dye solution, but the actual fixation of the dyes is a batch process.

10.5.2 Padding

Continuous application of dye solution to woven fabric is usually by padding but other procedures are also used, particularly for carpets. These include flowing or spraying dye liquor onto the moving carpet, or its application as foam.

The objective of padding is to impregnate the fabric with a solution or dispersion of dyes and chemicals as uniformly as possibly, both lengthways and side-to-side. To produce long lengths of fabric, all with the same colour, requires the maintenance of constant padding conditions over long periods of time. A pad or padder consists of a narrow trough, which is slightly wider than the fabric, and a pair of rubber-covered rollers under pressure (Figure 10.7).

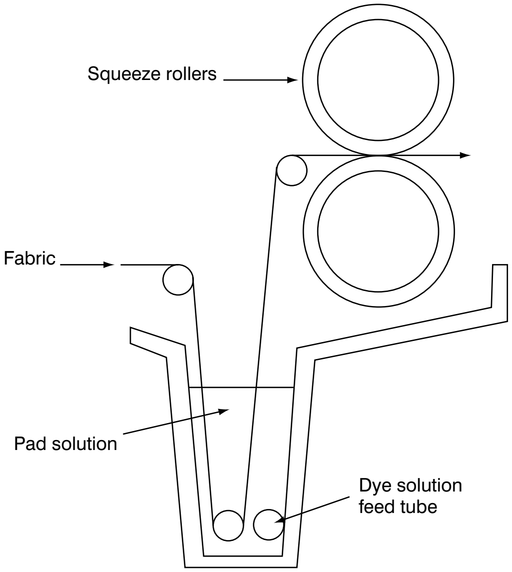


Figure 10.7 Schematic of a padder

The fabric first passes through the pad trough, where it is saturated with dye solution, and then between the rollers, where the pressure squeezes air out of the fabric and the solution into it. The nip is the zone where pressure is applied to the wet fabric. The material should be well prepared and very absorbent because the wetting time in the pad bath may be as short as 0.5 s. Dry fabrics of cotton and cotton/polyester are sometimes difficult to wet quickly and re-wetting agents are often dried into the material at the end of preparation. The fabric must, of course, be free of creases and have flat selvages. It is accurately centred on the rollers and runs under moderate tension.

The greater the applied pressure at the nip, the smaller the amount of dye solution retained by the fabric. The latter is called the wet pick-up, the weight of dye solution retained per 100 g of dry fabric. It should be high enough that there is sufficient solution to adequately wet the fibres and yarns and allow the dye to uniformly reach the fibre surfaces, but not so high that there is excessive migration on drying (Section 10.5.3). The wet pick-up cannot be decreased below a certain limit, no matter how high the nip pressure because it is not possible to squeeze out the water absorbed by the fibres and that adhering to the fibre surfaces. When the nip pressure decreases, after passage of the fabric, some of the expressed water is always re-absorbed. The minimum wet pick-up is usually around 55–60% for cotton/polyester materials, 60–70% for cotton, and higher for fabrics of the more absorbent viscose.

Under ideal conditions, the dyes will have no substantivity for the fibres being treated and the amount of dye in the fabric can be calculated from the liquor concentration and the wet pick-up. A 70.0% wet pick-up of a dye solution containing 1.80% of dye is 70 × 1.80/100 = 1.26 % dye owf.

$$\text{Amount of dye}\left(\frac{\text{g dye}}{100\,\text{g fibre}}\right) = \text{Wet pick-up}\left(\frac{\text{g soln}}{100\,\text{g fibre}}\right) \times \text{Dye concn}\left(\frac{\text{g dye}}{\text{g soln}}\right) \qquad (6)$$

Some dyes do exhibit substantivity for the fibres even in the very short time between wetting and the nip. Then, as the fabric runs through the trough and up to the nip, the fibres show preferential absorption of the dye rather than water. The material leaving the nip contains more dye than predicted from the wet pick-up and solution concentration. The liquor that is squeezed out at the nip and returns to the trough contains a higher proportion of water because of the preferential dye absorption. This causes the dye solution in the trough to gradually become more dilute. The consequence of these effects is that, if the fabric is being dyed with a single dye, it is initially dyed in too deep a shade, but, as the solution gradually becomes more dilute, the shade becomes paler and eventually no longer varies once a steady-state has been attained. This gradual loss of colour depth during the early part of a continuous padding operation is called tailing.

In dyeing with mixtures of dyes of different colours, which possess different substantivities for the fibre, some dyes may be absorbed more strongly than others and tailing then also results in unacceptable variations in hue. It can be minimised by padding under conditions of low substantivity. This involves using a trough of low volume, and running under conditions that cause more rapid replacement of the dye liquor, a higher fabric speed and a greater wet pick-up. For continuous dyeing, manufacturers often provide substantivity factors for appropriate dyes. These allow calculation of the dye initially retained by the material, the steady-state condition, and allow prediction of the degree of initial tailing. The pad bath can then be diluted to the predicted steady-state concentration before dyeing commences to avoid, or at least minimise, tailing.

Control of the shade over great lengths of material is a constant preoccupation of continuous dyers. It depends upon a number of factors. A major one is uniformity of the fabric absorbency, which depends upon its uniform preparation. Once initial tailing has been eliminated, the shade along the fabric should not vary provided that the pad roller pressure gives a constant wet pick-up, the dye solution fed to the pad trough always has the same concentration, and the conditions of fixation remain steady. Apart from lengthways variations in shade, side-to-side variations can also be a problem if the pressure across the nip is not uniform. A number of devices are used to ensure uniform nip pressure (Section 12.6.1). Other problems that the dyer must avoid are marks on the padded fabric from undissolved dye particles or undispersed pigment, or those arising from foam picked up from the surface of the dye liquor in the pad, which is squeezed onto the fabric surface.

10.5.3 Fixation procedures

Fixation procedures may be fully continuous or simple batch operations. Fully continuous fixation usually involves heating the material in saturated steam, in hot air, or by contact with heated metal cylinders. Sometimes, when using two different types of dyes, a second fixation step is preceded by application of additional chemicals in a second pad unit. In semi-continuous dyeing processes, fixation is usually a batch process. This can be as simple as storing a covered roll of impregnated fabric overnight, or fixation with an appropriate solution of chemicals in a conventional batch dyeing machine.

Before entering any unit in which the padded fabric will be heated, it must be completely dry. During drying, water evaporates from the surfaces of the yarns and fibres and more migrates from the capillaries in the interior to replace water lost by vaporisation. This migrating water will carry with it any unfixed dyes and chemicals in solution or fine dispersion. The extent of migration of unfixed chemicals depends on the yarn and fabric construction and is smaller the higher the absorbency of the fibres present, the lower the initial wet pick-up, the lower the rate of drying, the larger the particle size of pigments, and the higher the viscosity of the applied solution. It usually results in heavily dyed yarn surfaces, with a deeper perceived shade, and sometimes reduced fastness to washing and rubbing.

If the dye in the padded fabric is going to be fixed using heat, the fabric must first be pre-dried with a minimum of migration, reducing the water content to a value corresponding to the absence of significant amounts of water on the fibre surfaces or in the fibre capillaries. For 50/50 cotton/polyester fabric, migration is usually negligible at wet pick-up values below 20–25%, so the objective of pre-drying is to initially dry the fabric to this level with a minimum of migration. For fabrics of synthetic fibres that do not absorb water, the critical moisture content below which migration is negligible is often much lower, around 15% water for 100% polyester fabrics. The padded fabric usually passes between gas fired infrared heaters uniformly situated along each face of the fabric. The heating should be as uniform as possible and the rate of drying not too high. The padding liquor may contain migration inhibitors. These are usually polymeric materials that increase the solution viscosity, or which cause flocculation of pigment particles to mechanically hinder their movement. Once the wet pick-up has been reduced below the critical value, the fabric is fully dried using steam-heated cylinders.

A Thermosol unit is used to rapidly heat polyester fabric to temperatures up to 200–220 °C for 30–60 s to promote fixation of disperse dyes padded onto the polyester material (Section 12.6.2). It also serves for the fixation of reactive dyes on cotton. This type of unit is now widely used for cotton/polyester fabrics (Figure 10.6).

Various types of steamers allow the continuous fixation of direct, reactive, vat and sulphur dyes applied to cotton (Section 12.6.3). Fixation is achieved by heating the padded fabric in saturated steam for 20–60 s. For dyes sensitive to air-oxidation, such as reduced vat dyes, the steam must be air-free.

For the continuous dyeing of the important cotton/polyester fabrics, the different dyes required for coloration of the two different fibres necessitate heat fixation of the disperse dye in the polyester, in the Thermosol unit, and fixation of the cotton dyes in the steamer (Figure 10.6). The most impressive continuous dyeing ranges are therefore those for cotton/polyester dyeing. They include a dye pad, with all the dyes added, pre-dryer, dryer, a Thermosol unit for fixation of the disperse dye in the polyester, cooling cylinders, a second pad containing chemicals for fixation of the cotton dyes, a steamer to promote this, several sections of washing boxes and final drying cylinders.

The degree of dye fixation is never 100% and any unfixed dye must be removed from the fabric by rinsing and washing, otherwise the optimum fastness properties will not be attained. Washing may be carried out in a conventional dyeing machine or continuously. Continuous washers for removal of surface and unfixed dyes usually consist of several sections of coupled washing boxes with countercurrent flow of the washing solution. The box is either filled with water and the fabric passes up and down between rollers, or water is sprayed onto the fabric that passes horizontally between rollers. The dyed and washed fabric is finally dried on heated cylinders (hot cans). Section 12.6 has more information on continuous dyeing equipment.

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CHAPTER 11

Dyeing theory

Dyeing theory covers a wide range of subjects mainly in the area of physical chemistry. As for all theory, the aim is to provide a set of hypotheses that explain the behaviour of known dyeing systems, and which are capable of predicting what will happen in a new situation. Dyeing theory has many qualitative aspects that are useful in explaining practical dyeing, but the physico-chemical measurements on dyeing processes that provide quantitative data are often far removed from actual dyeing practice. Some of the subjects included in dyeing theory are:

(1) the state of dyes in solution and in the fibre during and after dyeing;
(2) the rates of dyeing processes and how these are influenced by mass-transfer of dye from the bath solution to the dye–fibre interface, and by diffusion of the dye from the interface into the fibre;
(3) the phenomena occurring at the dye–fibre interface such as dye molecule adsorption and the effects of surface potentials;
(4) the nature of the interactions between dye and fibre molecules, which are the origin of substantivity;
(5) the treatment of dyeing as a thermodynamic equilibrium and its description in terms of thermodynamic variables;
(6) the theory of fibre structure and how this influences dyeing rates and equilibria.

Many of these subjects are discussed briefly, and qualitatively, in other chapters of this book. This present chapter will introduce some of the more quantitative aspects of dyeing equilibria and kinetics.

11.1 DYEING EQUILIBRIA

In the study of dyeing equilibria, the fibre and dye solution are heated at constant temperature until a state of equilibrium is reached. After the initial increase in the degree of exhaustion, it eventually becomes constant, but a true equilibrium implies that the dye is also uniformly distributed throughout the fibres. On heating for the extended period required to reach a true equilibrium, there is always a risk of some decomposition of the fibre, or of the dye.

It is common practice to determine the amount of dye in the fibre from the initial quantity added to the bath, less that remaining in solution at equilibrium. The latter is readily obtained by spectrophotometric analysis of the dye solution (Chapter 24). A mass balance, however, is a necessary prerequisite to ensure that there are no losses of dye from decomposition. This involves completely extracting the dye from the fibre, or dissolving the dyed fibres and determining the dye in the polymer solution. Again, the dye should not decompose during these processes.

11.1.1 Adsorption isotherms

An adsorption isotherm gives the concentration of a substance adsorbed on a solid surface in relation to its concentration in the surrounding fluid when the system is at equilibrium at a constant temperature. The graph representing a dyeing adsorption isotherm has the adsorbed dye concentration (C_f in g kg^{-1} or mol kg^{-1}) plotted against the solution concentration (C_s in g l^{-1} or mol l^{-1}). Adsorption isotherms are useful for the information they provide on the dyeing mechanism. There are three main types of dyeing adsorption isotherm, usually referred to as the Nernst, Langmuir and Freundlich isotherms. Most dyeing systems involving only adsorption are completely reversible. Equilibrium isotherms, established by adsorption of dye from solution onto initially undyed fibres, are identical to those obtained by desorption of dye from dyed fibres into an initially blank dyebath.

The Nernst isotherm is the simplest and is given by the equation:

$$C_f = kC_s \tag{1}$$

where *k* a constant. This is also the equation describing the distribution or partition of a solute between two immiscible solvents. The graph of C_f against C_s is linear up to the point corresponding to the dye saturating the fibre and the water. The dyeing of many synthetic fibres with disperse dyes follows this type of isotherm (Figure 11.1). The fibre, in which the dye is soluble, extracts the disperse dye from the aqueous bath, in which it is only slightly soluble.

The Langmuir isotherm applies to adsorption on specific sites in the solid, of which there are often only a limited number. Such a situation exists in the dyeing of nylon with simple acid dyes by an ion exchange mechanism. The counter ion associated with an alkylammonium ion group in the nylon, under weakly acidic conditions, is exchanged for a dye anion (Scheme 4.4). The Langmuir adsorption

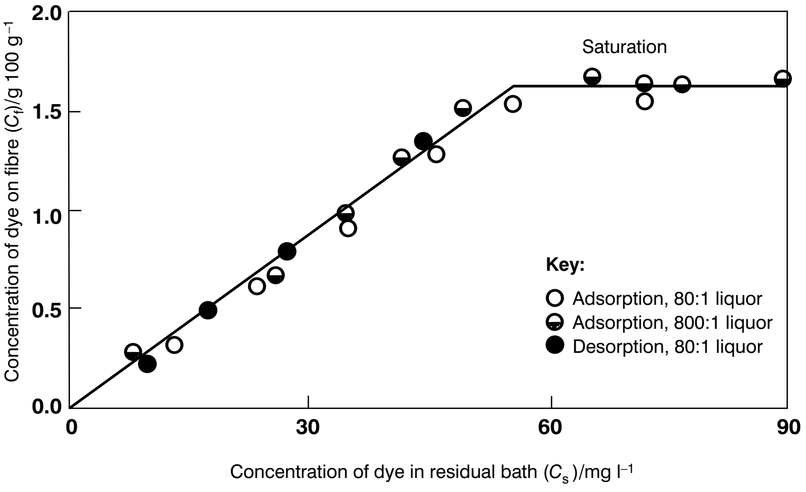


Figure 11.1 Example of a Nernst isotherm: adsorption and desorption of CI Disperse Red 19 on cellulose diacetate at 80 °C [1]

isotherm is easily derived. The rate of desorption depends only on the fraction of occupied sites (C_f/C_{max}). The rate of adsorption of dye onto the fibre from solution, however, depends upon the fraction of unoccupied sites ($1 - C_f/C_{max}$) and the concentration of dye in the solution (C_s). At equilibrium, the two opposing rates are equal and:

$$k_1\left(1-\frac{C_f}{C_{max}}\right)C_s = k_{-1}\frac{C_f}{C_{max}} \qquad (2)$$

where k_1 and k_{-1} are the rate constants for adsorption and desorption, and C_{max} is the maximum number of adsorption sites that dye molecules can occupy in the fibre. This leads to:

$$\frac{C_f}{C_{max}} = \frac{KC_s}{1+KC_s} \qquad (3)$$

where K is the value of k_1/k_{-1}. The graph of C_f versus C_s for the Langmuir isotherm ((a), in Figure 11.2) clearly shows that the fibre becomes saturated with dye when all the available adsorption sites are filled. The maximum number of sites in the fibre can be determined from the slope of the linear graph of C_s/C_f versus C_s, according to the equation:

$$\frac{C_s}{C_f} = \frac{C_s}{C_{max}} + \frac{1}{KC_{max}} \tag{4}$$

Figure 11.2 shows both forms of the Langmuir isotherm for adsorption of HCl by wool fibres. In the graph of C_s/C_f against C_s (b), the value of the slope is $1/C_{max}$. The value of C_{max} is 0.870 mol kg^{-1} – slightly higher than the presently accepted value of 0.820 mol kg^{-1}. This is a useful method of determining the number of ionic sites for dye adsorption in a fibre such as a polyamide or polyacrylonitrile, for which equilibrium dyeing often follows the Langmuir isotherm.

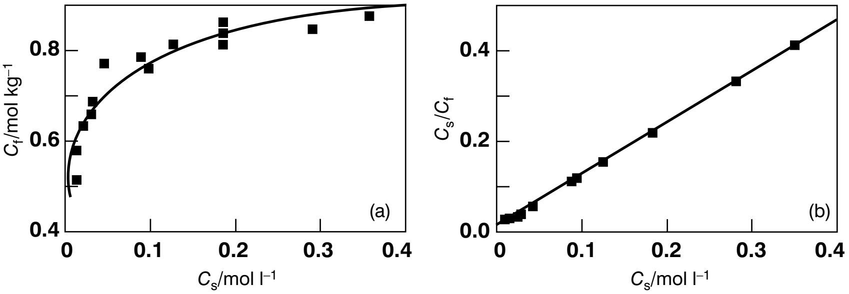


Figure 11.2 Graphs for a Langmuir isotherm: adsorption of HCl by wool [2]

The Nernst isotherm, given above, is a special case of the Langmuir isotherm for the condition where KC_s is very small compared to unity. Note that, for this condition, the initial portion of the plot of the Langmuir isotherm is linear as required for the Nernst isotherm.

The Freundlich isotherm applies to the situation where dye adsorption onto the fibre is not limited by a number of specific adsorption sites and the fibre does not become saturated with dye. The empirical equation describing this isotherm is:

$$C_f = kC_s^{\alpha} \quad \text{or} \quad \log(C_f) = \log(k) + \alpha \log(C_s) \tag{5}$$

where k is a constant, and the exponent α often has a value around 0.5 for the adsorption of anionic dyes on cellulosic fibres (Figure 11.3). The amount of dye adsorbed by the cotton fibres depends upon the available pore surface area. Initially, the dye molecules adsorb on the surfaces of the most accessible pores, but increasingly the dye must penetrate into the less accessible areas, so adsorption becomes more difficult. The dye molecules may even adsorb onto a layer of dye molecules already adsorbed on the pore surfaces. The equation for the Freundlich isotherm cannot be derived, as was the equation for the Langmuir isotherm.

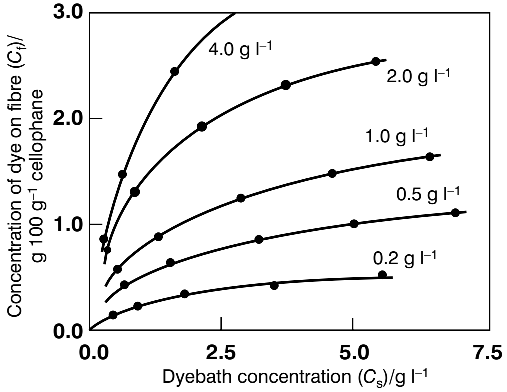


Figure 11.3 Graphs of the Freundlich isotherm: adsorption of Chrysophenine G on Cellophane sheet at 40 °C at varying salt concentrations (Source: [1])

11.1.2 Standard affinity of a dye

Chemical equilibria are usually discussed in terms of the change in the standard Gibbs free energy for the transformation that comes to equilibrium. The Gibbs free energy is, however, an extensive quantity depending upon the amounts of substance, and therefore varies with change in the composition. In treating dyeing equilibria, the alternative chemical potential is used. The chemical potential is defined as the change in free energy of a system that occurs when the composition changes by a unit molar amount of substance, all other variables such as the temperature, pressure and the amounts of other components remaining constant. It is a property akin to temperature or voltage. These determine the direction and rate of heat transfer, or the direction and size of charge transfer (current), respectively.

A transformation, at constant temperature and pressure, occurs so that the substance transfers from the state of higher to lower chemical potential until equilibrium is attained. In the case of dyeing, if the chemical potential of the dye in solution is higher than in the fibre, the dye will transfer to the fibre. The chemical potential in the solution falls; that in the fibre increases. At equilibrium, the chemical potential of the dye in the fibre is equal to the chemical potential of the dye in the solution. These are given by:

$$\mu_s = \mu_s^0 + RT\ \ln(a_s) \text{ and } \mu_s = \mu_f^0 + RT\ \ln(a_f) \qquad (6)$$

In these equations, μ_s and μ_f are the chemical potentials of the dye in the solution and in the fibre, respectively, and a_s and a_f are the respective activities or effective concentrations. $\mu_s{}^0$ and $\mu_f{}^0$ are the standard chemical potentials for the dye in its standard state in the solution and in the fibre. The standard states are those for which the dye activity in either phase is unity. *R* is the universal gas constant and *T* the absolute temperature. At equilibrium, $\mu_s = \mu_f$, so that:

$$\mu_f - \mu_s = 0 = \mu_f^0 - \mu_s^0 + RT\ \ln\left(\frac{a_f}{a_s}\right) \qquad (7)$$

The standard affinity of a dye for a fibre ($-\Delta\mu^0$) is defined as the difference of the standard chemical potentials of the dye in the two phases as follows:

$$-\Delta\mu^0 = -(\mu_f^0 - \mu_s^0) = RT\ \ln\left(\frac{a_f}{a_s}\right) = RT\ \ln(K) \qquad (8)$$

where *K* is the equilibrium constant for dyeing.

The standard affinity is a measure of the tendency of the dye to move from its standard state in solution to its standard state in the fibre, both at unit activity. For dyeing to have a large equilibrium constant, the standard chemical potential in the solution is larger than that in the fibre and the standard affinity $-\Delta\mu^0$ is positive when $K > 1$.

The problem in determining affinities in dyeing is to find suitable expressions for the activities, or effective concentrations, of the dye in the fibre (a_f) and in solution (a_s). This is difficult and usually molar concentrations must be substituted. For example, in dyeing a synthetic fibre with a pure non-ionic disperse dye, at equilibrium:

$$-\Delta\mu^0 = RT\ \ln\left(\frac{C_f}{C_s}\right) \tag{9}$$

The equilibrium constant for dyeing with a dye of given affinity is given by $K = C_f/C_s$ and depends only on the temperature. This is exactly the situation described by the Nernst isotherm from which the affinity can be calculated directly with the assumption that the term C_f/C_s is a correct approximation for the activity quotient a_f/a_s. The isotherm at 100 °C in Figure 11.4 gives the values for the saturation of the polyester fibre and the water as 34.8 g kg^{-1} and 0.0399 g l^{-1}, respectively. The ratio of these gives the slope of the line as 873 l kg^{-1}. This is the constant value of C_f/C_s that is equal to K, from which the affinity can be calculated.

$$-\Delta\mu^0 = 8.314(\text{J mol}^{-1}\ K) \times 373(K) \times \ln(873) = 21.0\ \text{kJ mol}^{-1} \tag{10}$$

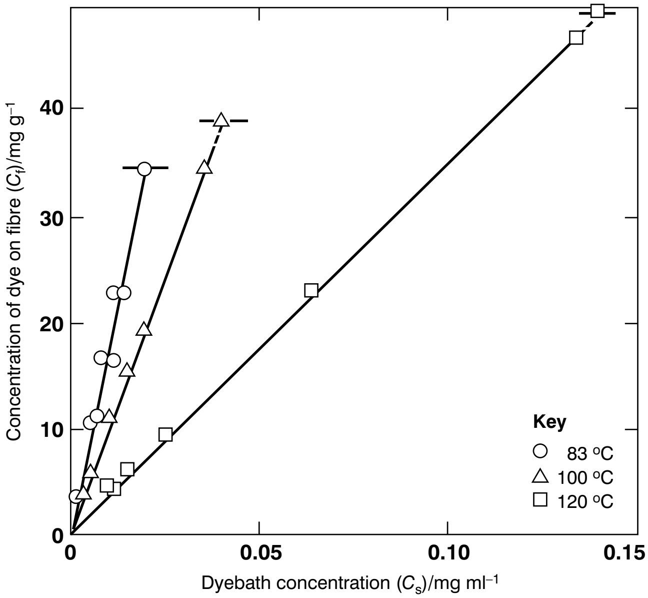


Figure 11.4 Adsorption isotherms for dyeing polyester with CI Disperse Red 15 (Source: [1])

This value for the standard affinity indicates a favourable equilibrium for dyeing. At equilibrium at 100 °C, the dye is almost 900 times more soluble in the polyester than it is in water.

For ionic dyes, the affinity equation is more complex and involves the activities of the individual ions and possibly a term for the fibre internal volume. For example, the sodium salt of a trisulphonated dye in solution has an activity approximated by:

$$a_s = [\mathrm{Dye}^{3-}]\,[\mathrm{Na}^+]^3 \tag{11}$$

This is derived from:

$$\mathrm{Dye(SO_3Na)_3(s) + H_2O(l) \rightleftharpoons Dye(SO_3^-)_3(aq) + 3Na^+(aq)} \tag{12}$$

The affinity equation for the adsorption by cotton of a polyvalent direct dye anion with a charge of $-z$ per molecule is:

$$\frac{-\Delta\mu^0}{RT} = \ln\left(\frac{C_f}{C_s}\right) + z\ln\left(\frac{Na_f}{Na_s}\right) - (z+1)\ln(V) \tag{13}$$

where the symbols C and *Na* represent concentrations, rather than activities. *V* is the internal volume of the cotton, usually given a value of 0.22 $\mathrm{l\,kg^{-1}}$. One can see that the calculation of the dye's affinity becomes quite involved.

The equation for the standard affinity shows that the dyeing equilibrium constant decreases with increasing temperature if $-\Delta\mu^0$ is positive. More dye adsorbs at lower temperature, although reaching equilibrium at lower temperatures takes longer. The standard affinity is the change in the chemical potential of the dye when one mole is transferred from the standard state in solution to the standard state in the fibre. It is therefore the standard molar free energy change for dyeing.

$$-\Delta\mu^0 = -\Delta G^0 = -\Delta H^0 + T\Delta S^0 = RT\ln(K) \tag{14}$$

The enthalpy of dyeing ΔH^0 can be derived from the temperature dependence of the standard affinity using the above free energy equation. A graph of $\ln(K)$ versus $1/T$ will be linear with a slope of $-\Delta H^0/R$. The data in Table 11.1 are derived from

Figure 11.4. The graph of ln(*K*) as a function of $1/T$ ((a), in Figure 11.5) has a slope $-\Delta H^0/R$ of 7393 K so that the enthalpy of dyeing ΔH^0 is −61.5 kJ mol^{-1}. As is usual, the enthalpy of dyeing is negative since dyeing is exothermic. This means

Table 11.1 Data derived from Figure 11.4 for dyeing of polyester with CI Disperse Red 15

Temperature (°C)	Solubilities			$-\Delta\mu^0$ (kJ mol^{-1})
	C_s (g l^{-1})	C_f (g kg^{-1})	$K = C_f/C_s$	
89.3	0.0207	30.89	1492.0	22.02
100.0	0.0402	34.81	865.2	20.98
120.0	0.1449	44.27	305.3	18.71

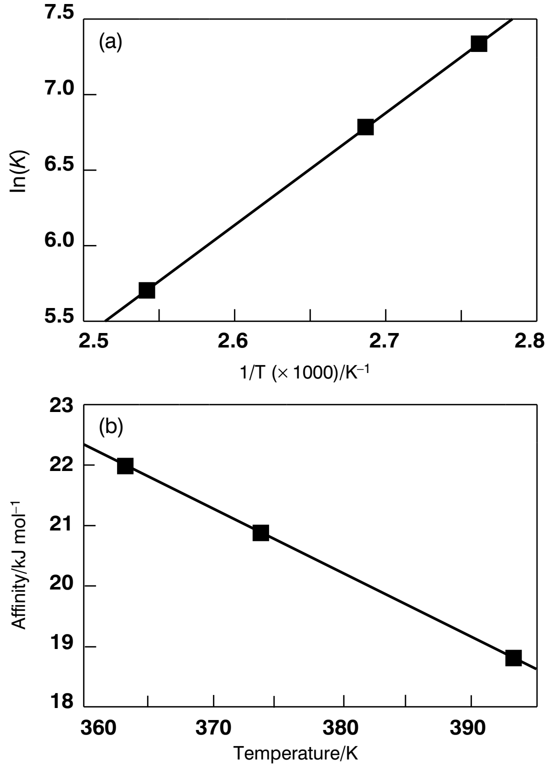


Figure 11.5 Graphs of ln(*K*) versus $1/T$ (T in Kelvin) (a), and of standard affinity versus T (b), for the determination of the enthalpy and entropy of dyeing

that the dye bonds to the fibre more strongly than it bonds to water in the external aqueous solution. The enthalpy of dyeing in this case corresponds to the enthalpy change for transfer of the dye from the aqueous solution into the fibre. It does not include the enthalpy change associated with dissolution of the dye solid in the water.

The standard enthalpy of dyeing can be measured quite rapidly from the concentrations of dye solutions in equilibrium with the same amount of dye in the fibre at different temperatures. A given mass of dyed material is equilibrated with a blank dyebath solution at a given temperature. The dilute solution of dye obtained by desorption is then re-equilibrated with a second identical sample of the original dyed material, so that almost no more dye is desorbed. The amount of dye in solution is then determined by spectrophotometry. Thus, the dye in solution at equilibrium at several temperatures is obtained for the same amount of dye on the fibre. The graph of the various values of $\ln(C_s)$ versus $1/T$ has a slope of $-\Delta H^0/R$, the value of $\ln(C_f)$ being constant for the series of samples.

$$\ln(K) = \ln(C_s) - \ln(C_f) = \frac{-\Delta H^0}{R} + T\Delta S^0 \qquad (15)$$

The standard entropy of dyeing (ΔS^0) can be calculated from the value of the standard affinity and the enthalpy of dyeing using the free energy equation. For the case examined above:

$$-\Delta\mu^0 = -\Delta G^0 = -\Delta H^0 + T\Delta S^0 = RT\ln(K) \qquad (16)$$

Alternatively, the graph of $-\Delta\mu^0$ versus T has a slope of ΔS^0, which gives the same value ((b), in Figure 11.5).

$$-\Delta\mu^0 = -\Delta G^0 = -\Delta H^0 + T\Delta S^0 \qquad (17)$$

The value of ΔS^0 provides a measure of the change of molecular freedom arising as a consequence of dye absorption. It seems reasonable that the immobilisation of the dye in the fibre, relative to its freedom of movement in the aqueous solution, would give a substantial decrease in entropy in agreement with the negative value of –108 J mol^{-1} K^{-1} for ΔS^0 in the above example.

In some cases, the entropy of dyeing is positive. This indicates an increase in molecular freedom as a consequence of the dyeing process. This probably involves an increase in freedom of water molecules that were initially in a highly structured, hydrogen-bonded cage surrounding the hydrophobic dye molecules in the solution. This cage collapses when the dye molecules transfer into the fibre, releasing water molecules. This is the same effect that causes the entropy of micelle formation to be positive (Section 9.2.2). Thus, the freedom gained by the liberated water molecules more than offsets that lost by the adsorbed dye.

The preceding analysis assumes that the standard affinity, as well as the enthalpy and entropy of dyeing, are independent of the temperature. Over a small temperature range this is a reasonable assumption but temperature variations must be considered in more precise studies.

The activity of the dye in the fibre cannot be determined and there is no choice but substitution of the molar concentration. For different types of dyes, different standard states are usually involved so that affinities of a dye for different types of fibres often cannot be compared directly. Although this thermodynamic approach is academically satisfying, it is based on some questionable assumptions. These, and the fact that it often bears little relation to practical dyeing, have limited studies in this field.

11.2 DYEING KINETICS

The rate of dyeing is of greater practical importance than dyeing equilibrium because few commercial dyeing processes reach equilibrium. The time required is simply too long. Unfortunately, dyeing rates are quite sensitive to changes in a number of variables. These include the degree of agitation of the bath, the liquor ratio, the type and construction of the material, the dyebath temperature and pH, the concentration of dyeing assistants, as well as the dye substantivity. This is one of the reasons why the fundamental study of dyeing kinetics has developed to an even lesser extent than has the study of dyeing equilibria.

Practical dyeing rates depend upon the way dyebath exhaustion changes as a function of time under the particular dyeing conditions. This may be determined at a constant temperature although, for most practical purposes, the temperature may vary during the test. The result characterises the dyeing properties of the dye and is useful for selecting compatible dyes that exhaust at about the same rate under the same conditions. Typical exhaustion curves show the initial rate of dyeing, the gradual decrease in dyeing rate as the bath becomes exhausted, and the equilibrium position (Figure 10.2). Exhaustion curves at different temperatures show how the dyeing rate increases with increasing temperature, and, in the usual case of exothermic dyeing, the suppression of the equilibrium exhaustion at higher temperatures (Figure 10.5).

The information in an exhaustion curve is often summarised in terms of the time of half dyeing and the equilibrium exhaustion. The time of half dyeing is the time required for the exhaustion to reach 50% of its equilibrium value. The rate of isothermal dyeing constantly decreases over time, becoming zero at equilibrium, and the half dyeing time gives a convenient measure of the dyeing rate. Thus, a dye with a short half dyeing time absorbs more rapidly than one with a long half dyeing time. This approach, however, has several limitations. A major criticism is that two dyes with different final exhaustions can have the same time of half dyeing, but do not necessarily have the same dyeing rate (Figure 11.6). Therefore, compatible dyes do not necessarily have the same half dyeing times. In addition, for pale shades, a dye often initially exhausts more rapidly and gives higher final exhaustion than when dyeing a deeper shade. The time of half dyeing therefore depends on the actual amount of dye being used.

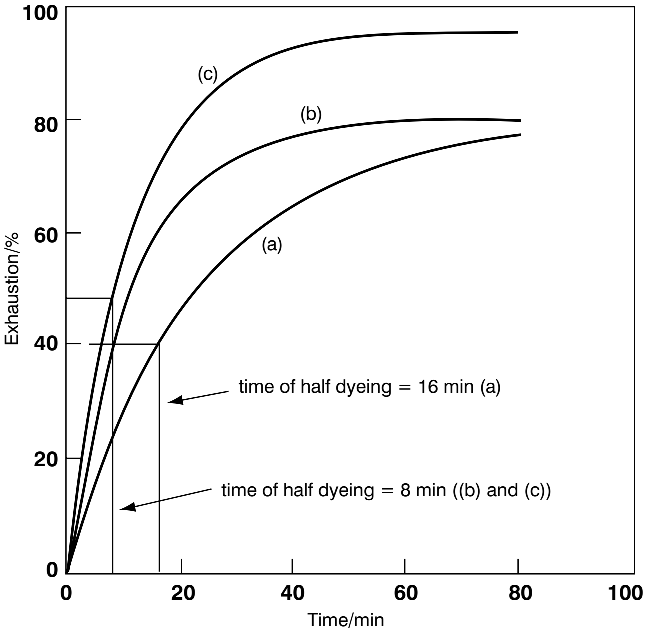


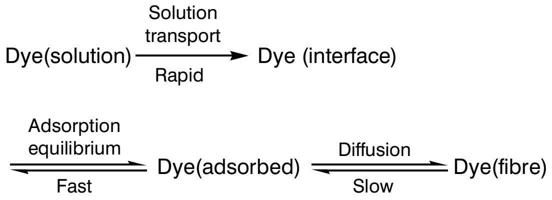
Figure 11.6 Graphs of exhaustion versus time to show variations in the time of half dyeing

Exhaustion isotherms can be described by different empirical equations. One or other of the following two equations sometimes gives a reasonable description of the dyebath exhaustion during the dyeing process.

$$\frac{E_t}{E_\infty} = 1 - e^{-kt} \quad \text{or} \quad \frac{1}{E_\infty - E_t} - \frac{1}{E_\infty} = kt \tag{18}$$

The symbol E_t represents the exhaustion at time t, and E_∞ represents the value at equilibrium (infinite time). The symbol k is the kinetic or rate constant. These two equations, however, describe quite different dyeing behaviour.

The transfer of a dye molecule from the dye solution into a fibre is usually considered to involve the initial mass-transfer from the bulk solution to the fibre surface, adsorption of the dye on the surface, followed by diffusion of the dye into the fibre. It is usually assumed that diffusion of the dye within the fibre is rate-controlling. Diffusion in a polymer is much more difficult than in solution because of dye–fibre interactions and mechanical obstruction by the fibre molecules in the pores. For example, the rate of diffusion of direct dyes in cotton is 10 000 times slower than in water. The concentration of adsorbed dye at the fibre surface therefore quickly reaches a steady-state equilibrium value. Any net transfer of dye from the solution to the interface then only occurs as the dye diffuses into the fibre (Scheme 11.1).



Scheme 11.1

Fick's equations describe the diffusion of a dye within a fibre. Fick's second law states that the rate at which the dye diffuses across a unit area in the fibre (dQ/dt in mol m^{-2} s^{-1}) is proportional to the concentration gradient across that area (dC/dx in mol m^{-3} m^{-1}), the proportionality constant being the diffusion coefficient D (m^2 s^{-1}).

$$\frac{dQ}{dt} = -D\frac{dC}{dx} \tag{19}$$

The negative sign gives a positive value of the diffusion coefficient because the concentration gradient is negative; the concentration decreases along the x axis, in the direction of diffusion. Considerable effort has been devoted to measuring diffusion coefficients and their correlation with dyeing kinetics. Diffusion coefficients are larger for dyes with lower molecular weights and for more porous, less compact fibre structures.

More complex forms of the diffusion equation apply for three-dimensional diffusion. Solutions to dyeing diffusion equations are mathematically complex and experimental studies are difficult. These differential equations, applied to real dyeing situations with fibres or films, usually require appropriate assumptions leading to an approximate solution. One simplification is to assume that the external dyebath has a constant concentration. This gives what is known as steady-state diffusion. Another simplification is based on conditions early in the dyeing when the centre of the fibre does not contain any dye. It can then be assumed that the dye is diffusing into an infinitely thick block of fibre. The amount of dye in the fibre at any time is then directly related to the square root of dyeing time:

$$\frac{C_t}{C_\infty} = 2\sqrt{\frac{D_f t}{\pi}} \tag{20}$$

A diffusion coefficient calculated from the slope of a graph of C_t/C_∞ against $\sqrt{t}$ gives an average apparent value that will differ from that obtained from a steady-state experiment at a constant concentration of dye in the material. One of the major problems in this field is that the diffusion coefficient of the dye in the fibre depends upon the amount of dye already present.

If the rate of dye adsorption at the water–fibre interface is rapid, the concentration of the dye in the solution, in immediate contact with the fibre, will be lower than in the bulk of the solution. The dye solution must first be transported to the fibre. The dye will then diffuse through the boundary layer, driven by the movement of the solution and the concentration gradient. It adsorbs onto the fibre surface and finally diffuses into the fibre. Figure 11.7 shows the relative concentrations of the dye in these stages once the adsorption equilibrium has been established. For a true equilibrium, the rate of diffusion of dye molecules through the liquid boundary layer equals the rate of diffusion from the interface into the fibre. If the rate of diffusion of the dye into the fibre is low, this will control the overall rate of dyeing and the boundary layer concentration gradient may be negligible. If, however, diffusion of dye in the fibre is faster, the rate of solution transport to the fibre surface may not be fast enough to maintain dye adsorption at equilibrium. In this case, dyeing will be faster the greater the degree of agitation of the solution as this increases the rate of transfer of dye across the boundary layer at the solution–fibre interface.

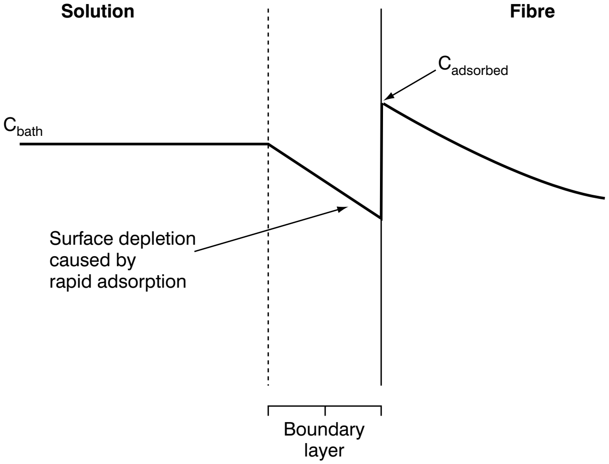


Figure 11.7 Dye concentration variations across the solution/fibre interface

In practice, increasing the relative rate of movement of solution and fabric, by increased circulation or agitation, will sometimes increase the dyeing rate (Figure 11.8). The effect is usually more pronounced for dilute dyebaths and at higher temperatures. At lower temperatures, the rate of diffusion into the fibre is lower and the effect of the initial mass-transfer is less apparent because the solution at the fibre–liquid interface is not depleted of dye. At low dye concentrations, the rate of supply of dye to the fibre surface becomes rate-controlling.

The practical significance of all this is that reproducible dyeing requires that the rates of mass-transfer are also reproducible. This means that a dyeing machine only gives reproducible dyeings when the relative rate of contact of fibre and solution is constant. High speed circulation of dye liquor under pressure through a wound package of yarn in a large dyeing machine does not give the same mass-

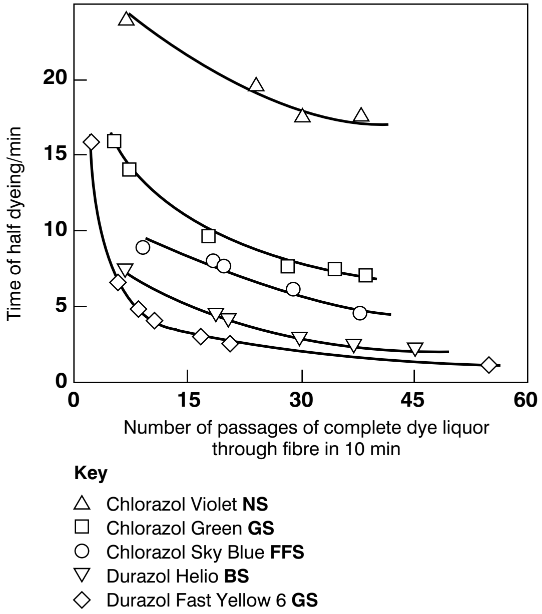


Figure 11.8 Influence of agitation on the rate of dyeing of direct dyes on cotton at 60 °[3]

transfer conditions as stirring a small sample in a laboratory dyeing pot. For this reason, dyeing recipes prepared on the basis of laboratory dyeings do not always give the same shade when the recipe is used in a large dyeing machine.

One of the classic examples of the determining role of dye diffusion in the fibre is that of the relationship between diffusion coefficients and times of half dyeing. Boulton studied the dyeing of viscose with direct dyes under conditions where each dye gave only 50% equilibrium exhaustion. This was achieved by adding the appropriate amount of salt to the dyebath for each dye. Figure 11.9 gives the values of the time of half dyeing plotted against Neale's values of the diffusion coefficients of direct dyes in cellulose films, using logarithmic scales. The data for Figure 11.9 are from reference [1]. It demonstrates that the time of half dyeing is a reasonable measure of the dye diffusion rate. For the series of direct dyes studied, the diffusion coefficients vary by a factor of about 300, and the times of half dyeing by a factor of over 2000. Practical dyeing rates of direct dyes on cellulosic fibres vary much less than Boulton's half dyeing times.

Rates of dyeing depend upon the dyeing temperature, the rate increasing with increase in temperature while the equilibrium exhaustion usually decreases.

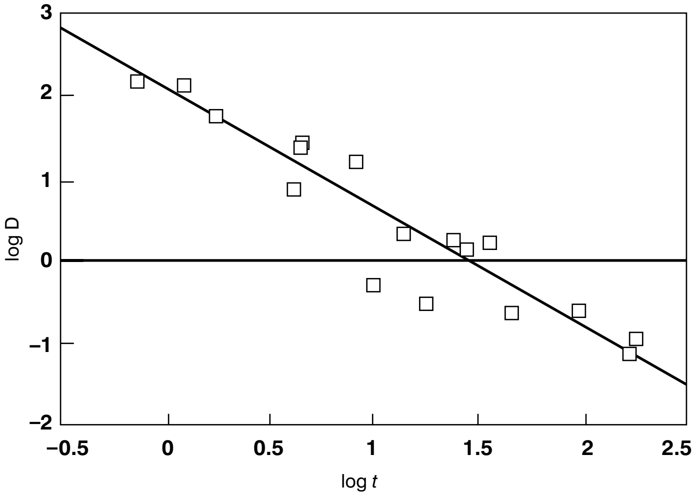


Figure 11.9 Times of half dyeing for viscose with direct dyes (log t), as a function of their diffusion coefficients (log D) into regenerated cellulose films

Therefore, for a dye that rapidly absorbs and that quickly comes to equilibrium, the best colour yield results from dyeing at lower temperatures. For a slowly absorbed dye, the best colour yield occurs at higher dyeing temperatures because dye adsorption is faster and dyeing does not approach equilibrium. Dyes often have an optimum dyeing temperature usually determined by a temperature range test. In this, the optimum dyeing temperature is that giving deepest shade for a convenient dyeing time under the given conditions. The effect of temperature on dyeing rate is that anticipated from the Arrhenius equation. Diffusion in solids has a high activation energy (E_a), which can be determined by examining the increase in the value of the diffusion coefficient D with increasing temperature:

$$\ln(D_f) = -\frac{E_a}{RT} + \text{const.} \qquad (21)$$

11.3 AGGREGATION OF DYES

Many types of ionic dyes appear to form aggregates or micelles in solution. The study of this phenomenon is limited by the lack of suitable precise experimental techniques. Aggregation numbers – the average number of dye molecules in a micelle – had been determined from diffusion coefficients, electrical conductivity measurements, osmotic pressures, membrane filtration, and light scattering. Almost all the data are of limited accuracy for one reason or another. Aggregation increases with increasing dye concentration and decreases with increasing temperature. Exact aggregation numbers and the number of incorporated counter ions, which determine the actual overall electric charge of the micelle, are imprecisely known. It is usually assumed that a rapid exchange occurs between free dye molecules in the solution and dye micelles of various sizes.

11.4 CONCLUSION

Opinions about the value of dyeing theory as a tool for developing dyeing technology are just as varied as those related to political parties. Much of dyeing theory is difficult to understand without an extensive background in physical chemistry. The results are often in a form that seems quite unrelated to practical dyeing. Nevertheless, dyeing is a reversible process governed by the fundamental laws of thermodynamics and kinetics. Studies in these areas, while they might seem far removed from the reality of the dyehouse, do explain the phenomena that are occurring. The problem is that textile dyeing occurs in a complex heterogeneous system. A dye solution does not behave like a simple solution of sodium chloride. The distribution of a dye between solution and a heterogeneous fibre is not the same as the partition of, say, benzene between water and hexane. Unfortunately, textile dyeing is complex and not easily amenable to simple experimental studies. Similarly, dyeing theory does not always provide simple conclusions.

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CHAPTER 12

Dyeing machinery

Dyeing machines come in all shapes and sizes to accommodate the various forms and quantities of textile materials. In one chapter, it is impossible to provide exhaustive coverage of this field. Therefore, the most important types of machine, and their problems, will be at the forefront.

Dyehouse machinery represents a large capital investment. The correct choice of equipment, and its effective use and maintenance, are important factors influencing the success of a dyehouse. Modern machines often have programmable microprocessors for automatic control of the process variables, particularly the dyeing temperature [1]. This subject is beyond the scope of this book. Equipment for fabric preparation, and for water removal and drying, will also not be discussed.

12.1 BASIC FEATURES OF BATCH DYEING MACHINES

Textile materials may be dyed at various stages during manufacture. They may be in the form of raw stock (loose fibre), sliver, top or tow (loosely constituted bands of parallel fibres or filaments), yarn, fabric or piece, or made-up articles such as hose or garments. The actual stage at which dyeing occurs in the production cycle depends on the associated costs, the subsequent processing required and the end-use of the goods, and on the colour fastness required at each stage. The modern trend is to delay coloration until as late as possible in the production scheme. This facilitates rapid response to market trends, as illustrated by the recent popularity of garment dyeing.

A dyeing machine has a container in which to hold the dye solution and the goods being dyed. It must be connected to a water supply for filling, and to a drain for discharge of the exhausted bath and rinsing water after dyeing. The first requirement for level dyeing is that all portions of the goods have equal access to the dye solution. The machine must allow uniform circulation of the dye liquor through the stationary material, or movement of the goods through the stationary dye bath, or, preferably, circulation of both the bath and the material.

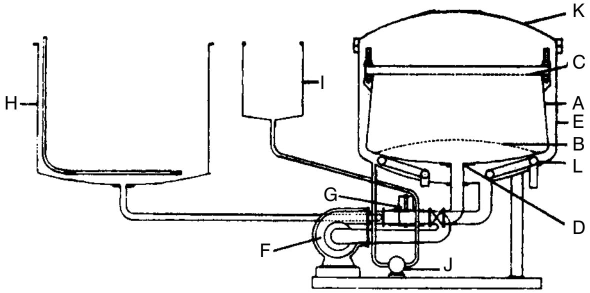
In modern dyeing machines, the surfaces and parts in contact with the dye liquor and the textile are invariably made from stainless steel. This has high resistance to wear and corrosion. Even then, there may be problems when using acidic, alkaline or salty solutions for dyeing. Some form of anti-corrosion treatment may be required.

The dyeing machine must have some means of heating the dye solution. Injection of live steam into the dye solution is the simplest method. Unfortunately, this is does not afford the best temperature control and the excessive condensation increases the liquor-to-goods ratio. For hot dyeing liquors, adequate means for removal of escaping steam are important to prevent condensation outside the machine. Heating with pressurised steam, circulated in a closed loop, is the preferred method. If cold water can circulate through the heating loop, or through an alternative set of tubes, controlled cooling of the dyebath is also possible. Many dyeing processes involve controlled heating to temperatures close to, or even over, the normal boiling point of water. The actual rate at which the dye is transferred from the solution to the fibre, and its rate of diffusion into the fibre, are frequently controlled either by the temperature of the dyebath, or assisted by the addition of chemicals. The machine should therefore preferably have some means of temperature control, and of adding the dye solution and any solid or liquid dyeing assistants. Modern machines have automatic controls for regulation of the dyeing temperature. These allow controlled heating at a given rate and maintenance of a set maximum dyeing temperature. Older machines used thermocouples and relays for this but today's machines have programmable microprocessors.

12.2 DYEING MACHINES FOR LOOSE FIBRE AND SLIVER

For the dyeing of loose staple fibres, level dyeing is less important than for piece goods. Yarn forming processes usually mix the dyed fibres sufficiently well to give satisfactory colour uniformity even when the initial colour of the fibres is not completely level. The fastness to subsequent wet processing of the dyed fibres, as well as to washing of the final product during the intended end-use, are more likely to be significant.

Similar types of dyeing machine serve for dyeing raw stock and various types of sliver. The most common types hold the goods in a conical pan with perforated inward sloping sides, or in a perforated cage. The fibres are gradually packed into the pan, then wetted and compressed by screwing down a solid plate laid on the top. The top plate prevents the dye solution from flooding the top of the pack. A flange on the bottom of the pan fits onto a central pipe delivering dye solution from the pump to the inside of the fibre mass. The entire pan or cage sits in an



A	Pan	G	Reversing valve
B	Perforated base	H	Open reserve tank
C	Detachable perforated lid	I	Small additional tank
D	Conical seating	J	Injection pump
E	Outer vat	K	Pressure vessel lid
F	Centrifugal pump	L	Closed steam coils

Figure 12.1 Illustration of a conical-pan machine

outer container, also with a closed lid, which collects the dye liquor that has flowed out through the fibres and returns it to the pump (Figure 12.1).

In this type of machine, the goods are stationary and the dye solution is pumped up through the packed fibres and out through the perforated walls of the container. In some machines, the top plate is perforated and the container walls solid so that the liquor circulates vertically through the packed fibres. In either case, level dyeing depends upon all fibres having equal access to the dye liquor. The uniformity of the fibre packing and of the liquor flow are key requirements. The machine is filled and drained through the pump. The dye solution is added to the outer pan, or through the pump. If the liquor ratio is high enough, the outer container is full of liquid, and the direction of flow can be reversed. The dye solution must be free of particles to avoid their filtration by the packed fibres. Over-compressing sensitive fibres such as wool, or dyeing at excessive flow rates, causes fibre damage that hinders subsequent carding and spinning.

Before further processing of dyed loose fibre or sliver, drying is necessary. Centrifugation in a hydroextractor removes the bulk of the adhering or unbound water. It is a slow batch process requiring considerable manipulation and does not eliminate absorbed or bound water. Thermal drying is therefore essential. This can be done by forcing hot air through a bed of fibres held on a continuously moving chain that passes through an oven. Sucking hot air through the fibres held on the surface of perforated drums is also effective.

There are also machines for the continuous dyeing of loose fibre and sliver. For loose fibre dyeing, suction onto a perforated drum or wire cage holds the fibres in place during application of the dye solution and subsequent heating with a mixture of steam and hot air to bring about dye fixation. This type of process requires large runs of one colour for economic operation. Only dyes that absorb and fix rapidly are suitable. In continuous sliver dyeing machines, the band of parallel fibres is impregnated with dye solution and then passed through a heated tunnel. The tunnel may be sectioned so that dyeing at high temperature occurs in the first section, washing-off of unfixed and surface dyes takes place in the second, and the fibres are dried in the third.

12.3 MACHINES FOR DYEING YARN

12.3.1 Hank dyeing

In a hank dyeing machine, the skeins of yarn usually hang from poles fitted into a frame that can be lowered into the dyebath. Rods inserted at the bottom of the frame keep the skeins fully extended. A spare frame allows preparation of one load while another is in the dyeing machine. The frame has a perforated top and bottom. The dye liquor gently circulates either down through the hanks, or in the reverse direction if the machine is completely filled. At the front of the machine, a compartment, separated from the hank frame, contains the impeller circulating the dye liquor. The steam and cooling pipes are at the bottom of this compartment. Dyes and chemicals are also added here. This type of dyeing machine is frequently referred to as a Hussong machine.

For level dyeing, equal exposure of all the yarn in the skeins to the circulating dye liquor requires even packing of the skeins. It is important that upward circulation of the liquor in the machine lifts the yarns in contact with the upper poles, otherwise these will dye paler because of poor contact with the liquor. The liquor ratio is usually in the range from 24:1 to 30:1. Such high liquor ratios require greater amounts of dyeing assistants and consume more steam than in package dyeing machines described in the next section. The rates of heating and liquor circulation are low.

Even though dyeing in a Hussong machine is less productive and less economic than dyeing yarn wound into bobbins, it is still widely used for dyeing skeins of wool and acrylic yarn. The Hussong machine preserves the yarn bulk and handle. Acrylic yarns, in particular, may shrink in the hot dyebath, opening channels within the packed skeins. The machine will therefore usually be over-packed so that after shrinkage has occurred the yarns just fill the machine with even circulation. When shrinkage of high bulk acrylic yarns is likely, any bottom poles are initially placed several centimetres above the bottom of the extended skeins.

There have been a number of refinements to the basic Hussong machine. Invariant downward flow of the dye liquor through the hanks keeps them extended so that bottom poles are not needed. In this case, the problem of contact between the solution and the yarns touching the upper poles can be avoided by pulsating the liquor flow. In another method, the dye liquor circulates through upward-pointing holes in the poles holding the skeins. There may be occasional problems of unlevel dyeing with dyes that do not migrate readily.

A major reason for the decline of hank dyeing is the problem of unwinding. After dyeing, the wet hanks are centrifuged, hung on poles or hooks, and passed through a hot air oven. They must then be mounted on a rotating frame to unwind the yarn. After package dyeing, yarn can be more easily unwound at much higher speed by pulling it over the top of a stationary bobbin.

12.3.2 Package dyeing machines

A package dyeing machine is typically a cylindrical vessel, about 2 m high and 2 m wide, with a rounded bottom and lid. The yarn is wound into cheeses, cones or cakes using perforated former tubes. The formers may be rigid or compressible, the latter allowing packages to be squeezed tightly together when mounted on top of each other in the machine. Cheeses are cylindrical with parallel sides, with a diameter usually larger than the length. Cones taper with a small angle. They usually have the shape of the former tube onto which the yarn is wound and uniform wall thickness. Cones allow easier over-the-top unwinding of the yarn than cheeses. Cakes are wound on a former tube that is then removed so the inside collapses. They are also produced by winding yarn or tow in a centrifuge or Topham box. High bulk acrylic yarn can be dyed in cake form.

The packages of yarn are inserted onto vertical, perforated spindles in the machine. Each spindle typically takes 8–10 packages but the vertical columns of packages do not touch. The packages may have a stocking over them to protect them and to act as a filter during dyeing. The spindles screw into holes in the base of a hollow, circular frame, at the bottom of which is a connection fitting onto the pump (Figure 12.2). The spacing of the spindles and hence the maximum load depends on the frame diameter and package size. The frame, with its load, can be

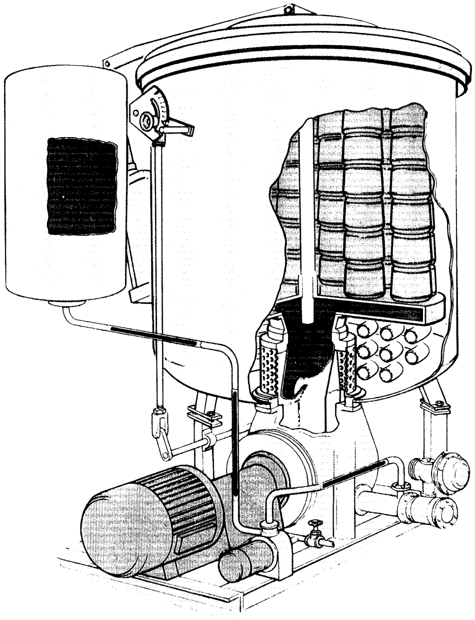


Figure 12.2 Illustration of a typical package dyeing machine (courtesy of Macart Textiles Ltd)

craned into and out of the machine. Thus, one frame is in preparation while one is in the machine.

The dye liquor is pumped into the base of the frame and up through the perforated spindles. Solid spacer plates seal the ends of each package on a spindle and force the circulating liquor to flow out horizontally through the package. Because of their regular cylindrical shape, however, cheeses on compressible formers can often be mounted on the spindles without spacer plates, and compressed together. At the top of the spindles, a screw-on plate presses the cheeses down and gives a good seal between them. Cones cannot be compressed lengthways to the same extent as cheeses and usually require solid spacer plates between them. Even then, the liquor flow through a cone is not usually as uniform as through a more regularly shaped cheese. The dye liquor flows up the perforated spindle and flows outward through the packages of wound yarn. It then flows back down over the outside of the frame and back to the pump. Heating is usually with super-heated steam in coils situated just below the frame carrying the spindles. The same coils, or a different set, can be used for cooling.

Fully filled, closed machines allow bi-directional flow that assists level dyeing. Even though the walls of a package may be of uniform thickness, the surface area of the package increases with distance from its centre. With in-to-out flow, this results in a decrease in the volume flow rate towards the outer edges of the package. To obtain level dyeing of the yarn throughout the package, the initial dye strike must be controlled. Less level dyeing dyes, of higher washing fastness, are used than when dyeing hanks. Frequent flow reversal gives improved levelness with such dyes of low migration ability. Package dyeing has many advantages over hank dyeing. It allows higher loads, lower liquor ratios, more rapid dyeing and easier unwinding of the dyed yarn.

Package preparation is a crucial step. Some of the factors influencing the stability of a package and its permeability to dye solution are:

(1) the denier or tex of the yarns or filaments;
(2) the degree of twist of the yarn;
(3) the extent to which the yarn traverses the package (cross-winding) and its tension;
(4) the degree of swelling or shrinkage that occurs in hot water;
(5) the actual shape of the package.

The yarn tension throughout the package must be even and winding must be as uniform as possible. The packing density should give a moderate resistance to flow but adequate and even penetration of the dye liquor throughout the package. The initial rate of dye liquor flow through a viscose filament package may drop sharply because of the fibre swelling that occurs in water. Non-textured nylon or polyester filaments, that tend to shrink in hot water, may have to be initially relaxed and re-wound before dyeing. Textured artificially made filaments give softer packages that do not require pre-shrinking and for which the permeability is much less dependent on yarn and filament characteristics.

All packages must have a stable construction and be as identical as possible. Depending upon the type of yarn, the packages must withstand some swelling, or alternatively some shrinkage. It is essential that the package is stable to the change in pressure that occurs when the liquor flow reverses direction. If the yarns move and become trapped, unwinding becomes difficult. The flow of liquor through the package must not cause any distortion or blowing out of the yarns. A blow-out results in an excessive local flow of dye solution and reduced flow to other packages. Typical flow rates in a package dyeing machine are around $30\ \mathrm{l\ kg^{-1}\ min^{-1}}$, giving complete circulation of liquor every 30 s, or even less. A typical liquor-to-goods ratio for a package dyeing machine is around 10:1, when the machine is fully flooded. Filling to just cover the packages, or even only to cover the circular base, decreases the liquor ratio. In the latter case, only flow up the spindles and out through the packages is possible. Dyeing at lower liquor ratios offers considerable savings in water, steam, chemicals and time.

Many machines have an expansion tank. This accommodates the excess liquor as it expands on heating the filled machine. This tank is used to add solutions of dyes and any required dyeing assistants, which are then pumped back into the machine. Almost all machines are pressurised, and can operate up to 135 °C. Even when apparently dyeing at the boil, the machine is under pressure since the lid is closed. Thus, more extensive safety precautions are required. Dyeing under pressure, and placing the pump at the machine base, where the liquid pressure head is highest, reduces cavitation. This arises from the formation of steam bubbles behind the pump blades where the pressure is less, and their subsequent explosive collapse when the pressure suddenly increases. This can cause noise and vibration, pitting of the blade surfaces and a loss of pump efficiency.

One problem with pressurised package dyeing machines is the difficulty of sampling to test that the dyeing has the correct shade. Some machines have an isolated pot containing a single package that can be easily depressurised, cooled and the yarn examined. Dyeing of a batch of yarn in package form, so that every package is uniformly dyed throughout and to the desired shade, still requires considerable experience. In package dyeing, it is difficult to reproduce the liquor flow conditions from batch to batch and the shade reproducibility is sometimes not completely satisfactory. For this reason, weaving or knitting of fabric with yarns from different dye batches should be undertaken with caution.

Beams of warp yarn are dyed using the same principle, in simple machines with unidirectional flow. Some machines may have four vertically mounted warp beams. The perforated beam is initially wrapped with a non-absorbent non-woven fabric before winding. This acts as a solution disperser and filter. As with other types of package, the uniform winding of the yarn onto the beam is a prerequisite for successful level dyeing.

Drying packages has always been a problem. Centrifuging packages in a basket removes much of the loosely held water but complete drying requires a lengthy period in a hot air oven. This type of process often takes as long as 24 hours to completely dry the yarn on the inside of the packages. An improved method dries the packages while they are still on the carrier frame. This is removed from the dyeing machine and fits onto a connection to a hot air blower. More recently, the use of radio frequency dryers has become popular. As much water as possible is removed by centrifuging and the packages then go into the RF dryer. The oscillating electromagnetic field causes oscillation of the polar water molecules in the package at the field frequency. This generates much heat. The degree of heating depends on the amount of water at a given point in the package so that drying is more uniform than in hot air. The power of the RF field is sufficiently high that drying only takes a few hours.

12.4 MACHINES FOR DYEING FABRIC

12.4.1 Winch dyeing

The winch or beck dyeing machine is quite simple and serves for all scouring, bleaching, dyeing, washing-off and softening processes. The machine contains a length of fabric with the ends sewn together, which is compressed to form a continuous rope. This rope passes from the dyebath over two elevated reels and then falls back into the bath (Figure 12.3). The first roller is free-running (jockey or fly roller). The second (winch reel) is driven and controls the rate of rope transport and the extent of pleating where the rope accumulates below and behind the winch. Both reels extend the full length of the machine and accommodate several fabric ropes running side by side. The fabric rope is held on the winch by

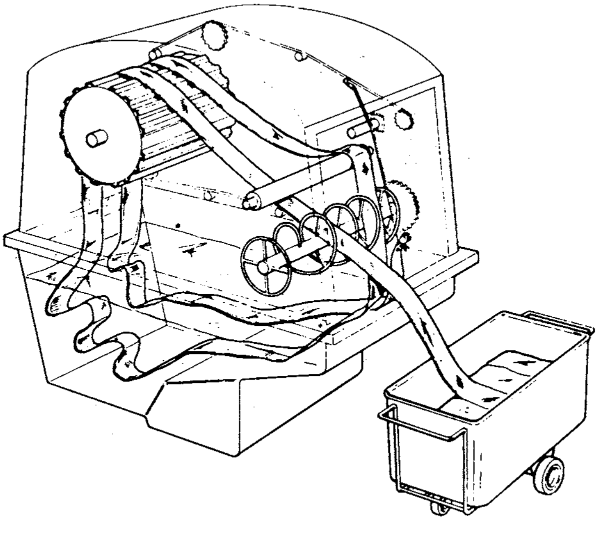


Figure 12.3 Illustration of a winch dyeing machine with Autoloda

friction and its own weight. Covering the winch with polypropylene or polyester tape increases the friction.

Deep-draught winches have circular or only slightly elliptical winch reels and the fabric falls into the back of the dyebath with little pleating. This type of winch is preferred when fabric stretching may occur. Shallower machines have more elliptical winches and plait the fabric into the back of the machine. The bottom of the machine slopes from back to front so that the fabric accumulating behind the winch easily moves forward. Tubular knitted fabrics, with a compact construction, tend to form a balloon filled with air just below the jockey roll. This is desirable since crease locations change with each cycle. An elevated driven roller at the front of the machine is used to load and unload the goods.

A perforated baffle separates the liquor in the front of the machine from the remainder. This part of the machine is called the salting box. Both dyes and chemicals are added to it during dyeing and gradually mix into the remainder of the solution. All additions must be made across the full length of the machine with stirring. Heating is by steam injection from a perforated pipe running along the length of the salting box. Careful design is necessary to ensure that steam condenses before reaching the liquor surface. Direct steam injection causes some bath dilution and can be quite noisy when steam bubbles collapse explosively on rapid cooling, or when they strike the walls. The machine is preferably closed to avoid steam and heat losses, particularly when dyeing at or near the boiling point. The problem of non-uniform temperature in the bath, caused by the cooled fabric falling into the back of the bath, can be minimised by use of a pump to circulate the bath solution. The liquor ratio is typically about 20:1. During dyeing, the bulk of the fabric is moving slowly in the dyebath. The rate of dyeing is partly controlled by the rate of rope cycling and usually increases with increasing winch speed. The winch is usually run quite fast but not at such a speed as to damage to fabric, or promote its elongation or felting.

As for all forms of rope dyeing, the fabric must be fairly resistant to lengthways creasing. Ideally, there should be constant lengthways folding and unfolding of the rope as it cycles around the machine. Lubricants are often added to the dyebath to promote this. A wide variety of materials that do not readily crease can be dyed using the winch machine. The good mechanical action promotes crimp in the yarns and improves the loop length of knitted materials. It gives thicker fabrics with a fuller handle. Open-width threading of the fabric in a winch machine is possible for heavy materials such as carpets and for fabrics that might be crushed in rope form.

Several ropes of equal length (50–100 m) are usually dyed side by side, being kept apart by pegs in a long rail below the fly roller. The hinged peg rail lifts if a tangled rope arrives, automatically turning off the winch drive. Short lengths of individual ropes require more sewing and more time to locate the seams for unloading. There is an obvious advantage if one long, continuous spiral of rope advances through the machine from one side to the other. It then returns to the start by way of a sloping trough or tube filled with dye solution at the back of the machine. In this case, a continuous helical metal spiral, whose pitch determines the loop spacing, replaces the peg rail. This type of loading is more uniform and allows a lower liquor-to-goods ratio.

12.4.2 Jig dyeing machines

The jig or jigger dyeing machine is one of the oldest types of machine for dyeing a variety of materials in full width. It is particularly useful for fabrics such as satins and taffetas that crease readily. The open-width fabric passes from one roller through the dyebath at the bottom of the machine and then onto a driven take-up roller on the other side. When all the fabric has passed through the bath, the direction is reversed (Figure 12.4). Each passage is called an end. Dyeing always involves an even number of ends.

The bath can be rapidly heated by live steam from an open perforated pipe, the perforations pointing down and away from the fabric. Closed-coil steam heating is slower but gives better temperature control during dyeing and avoids dilution of the liquor. As in winch dyeing, the fabric moves through a stationary bath, which is stirred only by the movement of the fabric through it. The bulk of the dyeing is usually carried out with a constant bath temperature. In the widest machines,

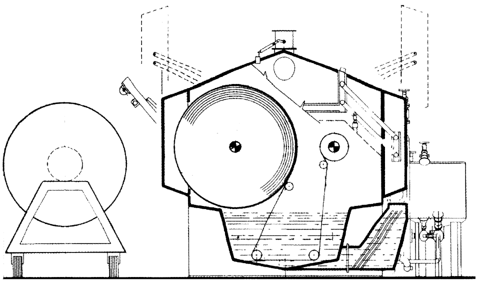


Figure 12.4 Illustration of a typical jig dyeing machine (courtesy of MCS SpA)

stirring the bath ensures uniformity of its temperature. During dyeing, the machine lid should be closed. This helps to maintain a high and uniform roll temperature and reduces heat loss and steam consumption. Any condensation on the lid must run into the dyebath without drops falling onto the fabric rolls. The lid limits air access and avoids rapid oxidation of reduced leuco dyes. Dyeing under pressure is also possible using jigs that roll into an end-opening autoclave.

The jig has a small bath containing the dye liquor (200 to 750 l) and gives a very low liquor-to-goods ratio of around 1:1. It is therefore useful for those dyes used on cellulosic fibres that normally give only low to medium exhaustion. Jig dyeing is a form of pad–roll dyeing repeated several times. Only a few metres of the total length of fabric are in the bath solution at any moment and dyeing occurs almost entirely in the roll of fabric outside the bath. The rate of dyeing depends on the amount of liquor retained by the fabric, the degree of exhaustion in the dwell period, and the extent of liquor exchange during the next dip. The latter is usually around 60–70%, but may be less for heavy fabrics.

The roll of fabric may vary in length from 1000 to 5000 m. The fabric must have constant width and be wound up so the selvages align exactly one on top of the other. The roll therefore has uniform, vertical sides, perpendicular to its axis. Expander bars ensure that the fabric winds up free from creases. Each end of the fabric has an attached end cloth. If several pieces of fabric are in the roll, the ends are cut straight and sown end-to-end without overlap or spaces. A heavy seam holds more dye solution and may transfer dye to adjacent layers of fabric that will show more deeply dyed stripes.

The modern jig often has both the take-off and take-up rollers driven to minimise lengthways tension. This is quite pronounced if only the take-up roller is driven. Regulating the relative roller speeds, or braking the free take-off roller, adjusts the tension. Lengthways tension elongates the fabric and reduces its width. In subsequent processes, relaxation of the strain introduced may also result in lengthways shrinkage. To promote uniform dyeing, and maintain a constant dip time in the bath, the linear velocity of the fabric is maintained fairly constant by gradually changing the angular speeds of the rollers.

There is little mechanical action in a jig machine and it is less suitable where vigorous scouring is required before dyeing. The major problems are side-to-centre colour variations, called listing, and lengthways colour variations, called ending. Ending is more pronounced with slow dyeing or temperature-sensitive dyes. The fabric at the end of the roll receives two closely spaced dips in the dyebath and tends to be dyed paler with slowly exhausting dyes. The end of fabric close to the roller may also have a lower temperature unless the roller is wrapped to minimise heat transfer to the metal. It is usual to add only half the dye solution at the beginning of the first end, the rest being added before the second. Before dyeing begins, an end cloth may be passed back and forth through the heated bath to heat up the draw roller. Listing can arise from non-uniform temperature across the width of the fabric, or from non-uniform pressure that squeezes the retained dye liquor across the fabric width between the layers. After dyeing, the roll of fabric slowly turns to avoid drainage of dye liquor into the lower layers of fabric. Moiré effects or water marks may arise on some acetate and nylon fabrics because of pressure flattening the structure of the rolled fabric. Larger diameter rollers, and a soft end cloth, avoid this.

12.4.3 Beam dyeing machines

In principle, beam dyeing is similar to package dyeing but with a single large package. As mentioned above, beams of warp yarns can be dyed by circulating dye liquor through the bed of yarns laid down on a perforated roller. Beam dyeing of fabric involves winding it onto a perforated beam and pumping dye liquor through this (Figure 12.5). This dyeing method is widely practised for those fabrics that might crease, extend or abrade when dyed in machines where the fabric is in motion. Obviously, it is not appropriate for compact fabrics that severely limit the flow of dye liquor through the many layers on the roll. Some early machines had an open bath with a vertical beam placed in it. The autoclave type with a horizontal beam is now more common. The autoclave allows higher dyeing temperatures and, if required, two-way flow through the roll of fabric. Beam dyeing under pressure is easier than jig pressure dyeing.

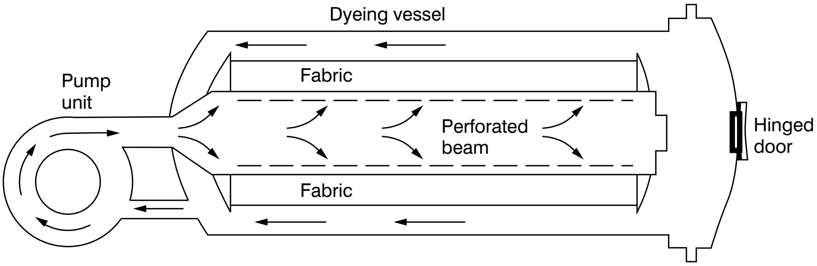


Figure 12.5 Sectional diagram of a high-temperature beam dyeing machine

The winding of the fabric onto the beam is a critical step. The beam is usually first wrapped with a few layers of cotton fabric. This provides a soft bed for the material, allows dispersion of the solution, and filters out any particles. The fabric is then wound onto the beam at constant speed with a uniform but not excessive tension. It is essential to avoid creases and to have evenly aligned selvages without any curling. A piece of polypropylene or calico is stitched to the end of the fabric, rolled around a few times and re-stitched. This prevents the centre of the roll from ballooning and keeps it clean. Tubular knit fabrics are usually slit along one crease before beaming. Although successive lengths of fabric can be joined and dyed on the beam, the number of seams should be kept to a minimum. As in jig dyeing, heavy seams tend to retain more dye solution and can cause deeper dyeing on adjacent layers in contact with the seam.

Beam barrels come in various diameters. They are smooth for about 20 cm at each end and the rest of the cylinder is perforated to allow good liquor flow. The perforations at the ends can be wrapped with flexible stainless steel sheets, and therefore blocked, to accommodate narrower fabrics. The degree of overlap of the fabric, beyond the end of the perforations at each end of the beam, must be carefully controlled. If there is too much overlap, the selvages receive less dye solution, but if the overlap is too small, much dye liquor escapes out through the sides of the roll. Both give unlevel dyeing near the fabric edges, particularly on the inner layers near the beam.

The fabric to be dyed must have good dimensional stability. If there is any length extension during dyeing, solution may leak out of the roll sideways between the layers of fabric giving unlevel edges. Shrinkage along the length of the fabric during dyeing causes excessive pressure that can flatten the fabric. Width shrinkage causes flow variations while width extension gives ballooning of the roll and reduced flow. Prior to rolling up the beam, fabrics made from thermoplastic synthetic fibres are therefore pre-set, using hot air or water, to relax tensions and eliminate possible dimensional changes during dyeing.

The beam of fabric is mounted in a cradle that glides on rails into the autoclave through an end door. When the door is closed, this seals the near end of the beam and provides good contact of the far end as it engages the tapered outlet of the liquor circulating pump. The machine is filled with water until water overflows into the expansion tank. The circulating pump forces water from the beam interior out through the layers of fabric. A wetting agent helps to eliminate air bubbles within the fabric roll. De-aeration is essential to avoid paler dyed spots. The level in the expansion tank rises as the temperature increases. Solutions of dyes and chemicals are added through this tank. From its bottom, the small pressure pump feeds the solution back into the machine. Complete circulation of the liquor takes about 45–120 s. The liquor ratio is usually around 10:1.

The fabric will then usually be scoured but the beam machine does not effectively remove solid impurities that are retained in the layers of fabric. Heating is by high-pressure steam passed through pipes running along the bottom of the autoclave. Cooling is achieved using the same tubes. Some larger beam dyeing machines have an external heating system.

Fast, even liquor flow through the roll of fabric is essential. This is usually in the in-to-out direction, but it can be reversed. Out-to-in flow can compress the material causing flattening and glazing, particularly on the inner layers. The main pump is a high capacity circulating pump. A secondary pump pressurises the vessel even when dyeing at temperatures below the boil. The major disadvantage of in-to-out flow is the risk of unlevel dyeing, with the inner layers of fabric having a deeper colour than those on the outside of the roll. The rate of exhaustion must be below about 2% per cycle of liquor. The high liquor flow rate helps to control the strike. The flow rate should be as high as possible without disturbing the layers of fabric. It depends on the pump, the fabric permeability, and the number of layers in the roll. Unlevel dyeings are difficult to correct unless readily migrating dyes are used.

Sampling during beam dyeing remains a problem. Small samples placed in the liquor flow can be withdrawn through a pressure lock but have not been exposed in the same way as the layers of fabric in the roll. In many cases, it may be necessary to cool, drain the liquor to storage, sample the roll and then refill with additional dye solution. This is expensive.

12.4.4 Jet dyeing machines [2]

The first jet dyeing machine, based on a design by Burlington Industries in the USA, was introduced by the Gaston County company in 1961. Jet machines essentially all use the same principle (Figure 12.6). Dye liquor is injected at high speed from an annular orifice around a rope of fabric as it passes through a venturi tube. This is a tube with a constriction. The high linear velocity of the jet of liquid, and its flow around the fabric rope in the venturi, pull the fabric along towards the back of the machine. Fabric speeds are usually about 200–250 m min^{-1} but can be much higher. The fabric then falls into the back of machine and slowly moves to the front where it rises to the jet again. A typical cycle takes about 1 min.

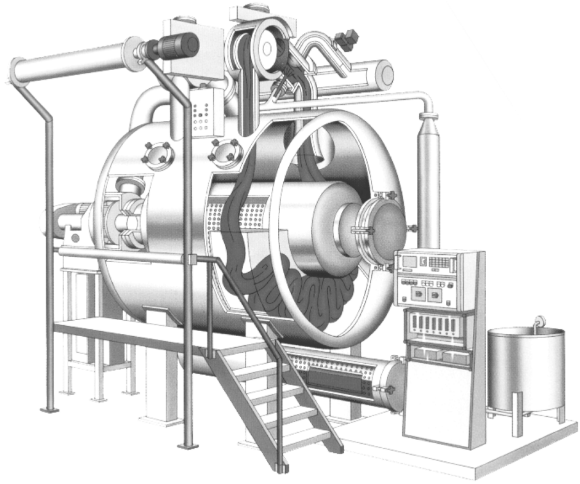


Figure 12.6 Illustration of a typical jet dyeing machine

The lifting of the fabric is mainly by the action of the jet. A non-driven lifter roller, or a small driven winch, in front of the jet, guides the fabric into the venturi tube. In large machines, several jets arranged side by side with one rope in each tube, share a common bath. Dye liquor that collects in the bottom of the vessel is pumped through a heat exchanger and back into the jet. Solutions of dyes and chemicals are added from a tank using a secondary pump.

This type of machine is usually fully enclosed and can be pressurised by heating the bath to temperatures above 100 °C or with compressed air. Jet dyeing machines have proved particularly suitable for dyeing textured polyester fabrics under pressure at temperatures of 120–130 °C.

In the jet machine, the fabric being dyed and the dye liquor are in constant motion and the vigorous exchange between them results in rapid dyeing. Considerable dye adsorption can occur even during the short period of about 1 s that the fabric rope spends in the venturi tube. In the remainder of the cycle, which lasts about 1 min, when the fabric is moving more slowly through the bottom of the machine, dye is diffusing into the fibres.

Jet dyeing machines have their limitations. Like closed package and beam dyeing machines, sampling to check the shade is often difficult. The machines are usually quite expensive and are difficult to load and unload. A tape is left in the machine and the end of it passing into the jet attached to the end of the fabric being introduced. The other loose end of the tape is slowly withdrawn as the rope feeds into the machine and is finally used to lift the end originally inserted back up to the entrance port. The two ends are then sewn together to form a 300–400 m continuous rope. After dyeing, the seam between the fabric ends is cut and the tape reattached to the end that will pass through the jet. It is pulled into the machine as the fabric is unloaded and remains there.

Because the interior of most jet machines is not easily accessible, they are difficult to clean. In particular, polyester oligomer deposits may develop on the hot surfaces and later dislodge. Cleaning with circulating NaOH and $Na_2S_2O_4$ solution is common. The inside surfaces must be smooth to avoid snags.

Jet dyeing machines have liquor-to-goods ratios in the range from 5:1 to 15:1. The lowest liquor ratios require using only partly filled machines and are useful for dyeing cotton knits with reactive dyes because of the lower quantities of chemicals consumed. Partly filled jet machines, however, tend to produce copious amounts of foam from the turbulent passage of dye liquor and fabric through the venturi. Even when low-foam chemicals are used in dyeing, an anti-foaming agent such as a silicone or fatty alcohol will be required.

The venturi tube may be inside the main body of the machine, or in a separate tube on its outside. The size of the actual orifice depends on the fabric weight and width. For a given rope of fabric, too small a jet produces more creases because the fabric rope is more compressed in the jet and may even jam. Too large a jet gives inferior rope transport. In some machines, jets of varying diameter are interchangeable, while others have adjustable jets. Accurate positioning of the jet avoids giving a circular motion to the liquor that might cause twisting of the rope and more creasing. Rectangular jets help to open up the fabric rope.

Jet machines can be quite hard on the fabric. Lifting the dripping rope from the base of the machine to the jet, and the force of the jet, cause longitudinal tension and creasing. Although the frequent fabric movement, and the ballooning of the fabric after the jet, minimise lengthways creases, this type of machine is not suitable for many delicate fabrics. Fabrics from spun yarns of staple fibres may tend to become quite hairy in appearance because of abrasion.

Much gentler jet dyeing machines avoid some of these effects. Some limit the fabric tension by providing mechanical assistance in moving the plaited fabric through the machine and back to the jet. Fully flooded jet machines are useful for more delicate fabrics. They will have a higher liquor ratio (15:1). In a fully flooded machine, the fabric rope is always immersed in the dye liquor. Fabric from the venturi passes into a wider storage tube along with the dye solution. The rope speed is much slower than in the jet section. At the end of the storage tube, the fabric is drawn off into a narrower tube and returns to the venturi. The dye liquor is pumped from both ends of the storage tube to a heat exchanger and then to the jet. Some machines have a long narrow vertical U-tube whereas in others the tube is horizontal. Several tubes may be situated mounted side by side and share a common dyebath. They can be isolated for dyeing small lots.

In the so-called soft-flow machines, tension and creasing problems are minimised. The fabric rope is gently lifted over the short distance between the dyebath and the transport tube using a circular driven reel. Once in the tube, the gentle flow of dye solution and gravity carry it around to the exit (Figure 12.7). The tube supports the fabric and there is no tension. The tube is filled to overflowing with dye liquor. A typical liquor ratio is about 15:1. Several machines may share heating and circulation systems.

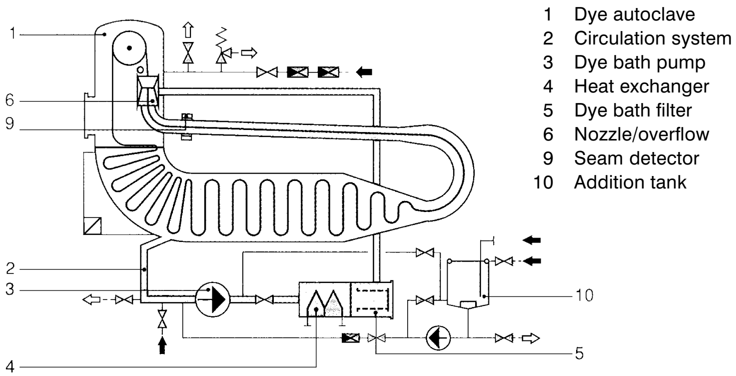


Figure 12.7 A typical soft-flow (THENFLOW) jet dyeing machine (courtesy of Then GmbH)

For lightweight or narrow fabrics, dyeing with several parallel ropes in the same jet is not usually satisfactory because equal lengths are needed and they may give different degrees of shrinkage. The flyer method of dyeing is used. For this, lengths of fabric are stitched onto a main carrier rope by their leading edges. They are slightly shorter than the main rope. Ideally, the fibre of the carrier rope will not be dyed.

12.5 DYEING MACHINES FOR SPECIFIC ARTICLES

12.5.1 The star frame

The star-frame has a central shaft with many horizontal radial arms with hooks on the underside that hold the suspended fabric by the selvages as it winds around in ever increasing circles. The dye liquor circulates over a perforated plate above the frame and evenly distributes itself over the fabric. The frame may even be raised and lowered in the bath during dyeing. The liquor ratio is often about 50:1. The frame only takes about 200–250 m of fabric. Dyeing using the star-frame is fairly expensive because of the time required for mounting the fabric on the frame. This machine is usually reserved for dyeing expensive fabrics such as high quality velvets.

12.5.2 Garment dyeing machines

In paddle dyeing machines, the goods pass around a central island as a rotating paddle circulates the dye liquor. The walls of the island are perforated and the central section is flooded. It serves for dye and chemical additions and for draining the machine. The paddle is usually located along one of the straight sides of the oval shaped vessel with its axle passing through the island above bath level. The paddle blades dip to about half the depth of the bath and the paddle speed is about 5–10 rev min^{-1}. This type of machine is used for dyeing loose articles such as hose and small garments. These are preferably held in mesh bags made of a non-dyeable material since this facilitates loading and unloading and minimises tangling. The liquor ratio is fairly high, with a minimum value of about 25:1. Live steam heats the bath, issuing from pipes in the bottom of the vessel.

Rotating drum machines are also useful for dyeing hose and garments. These have an inner perforated drum that rotates in either direction inside a sealed drum of slightly greater size. Baffles divide the inner drum into quadrants to ensure that the goods move as it rotates. The rate of rotation is quite low, about 3–4 rev min^{-1}, with frequent reversals of direction. Again, the goods are preferably bagged. As for all dyeing machines, a smooth interior is essential to avoid snagging. A variety of tumbling machines have higher rotation speeds and can spin dry at the end of the cycle. These are similar to dry-cleaning machines. Rotating drum machines are more efficient and cleaner to operate than paddle machines. The more vigorous mechanical action often promotes more shrinkage and bulking, which may be desirable for some articles.

Nylon hose can be mounted on appropriately shaped boards that are placed in a type of autoclave that allows dyeing, drying and heat setting to be carried out in sequence. Garment dyeing machines are also available that allow pressure dyeing of polyester articles.

12.6 CONTINUOUS DYEING EQUIPMENT

Some of the techniques and problems of continuous dyeing were outlined at the end of Chapter 10. This section now considers the equipment routinely used in continuous dyeing.

12.6.1 Padding mangles

During padding, the fabric passes into a solution of chemicals, under a submerged roller and out of the bath. It is then squeezed to remove excess solution (Figure 10.7). The objective of this process is to mechanically impregnate the fabric with the solution or dispersion of chemicals. This must be as uniform as possible both along the entire fabric length and across its width. Pad impregnation is common for the dyeing of fabric and for the application of finishing chemicals.

The uniformity of the distribution of any chemical in the padded fabric depends on having a constant immersion time in the bath and between the bath and squeeze rollers, an even pick-up of the solution, and uniform wetting of the fibres. The bath conditions must also remain constant. These conditions are largely met by running the fabric at constant speed through a bath maintained at constant level, and by adjusting the pad roller pressure so that it gives uniform pick-up of solution. A key requirement for successful pad dyeing is uniform preparation of the fabric.

The bath level must remain constant. A simple mass balance for the dye solution shows that the rate of flow of solution (kg soln min^{-1}) from a supply reservoir into the pad bath must equal the rate at which solution leaves the bath in the fabric. The latter is equal to the fabric pick-up (kg soln kg^{-1} fabric) times the mass flow rate of fabric (kg fabric min^{-1}). At a typical running speed of 15 kg fabric min^{-1} with 60% solution pick-up, 9.0 kg soln min^{-1} must flow into the pad bath. Since the volume of solution in the bath is around 30–40 l, fresh solution completely replaces it in about 3–4 min. The dye solution from the supply reservoir feeds into a perforated pipe running along the bottom of the pad bath at the back of the fabric, the holes pointing away from the fabric. A controller maintains a fixed bath level or depth and activates the feed from the dye solution supply reservoir.

The pad rollers are called bowls and may be horizontally or vertically opposed. The region where they are in contact and exert pressure on the wet fabric is called the nip. On leaving the bath, the fabric passes vertically into the nip of horizontally opposed bowls, or over a small free-running smooth roller in front of the nip of vertically opposed bowls (Figure 10.7). After the nip, the fabric should leave both bowl surfaces at the same time to avoid back-to-face colour differences. In fact, after leaving the nip, contact of the wet fabric with any roller or guide should be minimal. The heavy padder must be on a firm floor with the fabric accurately centred.

The bath volume should be as small as possible (30–40 l). This helps to minimise waste residual solution after padding is over and promotes a rapid turnover of the bath solution. This ensures better constancy of the solution composition in the bath and minimises initial colour tailing from the preferential absorption of the dyes (Section 10.5.2). Ideally, padding should occur under conditions for which dye substantivity is negligible. Padding at room temperature is most common. For dyes with appreciable substantivity at room temperature, padding is often done at higher temperatures where the dyes are less likely to cause colour tailing. Various types of displacement devices are used to minimise the volume of liquor in the pad. If the fabric is not as wide as the pad trough, heavy, hollow metal blanks are added at the ends of the bath. A similar metal displacer is often placed in between the descending and ascending fabric, above the submerged guide roller. Such devices minimise the bath volume and ensure rapid turn-over of the dye solution. Liquor circulation in wide troughs ensures uniformity of the dye concentration across the width.

The two pad rollers are called bowls and their axes may be horizontally or vertically opposed. They are typically about 2 m long and 35–40 cm in diameter. The roller axes are usually exactly aligned. A pneumatic system applies a pressure of up to about 50 kg cm^{-1} of bowl length at both ends of one of the mandrels, the upper one when they are vertically opposed. This gives a contact width of about 1 cm where the rubber flattens. The higher the applied pressure, the greater the degree of deformation of the rubber surface, the lower the solution pick-up, but the greater the extent of wear over time. The rubber surface should be treated with great care. Any surface damage holding dye solution may transmit repeating colour spots onto the padded fabric. The bowls should be hosed down immediately after use and the pressure released. The pressure should only be applied when the rollers are rotating to avoid forming a permanent flattened zone that can cause an irregularly coloured stripe on the fabric.

The pressure at the ends of the mandrel causes some bending. This gives higher pressures towards the fabric selvages and a higher solution pick-up in the centre. To counteract this, the surface camber of one or both bowls can be modified to give even pick-up across the nip width under pressure. The rubber surface is ground so that it tapers slightly towards each end. The camber introduced will only give a uniform pressure across the width of the nip for one application pressure. Alternatively, the axes of the two bowls can be skewed slightly so the applied pressure is greater in the middle and less at the ends. The degree of skew can be varied for different applied pressures.

The swimming roller developed by Küsters is a more sophisticated method of compensation for mandrel deflection under pressure. This type of roller has a stationary mandrel with an outer rubber shell that rotates on bearings. The space between the mandrel and the rubber shell is divided into compartments in such a way that the central region oriented towards the nip can be pressurised. In this way, the surface pressure at the nip in the middle of the roll can be increased to compensate for deflection of the mandrel. By controlling the pressure of oil pumped in, and the load on the mandrel, the surface pressure at the nip is more uniform across the width.

Some pads provide two dips into the dye solution. This may involve two sets of pad rollers with two separate baths of dye solution, or two nips between a set of three bowls with a single bath. When padding dry fabric using two baths, much more solution is removed from the first bath during the first dip. The second bath is fed from the supply reservoir and usually overflows into the first, which has a level controller.

The wedge nip has the solution held in the nip between two horizontally opposed bowls. Side plates at the ends just touch the rollers' surface and hold the solution above the nip. Using this type of pad, it is vital that the descending fabric wets immediately on contact with the liquor as the immersion time is very short. The wedge nip is useful for lightweight fabrics but tends to give excessive foam as air is squeezed out of the fabric into the bath. It is most frequently encountered as the second nip in a double pad system.

12.6.2 The Thermosol process

The Thermosol process is mainly used for the continuous dyeing of fabrics containing polyester fibres. When polyester fabrics that have been padded with a disperse dye suspension and dried, are heated to temperatures around 200–220 °C for 30–60 s, the dye sublimes. The dye molecules dissolve directly in the polyester fibres from the vapour phase. At such high temperatures, there is quite rapid diffusion of the dye molecules into the polyester.

This type of dyeing process is widely used for cotton/polyester blends, using a disperse dye for the polyester fibres and another type such as a reactive, vat or direct dye for the cotton. The fabric is initially padded with all the dyes required for dyeing the cotton and polyester. There may be as many as 6–8 dyes in the mixture. Because the disperse dyes will be fixed using dry heat, the padded fabric is first dried. This is a two-stage process. Infrared heaters gently pre-dry the fabric to a water content below the critical value for migration (Chapter 10.5.3). Once migration is no longer possible, drying is completed on steam heated cylinders.

The required heating for the Thermosol process can be done using a tenter frame but this is not ideal. The oven would have to be quite long to run at high speeds and there are problems from over-heating of the metal pins and plates that hold the selvages. Hot flue fixation is common in Europe. The hot flue is a chamber with a set of driven upper rollers and free lower ones. The fabric loops up and down through these as it passes through the heated chamber. Hot air, from oil- or gas-fired burners, blows up between the loops of fabric held on the rollers. If combustion gases such as nitrogen oxides are likely to cause dye fading, the air may be heated indirectly. The fabric is running at speed under some tension and may extend so the exit rollers must be driven slightly faster to account for this. There is no width control and the rollers must have quite large diameters and be accurately aligned to avoid creases. The fabric enters and leaves through narrow slots to retain the hot air.

Contact heating gives a more rapid temperature increase than convective heating. This is important because sublimation and diffusion of the disperse dyes probably occur quite rapidly once the required temperature is reached. The total dyeing time in a typical contact Thermosol process is reduced to around 20 s. This type of heating is used mainly in the USA where 60 cm diameter cylinders in banks are fired using natural gas. Perforated suction drums can also be used in which heated air is sucked through the fabric in contact with the drum. Care is required to ensure that the flow of air does not carry away any vapour of the sublimed dye.

12.6.3 Roller steamers [3]

Steamers are used for the continuous fixation of vat, sulphur, reactive and direct dyes on cotton, particularly in blends with polyester. The padded fabric passes through a zone filled with saturated air-free steam for about 20–60 s. If the polyester component has already been dyed by the Thermosol process, the dry fabric already contains the dyes for the cotton. Before entering the steamer, it is padded with chemicals for assisting the dyeing of the cotton. The steamer usually has a bank of driven rollers at the top and a set of free rollers at the bottom, the fabric being interlaced up and down through the two sets. A steamer typically holds about 30–60 m of fabric. Again, good roller alignment is necessary to avoid lengthways creases.

The roof of the steamer must be well insulated. In the roof, heated pipes or plates circulating pressurised steam at a temperature above 100 °C prevent condensed water from forming and dropping onto and marking the fabric. The saturated steam in the box should be slightly superheated (105 °C). It is fed into the sump water, which boils, the ceiling pipes or plates adding the required degree of superheat. The amount of air in the steamer should be minimum, particularly when dyeing with leuco vat dyes that are readily oxidised. The fabric enters through a narrow slot and exits through a water seal that is often filled with warm rather than boiling water.

12.6.4 Continuous washing units [4]

Continuous washing units are used both for washing after continuous scouring and bleaching of grey cotton, and also for removing unfixed dye and chemicals after continuous dyeing. The vertical types have horizontal banks of rollers along the top and bottom. The upper rollers are driven and are not in the wash liquor. The lower set are free-running and immersed. The fabric being washed therefore undergoes a series of dips into the washing liquor. This flows countercurrent from one washing box to the previous one, often by overflow of the compartment wall, provided that the water is not overly contaminated. They usually operate at temperatures up to around 95 °C. Direct steam injection into the in-coming water is used to heat the washing solution. A number of devices are used to increase the efficiency of such units to minimise heat and water consumption. The dirty hot water discharged to the drain may pass through a heat exchanger to heat up the in-coming water. Carry-over of dirty liquor between compartments, or between adjacent washing units, can be minimised using a squeeze roller in contact with the last top roller.

The horizontal types of wash box have vertical banks of rollers at each end and the fabric passes up through the unit moving horizontally from one side to the other. Water enters at the top and flows downwards over the layers of fabric so the flow is again countercurrent. Horizontal washers work better with more open fabrics. Compact fabrics give too much water dropping off the sides of the fabric into the machine bottom. This type of washer contains a smaller amount of water but the fabric is under greater tension than in a vertical type washing unit.

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