Cellulosics Dyeing

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Preface

This book is another in the series on colour and coloration technology initiated by the Textbooks Committee of the Society of Dyers and Colourists under the aegis of the Dyers' Company Publications Trust Management Committee, which administers the trust fund generously provided by the Worshipful Company of Dyers.

It has been written to replace the previous work in this series entitled *The dyeing of cellulosic fibres*, which is now out of print. Assembled mainly about fifteen years ago under the editorship of Cliff Preston and eventually published in 1986, that multi-author book had become somewhat outdated. Rather than prepare a formal second edition, Textbooks Committee decided to go for a modified approach. A smaller team of authors was appointed with a view to completing the update more quickly and achieving a more coherent presentation of the contents.

To take due account of technological changes in the dyeing of cellulosic materials over recent years, at least half of the book has been completely re-written and the remaining less active topics have been updated and rearranged considerably. Much new illustrative material has been added and the presentation of those illustrations retained from the 1986 book has been much improved. Discussion of the preparation and dyeing of cellulosic blend materials has been deliberately omitted, in view of the decision by Textbooks Committee to produce a separate publication on the dyeing of fibre blends. This present work has been completely re-indexed and the lists of references at the end of each chapter have been revised, extended and updated throughout.

In many of the areas covered, of course, we have retained material or ideas originated by our fellow authors of the chapters in the 1986 book and we should like to record our sincere thanks to them for helping us in this way to build on their contributions. These individuals are: Ulrich Baumgarte, David Clarke, Ken Dickinson, Maurice Fox, Hans Herzog, Ian Holme, Bernard Kramrisch, Bill Marshall and Harry Sumner.

The authors and editor of this book are indebted to our referees for valuable comments and suggestions for improvement. Our grateful thanks are due to Paul Dinsdale (the editor of the Society), Ros Amery (copy editing and proof reading), Carol Davies (artwork and layout) and Sue Bailey (typing). We are particularly impressed by the quality of the illustrations, which are a notable improvement on those in the 1986 book on this subject.

JOHN SHORE

CHAPTER 1

Cellulose: structure, properties and behaviour in the dyeing process

Thomas P Nevell

1.1 INTRODUCTION

Cellulose is the most abundant of all naturally occurring organic polymers, thousands of millions of tonnes being produced by photosynthesis annually throughout the world [1]. Although exploited for several millennia in the forms of cotton, flax and other textile fibres, and in the form of wood for papermaking and constructional purposes, our knowledge of its chemistry is comparatively recent. It was first recognised in 1838 as the common structural material of many of the higher land plants by Payen, who invented the name cellulose [2]. However, it was not until the 1930s that its constitution as a linear high polymer of anhydroglucose units was unequivocally established [3,4]. This did not prevent much academic and industrial research from being done from the 1850s onwards. Notable technological advances were made long before they could be explained on a molecular basis, e.g. the development of viscose fibre manufacture at the turn of the century. The progress of research has not slackened – indeed it appears to be accelerating [5]. A vast and complicated literature has arisen which may well appear daunting. The purpose of this chapter is to describe the basic facts as they are understood at the present day. It owes much to several standard works on the subject [1,3,6–47].

1.2 CELLULOSIC TEXTILE FIBRES

1.2.1 Cotton

Cotton, the purest form of cellulose found in nature, is the seed hair of plants of the genus *Gossypium* [44,48]. Many species are grown commercially, but they may be conveniently divided into three types. Type 1 fibres have staple lengths (i.e. average fibre lengths) varying from 25 to 60 mm, including high-quality fine cottons such as the Egyptian, Sudanese and Sea Island varieties. Type 2 are coarser species with shorter staple lengths (about 13–33 mm), such as American upland cottons, and type 3 species of still shorter staple lengths (about 9–25 mm), commonly produced in various Asian countries. Major cotton producers at the present time are the USA, China, India, Pakistan and the Central Asian republics; other countries producing small but not insignificant quantities include Mexico, Turkey, Brazil, Egypt and Sudan.

The mature cotton fibre forms a flat ribbon varying in width between 12 and 20 µ m. It is highly convoluted, probably on account of the twisting that takes place when the tubular shape formed during growth collapses on drying. The number of convolutions varies between four and six per millimetre, reversing in direction every millimetre or so along the fibre. These characteristics make cotton easy to recognise under both optical and electron microscopes (Figures 1.1 and 1.2).

Cotton fibres are also illustrated in cross-section in Figures 1.1 and 1.2. Their bean-shaped appearance is sometimes described as a *bilateral structure*, which indicates that the density of packing of cellulose chains is not uniform across the fibre. Hence the accessibility of the chain segments to various reagents varies across the fibre. Three main zones (A, B and C in Figure 1.3) have been identified by means of enzymic degradation [49]. The rate of degradation increases from A to B to C, which is the order of decreasing density of packing. Between zones A and C there appear to be limited areas (denoted by N) even more accessible then zone C.

As well as ‘normal’ (i.e. mature) fibres, a typical batch of cotton may also

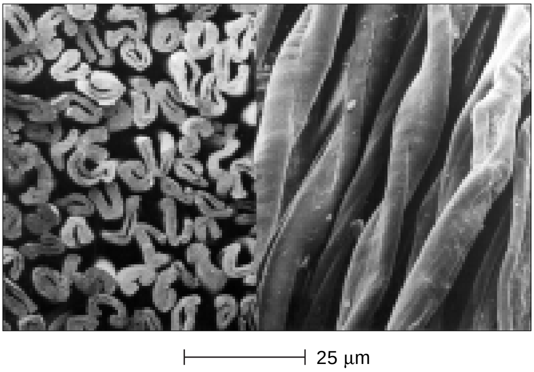

Figure 1.1 Scanning electron micrographs of raw cotton fibres. (*Source:* BTTG-Shirley, Manchester.)

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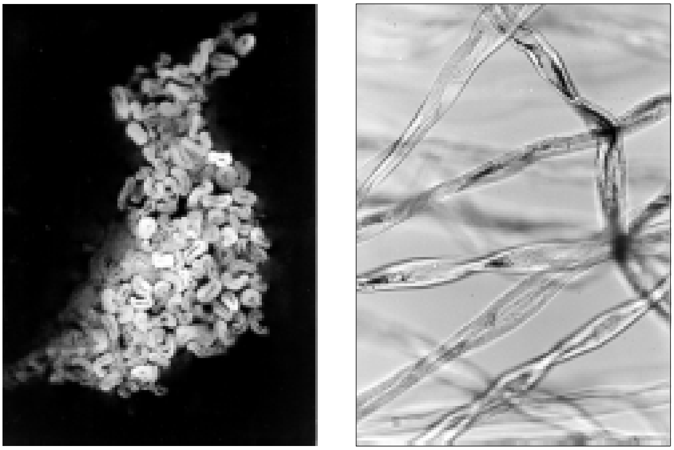


Figure 1.2 Optical micrographs of raw cotton fibres × 184. (*Source*: Mr J T Jones, Dept of Textiles, UMIST, Manchester.)

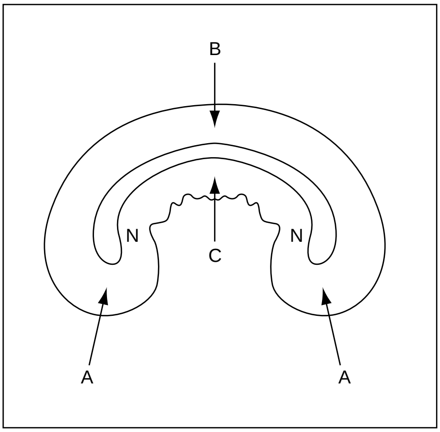


Figure 1.3 Bilateral structure of mature cotton (zones A, B, C and N differ in fibrillar packing density). (*Source:* [49].)

contain some immature and dead fibres. A normal fibre may be defined as one that, after being swollen in aqueous sodium hydroxide, appears rod-like with no continuous lumen and no well-defined convolutions [50]. The lumen is what remains of the central canal from which the layers of cellulose were laid down in the secondary wall while the fibre was growing; it contains some residual protein. In dead fibres the wall thickness after swelling is one-fifth or less of the maximum ribbon width (usually found about midway between two convolutions). Immature fibres are thin-walled because the secondary walls have not fully developed between their ceasing to grow in length and the bursting open of the boll. The boll is the pod remaining on the plant after the flower has fallen; it may contain 20 or more individual seeds.

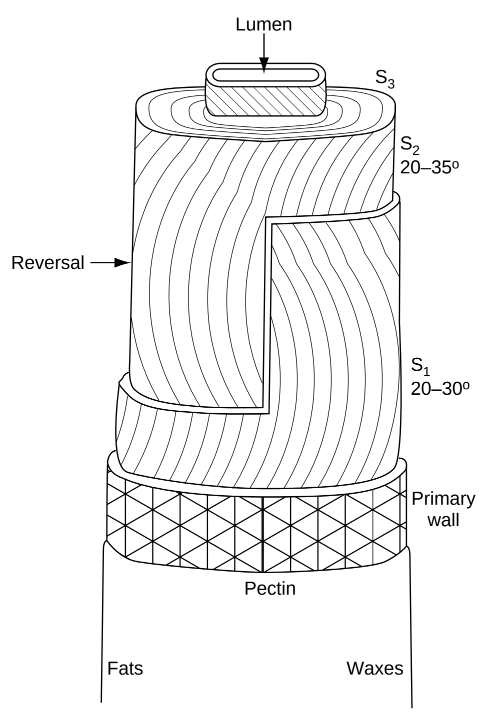


Figure 1.4 Idealised diagram of cotton morphology. (*Source:* J O Warwicker, in *Liquid ammonia treatment of textiles*, Shirley Institute, Manchester,1970.)

Cotton fibres have a fibrillar structure. Their morphology, illustrated schematically in Figure 1.4, exhibits three main features: primary wall, secondary wall and lumen. The primary wall consists of a network of cellulose fibrils covered with an outer layer, or cuticle, of pectin, protein, mineral matter and wax. The wax renders the fibre impermeable to water and aqueous solutions unless a wetting agent is present. The secondary wall constitutes the bulk of a mature fibre and consists almost entirely of fibrils of cellulose arranged spirally around the fibre axis, the direction of the spiral reversing (i.e. changing between S and Z twists) many times along a single fibril. Reversal points frequently correspond with reversals of the exterior convolutions. The secondary wall consists of several layers and the spiral angle of the fibrils varies from one layer to the next, from about 20° to 35°. Although fibrils may be seen under a high-power microscope, there is considerable uncertainty about their dimensions. The resolution limit of the optical microscope is around 0.2 µ m, but the fibrils seem to be bundles of smaller microfibrils, which appear in the electron microscope to be 0.02–0.03 µ m thick and at least 10 µ m long. The microfibrils are themselves believed to consist of still smaller 'elementary' fibrils that are approximately 0.004 × 0.006 µ m in cross-section.

Thus the cotton fibre consists of an assembly of fibrils in which the cellulose is

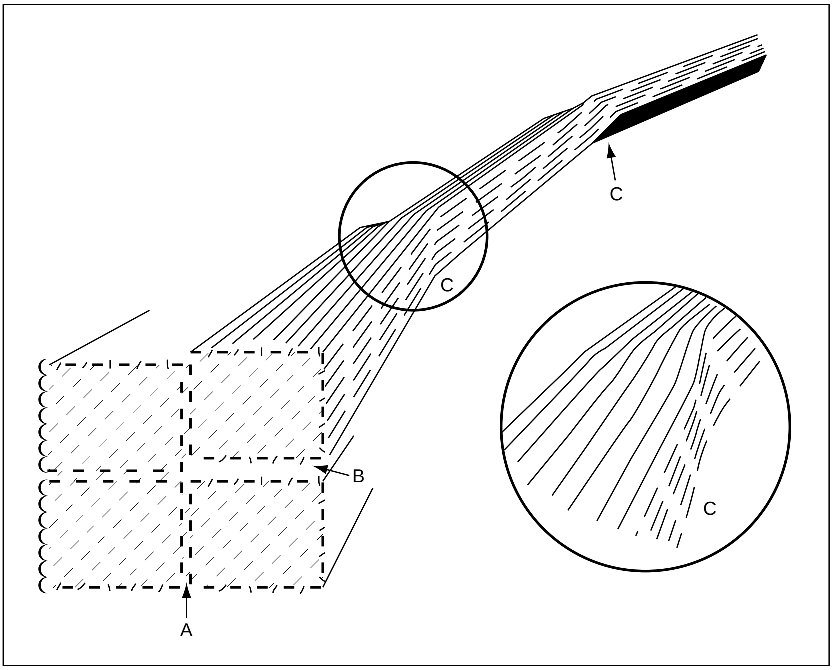


Figure 1.5 Idealised diagram of elementary fibrils in cotton. A, coalesced highly ordered surfaces; B, readily accessible disordered surfaces; C, readily accessible surfaces of tilt/twist regions. (*Source:* [53].)

accessible to most reagents only at fibrillar surfaces by way of a system of voids and channels [51,52]. The 'crystalline-fibril' concept of the fine structure of cotton has been further refined by Rowland and Roberts (Figure 1.5) [53]. Some surfaces (A) of the elementary fibrils are so close to one another that they are inaccessible to all chemical reagents unless swelling has been induced. Others (B) are relatively disordered and are more accessible; in addition there are readily accessible surfaces (C) in the tilt–twist regions that connect the more ordered regions.

It is instructive to compare the composition of the primary wall with that of the cotton fibre as a whole, since it is the primary wall that becomes disintegrated when preparing cotton for dyeing and printing. Although the primary wall accounts for only 5% by weight of the fibre, it contains most of the non-cellulosic constituents. Table 1.1 gives comparative data for a typical cotton [54]. The 'other substances' are mostly water-soluble organic acids and sugars. The table illustrates the very high cellulose content of cotton, which surpasses all other natural sources in this respect.

Table 1.1 Composition of a typical cotton

	Proportion of dry weight/%	
Constituent	Whole fibre	Primary wall
Cellulose	94.0	54.0
Protein (%N × 6.25)	1.3	14.0
Pectin	1.2	9.0
Wax	0.6	8.0
Ash	1.2	3.0
Other substances	1.7	12.0

1.2.2 Bast fibres

The bast fibres [45,46,55] are obtained from the stems of certain dicotyledonous plants, the most important of which is *Linum usitatissimum*, generally known as flax. They form a strength-giving protective layer around the woody central portion of the stem, and are themselves protected by an outermost cuticle which contains waxes and other substances. The fibres consist of bundles of thick-walled cells held together by gummy substances. The ultimate fibres vary in dimensions from one species to another. For example, in flax the length varies from 25 to 30 mm and the diameter from 15 to 35 μm. On the other hand, the individual cells of ramie are unusually long (about 150 mm), whilst their width (30–50 μm) is of the same order as that of flax. In the bast bundles the ends of the individual fibres overlap, forming continuous filaments extending along the length of the stem. Most bast fibres are used as full-length bundles, but flax is separated into its ultimate fibres for the production of fine linen yarns, and ramie is also similarly separated before spinning. The commercial use of ramie is limited, but the supramolecular structure of the fibre is of particular scientific interest. The microscopic features of flax, jute and ramie are illustrated in Figures 1.6–1.8.

Separation of the fibre bundles from the harvested stems is complicated and time-consuming. Usually, the first stage is ‘retting’, i.e. soaking the stems for several weeks in water, traditionally in slow-moving rivers or bogs, until the effect of bacterial action on the intercellular material loosens the fibres sufficiently for mechanical separation. The treatment time can be reduced to a few days by retting in tanks at temperatures between 27 and 32°C. This applies particularly to the production of linen from flax. Subsequent mechanical

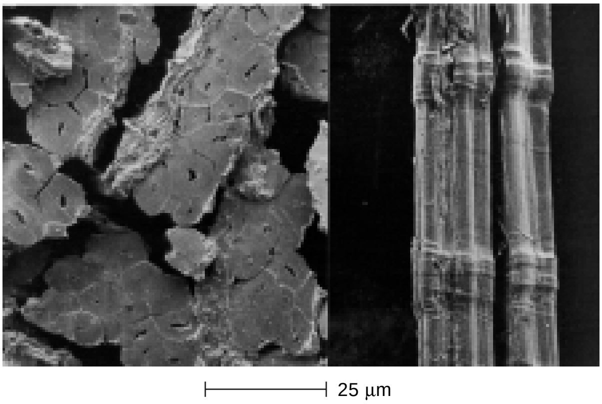


Figure 1.6 Scanning electron micrographs of flax. (*Source:* BTTG-Shirley, Manchester.)

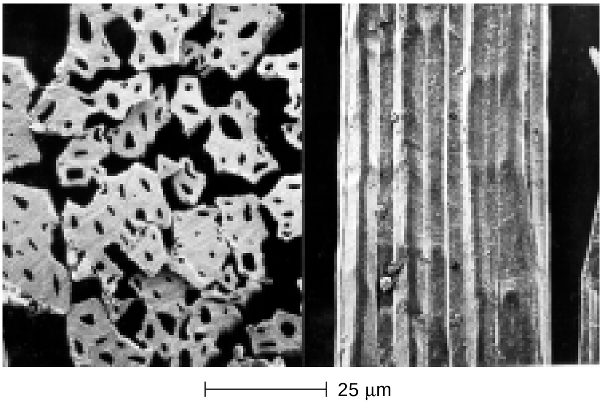


Figure 1.7 Scanning electron micrographs of jute. (*Source:* BTTG-Shirley, Manchester.)

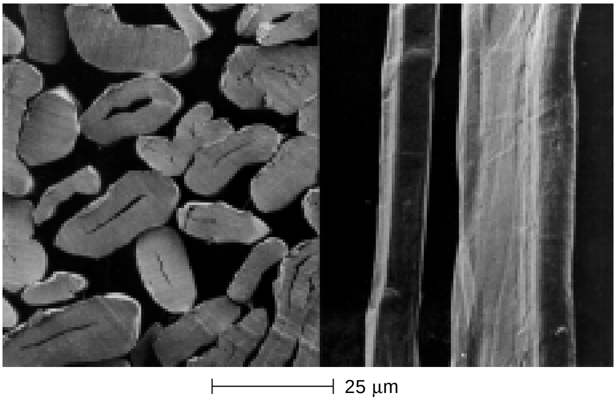


Figure 1.8 Scanning electron micrographs of ramie. (*Source:* BTTG-Shirley, Manchester.)

separation is described as stripping (jute), or scutching and hackling (flax). The decortication of ramie is carried out without preliminary retting.

The crude fibres contain far less cellulose than cotton, as may be seen from Table 1.2. The intercellular material consists of pectins, hemicelluloses (both complex polysaccharides) and lignin (a highly complex crosslinked polymer based on substituted phenylpropane units, found in large quantities in wood). Jute is frequently used without further purification, but flax and ramie are usually scoured and sometimes bleached. Much of the non-cellulosic material is removed, to an extent depending on the quality required in the product. Flax containing 'sprit' (remains of the woody core of the stem of the plant) may be difficult to dye level because the flax fibre and sprit differ in dyeability. The problem is similar to that of motes (remnants of seed coat) in raw cotton. Jute for dyeing is prescoured, but considerable quantities of lignin usually remain, leading to poor light fastness.

Table 1.2 Composition of some typical bast fibres

	Proportion of dry weight/%		
Constituent	Jute	Raw flax	Decorticated ramie
Cellulose	71.3	80.1	83.3
Intercellular material	27.1	10.5	7.5
Wax	0.4	2.6	0.2
Ash	0.8	1.5	2.1
Other substances	0.4	5.3	6.9

1.2.3 Regenerated fibres

The most abundant source of cellulose is wood, of which it constitutes about 40–50%. Wood fibres are too short to spin into textile yarns but they are ideal for making paper, which is essentially a random mat of cellulosic fibres held together by hydrogen bonding. For wood fibres to be converted into textile yarns they must first be dissolved in a suitable solvent from which they can be regenerated as continuous filaments after the solution has been extruded through a fine orifice. The first such conversion was achieved by Chardonnet [47,56] around 1885. Cellulose was nitrated and dissolved in a mixture of diethyl ether and ethanol. The solution was extruded either into water (wet spinning) or into a hot-air chamber (dry spinning) to produce filaments of cellulose nitrate. Since these were highly inflammable they were denitrated with ammonium hydrosulphide. The final product was the first regenerated cellulose to enjoy any commercial success, but it is now obsolete. It has been superseded almost entirely by various types of viscose, although very small quantities of cupro (cuprammonium rayon) are still produced for special purposes.

The main raw material from which regenerated fibres are manufactured is specially purified wood pulp. In the past, particularly for cupro, cotton linters have also been used. These are the very short cotton seed hairs left after those suitable for spinning directly into yarns have been separated. Although easier to purify, they were always more expensive than wood pulp.

Cupro was first produced commercially in 1901, although it had been made experimentally some years earlier [31,56]. Linters or wood pulp are dissolved in cuprammonium hydroxide and the solution is extruded into water. The filaments are stretched and passed through dilute sulphuric acid to complete the regeneration of the cellulose.

Viscose

The viscose process [31,47,56] was discovered by Cross and Bevan in the last century, but it was not until 1910 that appreciable quantities of what is now called regular viscose were produced. Even then it was a comparative rarity. The viscose solution consists of sodium cellulose xanthate dissolved in aqueous sodium hydroxide. Cellulose filaments are obtained by extruding the solution through a spinneret into an aqueous bath containing sodium sulphate and sulphuric acid. The chemistry of the process will be described later (section 1.6.2). The filaments are stretched mechanically during regeneration and their properties are determined by the concentration of the viscose solution, the rate at which it is allowed to coagulate, the rate of stretching and the point at which stretching occurs during coagulation. The rate of coagulation is controlled by temperature and additives such as zinc sulphate or glucose and, for some types of fibre, small amounts of so-called ‘modifiers’, e.g. dimethylamine or cyclohexylamine [57,58].

Regular viscose differs from cotton in being non-fibrillar, having no lumen, and having a much lower degree of polymerisation (DP) (section 1.3). Although viscose filaments consist wholly of cellulose, their skin and core differ somewhat in supramolecular structure. The skin contains numerous small crystallites, whilst the core has fewer but larger crystallites [59] (section 1.4.3). The relative proportions of skin and core vary according to the conditions of coagulation. Under the microscope viscose fibres appear striated longitudinally and in cross-section their circumference is irregularly serrated due to the contraction of an originally cylindrical shape during the later stages of their formation (Figure 1.9).

Modal fibres

Compared with cotton, regular viscose suffers from the disadvantage of much lower breaking strength, particularly when wet. This is seldom a problem in apparel, but renders it unsuitable for more critical end uses. High-tenacity viscose fibres have been produced for at least half a century. They are highly oriented all-skin filaments with a near-circular cross-section (Figure 1.10). Originally developed for reinforcing cord in rubber tyres, they have been partly supplanted for this purpose by nylon and, more recently, polyester. The first high-tenacity fibres still had the disadvantage of a low wet modulus, and it was to overcome this that modified high wet modulus (so-called because of 'modifiers' in the spin bath) and polynosic fibres were introduced.

The polynosic fibres were first developed in Japan [16,60]. The distinctive features in their method of production are:

(1) a solution of viscosity higher than that used for regular viscose (achieved by using an aged pulp of higher DP rather than a more concentrated solution);
(2) a spin bath of low salt concentration with no modifiers or other additives; and
(3) a lower than usual spinning temperature.

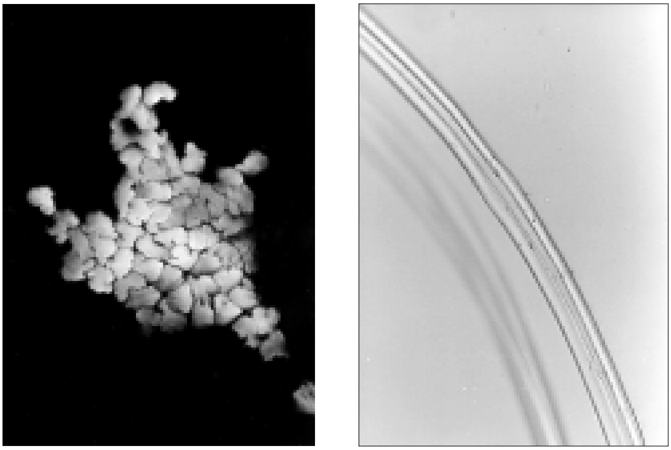


Figure 1.9 Optical micrographs of Evlan (a coarse crimped regular viscose fibre used for carpets) × 92. (*Source:* Mr J T Jones, Dept of Textiles, UMIST, Manchester.)

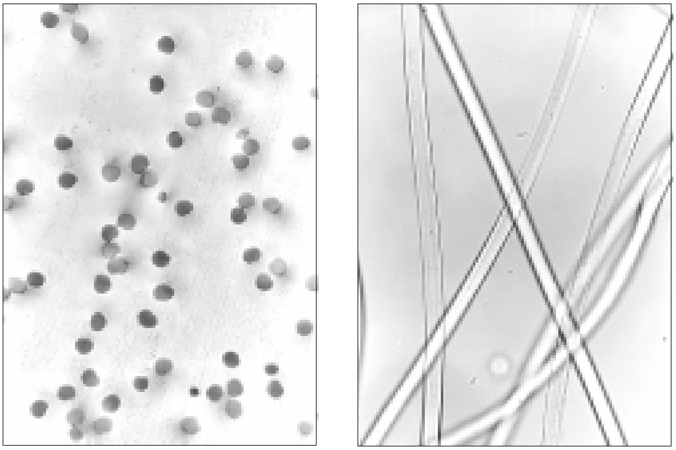


Figure 1.10 Optical micrographs of modal fibres × 184. (*Source:* Mr J T Jones, Dept of Textiles, UMIST, Manchester.)

Under these conditions, high stretch (up to 300%) can be obtained. The product is a highly oriented fibre much more like cotton than other viscose fibres. Polynosic fibres have stress–strain curves similar to those of cotton and are largely unaffected by dilute sodium hydroxide solutions (up to 8%), which dissolve as much as 25% of regular viscose. They appear to be fibrillar in structure.

More details of the preparation and properties of regenerated fibres are available in several reviews [16,31,47,61]. The term modal has been introduced to embrace all regenerated viscose fibres having tenacities in the conditioned state and wet moduli at 5% extension above certain defined values. *Textile terms and definitions* [62] defines a modal fibre as one satisfying conditions (1.1a) and (1.1b):

$$B_c \geq 1.3\sqrt{T} + 2T \tag{1.1a}$$

$$B_m \geq 0.5\sqrt{T} \tag{1.1b}$$

where B_c is the breaking strength in the conditioned state (in cN), B_m is the force required for 5% extension in the wet state (in cN) and T is the linear density (in dtex). For a single filament of linear density 1.7 dtex these formulae give a minimum tenacity of 30 cN tex^{-1} and a minimum wet modulus at 5% extension of 76 cN tex^{-1}.

Miscellaneous speciality viscose fibres

Numerous variants of regular viscose have been developed for special purposes. A few of these will now be mentioned briefly.

Chemically crimped viscose is produced by modifying the regeneration conditions so that the skin of the filament ruptures while in the spin bath [63]. The liquid viscose exposed is thus regenerated under different conditions from the skin, and a bicomponent structure results. A permanent crimp develops as a result of the differential shrinkage in subsequent washing and drying. In the wet processing of such fibres, excessive tension results in loss of crimp and should be avoided. Chemically crimped viscose is usually used in staple form and has an attractive handle.

Hollow fibres have been produced in an attempt to simulate the lumen of cotton [64–70]. One method of doing this is to extrude viscose solution containing sodium carbonate into the acid spin bath. The carbon dioxide produced inside the filament creates a continuous channel, similar to the lumen in cotton but usually larger. Hollow viscose fibres have a lower density (1.15 g cm^{-3}) than regular viscose (1.52 g cm^{-3}) and a higher water imbibition value (130% compared with 90%). They provide greater bulk and fabric cover than regular viscose at the same fabric density and have a soft handle like that of combed cotton.

By a careful choice of spinning conditions it is possible to produce hollow fibres with water imbibition values as high as 200% – the so-called super-absorbent fibres designed for surgical and sanitary purposes [71,72]. An alternative approach [73,74] is to add water-retentive polymers such as sodium polyacrylate or sodium carboxymethylcellulose to the viscose solution before spinning.

Flame-retardant fibres have been produced by dispersing a suitable agent in the viscose solution before spinning [75,76]. One of the most successful agents was tris(2,3-dibromopropyl) phosphate (used in such fibres as Darelle), but in the late 1970s it was suspected of being carcinogenic and had to be abandoned. Little flame-retardant viscose is now manufactured for apparel, although some intended for other uses, containing flame retardants that are less hazardous, is still produced.

Viscose fibres of modified dyeability have been produced for use in the dyeing of wool/viscose blends [77,78]. Additives with free amino groups incorporated into the viscose solution resulted in fibres that could be dyed with acid dyes. Although effective they were too expensive for commercial exploitation.

Producer-coloured viscose is known as ‘dope-dyed’ yarn because insoluble pigments are dispersed in the viscose ‘dope’ from which it is spun. It exhibits excellent fastness to both light and laundering, but represents only a tiny fraction of fibre production.

Regeneration from amine oxide solution: Tencel (Courtaulds)

One of the most exciting recent developments in the production of regenerated cellulosic fibres has been the introduction of an alternative to the viscose process. The objectionable effects of viscose manufacturing plants on the environment have been universally recognised for a long time, but it was not until the 1970s that the possibility of using some other solvent for wood pulp began to emerge. The 'new' non-aqueous solvents for cellulose will be described later (section 1.8.3). The only one that so far has proved suitable for development is *N*-methylmorpholine-*N*-oxide (NMMO). Satisfactory fibres have been regenerated from it on a small scale from time to time [79,80], but now Courtaulds PLC has established full-scale manufacture [81]. Wood pulp is dissolved in NMMO monohydrate and the solution extruded into dilute aqueous NMMO, with appropriate stretching and drying of the regenerated fibre. The solvent is totally recoverable for reuse so that the process is environmentally innocuous. The fibre is called Tencel (Courtaulds) and is illustrated in Figure 1.11. It is fibrillar in structure and approximates to cotton in its behaviour under stress and capacity for absorbing liquid water even more closely than modal fibres. Because of the close similarity of its stress–strain curve to that of cotton it can contribute to the

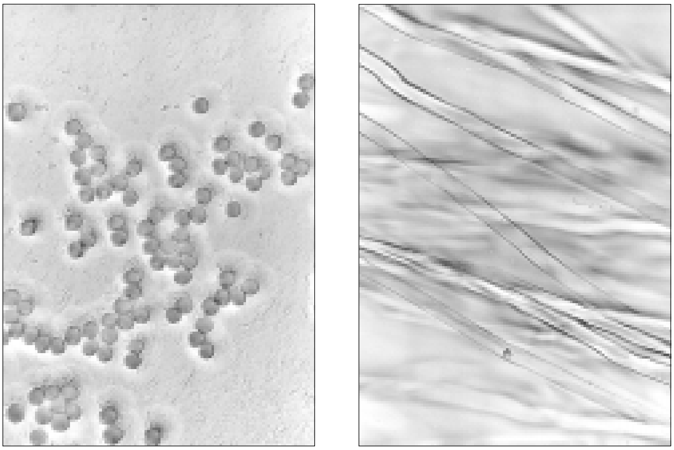


Figure 1.11 Optical micrographs of Tencel fibres × 184. (*Source:* Mr J T Jones, Dept of Textiles, UMIST, Manchester.)

strength of yarns blended from the two fibres, even at low blend levels. The chief mechanical properties and water imbibition of cotton, regular viscose, modal and Tencel fibres are compared in Table 1.3.

Table 1.3 Comparison of typical fibre properties[a]

Fibre (titre 1.7 dtex)	US Middling cotton	Regular viscose	Modal	Tencel
Tenacity/cN tex^{-1}	22	24	35	40
Elongation/%	8	22	14	15
Wet tenacity/cN tex^{-1}	28	13	20	36
Wet elongation/%	13	27	14	17
Wet modulus at 5% extension/cN tex^{-1}	100	50	110	270
Water imbibition/%	50	90	75	65

[a] From Courtaulds Tencel Technical Information pamphlet.

1.3 MOLECULAR STRUCTURE

The main features of the chemical structure of cellulose are well known [30,82]. It may be most conveniently described as a 1,4-β-D-glucan, i.e. a condensation polymer of β-D-glucopyranose with 1,4-glycosidic bonds.

The pyranose rings are in the $^4C_1$ conformation (Figure 1.12(a)). For the sake of clarity and in accordance with convention the ring carbon atoms and the hydrogen atoms attached to them are omitted. Some authors also omit the C–H bonds. Hydroxy groups are always, and methylol groups are sometimes, printed in full. Although the Haworth projections formula (Fig 1.12(b)) is easier to write quickly it obscures some important stereochemical aspects of the glucopyranose ring [83]. Thus all the substituents, including the glycosidic bonds, are in the mean plane of the ring (equatorial) and not perpendicular to it (axial) as might be supposed from the Haworth formula. Only the C–H bonds are axial. The essential features of the polymer chain are the main sequence of intermediate units (I), the non-reducing end group (II), the reducing end group (III) and glycosidic linkages. The intermediate units possess one primary and two secondary alcohol groups each. The non-reducing end group possesses one extra secondary alcohol group at C4, and the reducing end group (so-called because it reduces Fehling's solution and ammoniacal silver nitrate) is a cyclic hemiacetal. It

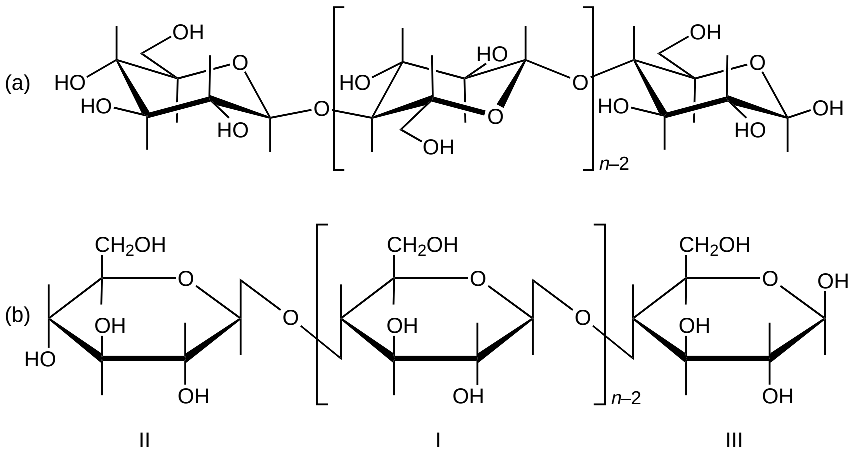
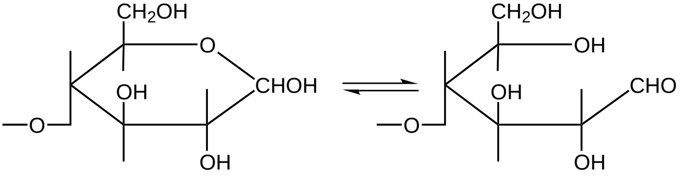


Figure 1.12 Cellulose: (a) fully extended conformational formula; (b) the Haworth projection formula. *n* = degree of polymerisation (DP).



Scheme 1.1

exhibits the characteristics of both an alcohol and an aldehyde under appropriate conditions (Scheme 1.1).

The degree of polymerisation (DP) of cellulose varies with its source and is usually expressed as an average, since a wide distribution is found in most samples. In native cellulose it may be as high as 14 000 [32,84], but purification involving treatment with alkali usually reduces this to about 1000–2000. Furthermore, the hemiacetal end groups are converted to acid groups (section 1.5.3); thus purified native cellulose is normally devoid of reducing power. The DP of cellulose regenerated by the older methods is about 250–300, but that of modal fibres is higher (about 500–700). All fibres regenerated from viscose solution contain a very small number of aldehyde, ketone and carboxylic acid groups introduced during manufacture. Thus chemically, regenerated cellulose differs from native cellulose only slightly. Differences in properties arise mainly from differences in supramolecular structure.

1.4 SUPRAMOLECULAR STRUCTURE

1.4.1 Introduction

Cellulose is a highly crystalline material, but it does not form discrete crystals like those of glucose from which it is derived. As already indicated, native cellulose fibres consist of crystalline fibrils varying in complexity and length. This fibrillar structure is interspersed with material in which the chain molecules are less well ordered than in a crystal. The same chain molecule may participate in crystalline and less crystalline material along different portions of its length. Native cellulose contains very little genuine non-crystalline material. What used to be regarded as amorphous is generally believed to be the accessible surfaces of some of its crystalline fibrils (section 1.4.3). Regular viscose and cupro fibres do seem to contain some genuinely amorphous material, but modal fibres are essentially fibrillar in nature. The supramolecular structure of cellulose, i.e. the overall arrangement of chain molecules in a fibre, may be considered under two headings: crystalline structure and fine structure.

1.4.2 Crystalline structure [17–19,33,44]

Five allomorphic forms of cellulose (often incorrectly referred to as polymorphic forms) have been identified [33], but only cellulose I and cellulose II are important in textile processing. Cellulose I is the form found in nature, and cellulose II (formerly, and misleadingly, called ‘hydrate cellulose’) is the thermodynamically stable form produced when cellulose is regenerated from solution or subjected in the solid state to the process of mercerisation (section 1.9.1). The main features of the crystal structures of the two forms were established in the 1930s by X-ray analysis [85,86]. They have been frequently refined during the intervening years, but some uncertainties in their precise details remain [33].

X-ray analysis alone proved insufficient to define the unit cells of cellulose I and II precisely, and more detailed information was obtained with the aid of electron diffraction and especially i.r. spectroscopy. The latter was used by Liang and Marchessault [87] to study the hydrogen-bonding system in cellulose I and this enabled them to conclude that the so-called ‘bent-chain’ model originally proposed by Hermans [88] was nearer the truth than the Meyer and Misch model. In the latter, the glycosidic bonds are in a plane perpendicular to the mean planes of the adjacent rings. In Hermans’ model, however, they are inclined at a small angle alternately positive and negative to these planes. The chain molecules are thus fully extended to the form of flat ribbons having the minimum possible thickness in the direction perpendicular to the mean planes of the rings. It should be possible to visualise this structure from Figure 1.12(a), but it is much easier to do so with the aid of skeletal atomic models.

The flat ribbons just described pack together into a monoclinic unit cell of dimensions approximately $a = 0.82$, $b = 0.79$, $c = 1.034$ nm (fibre axis) and $\gamma = 97°$ in the case of cellulose I. A cross-section of the cell in the *ab* plane, looking along the fibre axis, is shown in Figure 1.13(a). Originally Meyer and Misch believed that the centre and corner chains were antiparallel to one another, but the latest evidence [33,89] strongly favours the parallel arrangement with the centre chains staggered by approximately 0.25*c* (0.26 nm) with respect to the corner chains, as in Figure 1.14(a). Adjacent chains are held together in a system of hydrogen-bonded sheets in the *ac* planes as shown in Figure 1.15, alternate sheets being staggered with respect to each other in accordance with the arrangement indicated in Figure 1.14(a). Thus there are two interpenetrating sets of sheets, one comprising the corner chains and the other the centre chains. There is no hydrogen bonding between corner and centre chains. Furthermore, the surfaces of the sheets are hydrophobic, which means that they are held together by van der Waals forces.

Three features of the structure of cellulose I should be emphasised. Firstly, the chains are fully extended. Thus the repeat distance in the chain direction is equal to the length of two anhydroglucose units, i.e. one anhydrocellobiose unit. The degree of polymerisation is the average number of anhydroglucose units per chain molecule. Secondly, the unit cell parameters are stated according to the modern crystallographic convention for fibrous polymers [90,p.713]. Unfortun-

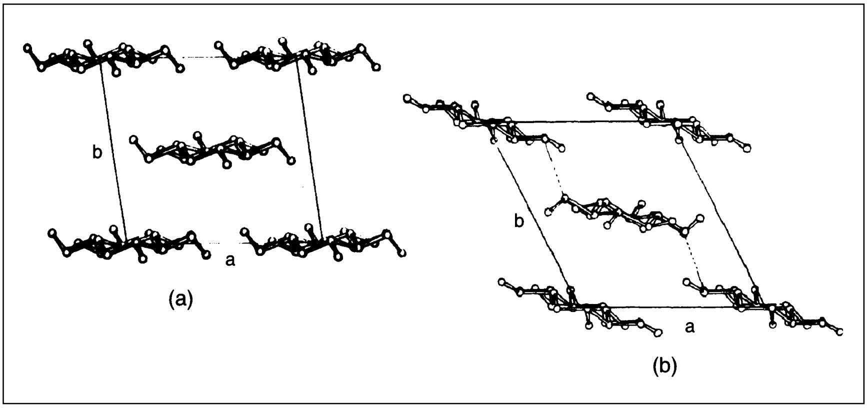
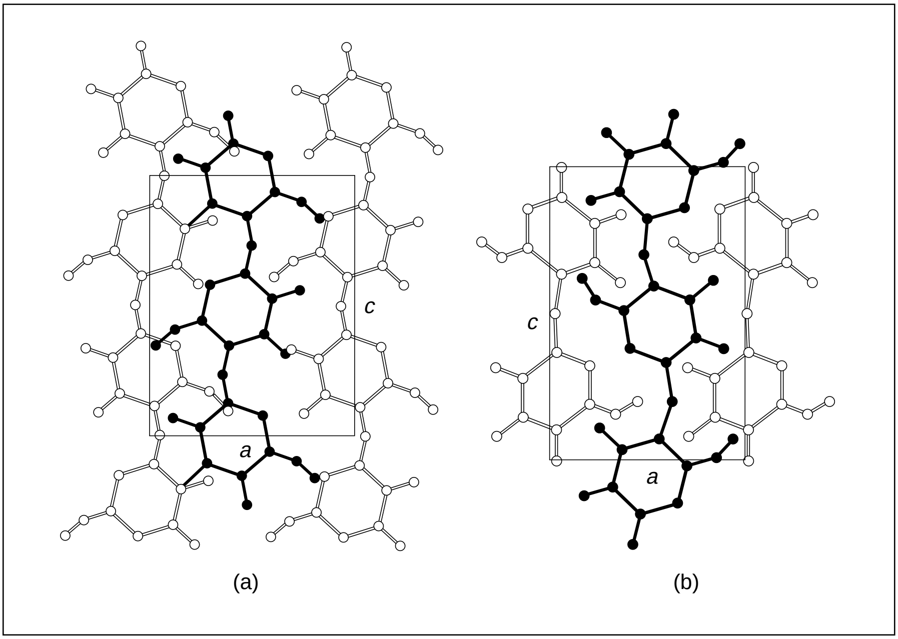


Figure 1.13 Cross-section of unit cell in the *ab* plane (looking along the fibre axis): (a) cellulose I; (b) cellulose II). (*Source:* [89].)



(a) (b)

Figure 1.14 Unit cell in the *ac* plane: (a) parallel-chain model of cellulose I; (b) antiparallel-chain model of cellulose II. (*Source:* [89].)

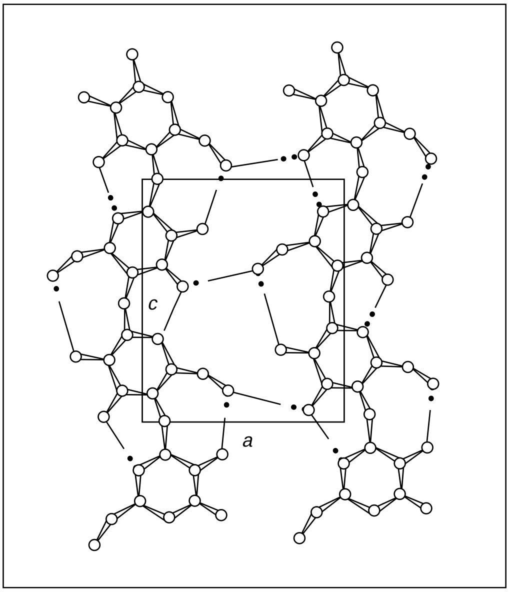


Figure 1.15 Hydrogen bonding in cellulose I. (*Source:* [89].)

ately in all the older papers, and even in some (e.g. [44]) of the current literature of cellulose structure, the fibre axis has been identified with the *b* direction; with this usage the parameters of the unit cell would be a = 0.82, b = 1.034 (fibre axis), c = 0.79 nm and $\beta\,(180° - \gamma)$ = 83°. Care must be taken to avoid confusion between the two conventions and it is much to be hoped that the older will soon die out. Lastly, the unit cell dimensions are quoted with a lower degree of precision than X-ray analysis is capable of achieving. This is because they are averages of values that may differ by as much as 1% between samples of cellulose from different sources.

The unit cell of cellulose II is also monoclinic, its average dimensions being a = 0.81, b = 0.91, c = 1.034 nm and γ = 117°. A cross-section in the *ab* plane is shown in Figure 1.13(b). The chain arrangement differs from that in cellulose I in two respects. Firstly, the planes of the glucose rings are inclined at a small angle to the *ac* plane. Secondly, the centre chains are oriented antiparallel to the corner chains. They are still staggered with respect to the corner chains in the *c* direction in the same way as in cellulose I, as Figure 1.14(b) shows. However, the hydrogen-bonding system is rather more complicated than in cellulose I. Not only are there hydrogen bonds in the *ac* planes between parallel corner chains and between parallel centre chains, but there are also hydrogen bonds between antiparallel corner chains and centre chains. Detailed illustrations of the system have been published [89], along with X-ray evidence for the antiparallel orientation of alternate chains. Such an arrangement would be expected in regenerated cellulose since there is no reason to suppose that the molecules would be other than randomly oriented in solution. It is more difficult to reconcile with the fact that cellulose I is converted into cellulose II by mercerisation (a process that does not involve dissolution of the material) but a plausible mechanism for the process has been proposed [33,91].

Chain folding in cellulose has been postulated [17,18], but the existence of a parallel-chain structure effectively disposes of the suggestion for cellulose I, since it is incompatible with any reasonable picture of the synthesis of cellulose in nature. It would also be difficult to reconcile with the low extensibility of native cellulosic fibres. The antiparallel arrangement in cellulose II is compatible with chain folding but it seems unlikely that the two forms would differ, especially since some regenerated cellulosic fibres have properties similar to those of cotton. Rejection of the folded-chain hypothesis for cellulose in fibrous form does not mean that chain-folded structures may not be formed under special conditions. For example, single crystals of cellulose triacetate containing folded chains can be obtained from solution in a mixture of nitromethane and butan-1-ol, and it is possible that some of the folds survive saponification [92]. Similarly, under suitable conditions, cellulose of moderate DP can be crystallised from solution in aqueous sodium hydroxide in folded-chain form [93].

Cellulose III is not itself important in textile applications, but is mentioned here because it sometimes results from treating cellulose with liquid ammonia or aliphatic amines (section 1.9.3). It has a monoclinic unit cell with the following dimensions: $a = 0.77$, $b = 1.00$, $c = 1.03$ nm and $\gamma = 122°$ [19].

1.4.3 Fine structure

A knowledge of the fine structure of cellulose is essential for a full understanding of dyeing processes since it is important to know precisely where a dye becomes attached to the fibre. It is generally accepted [77,94] that reagents cannot penetrate the crystalline regions unless they can simultaneously disrupt them. The nature of the less ordered, and therefore more accessible, regions of cellulosic fibres will now be discussed.

The subject is still somewhat speculative. As long ago as 1967 Statton [95] pointed out that theories and models of fine structure are no more than theories and models, and broadly speaking the same is true today. Nevertheless, these concepts are helpful in considering the dyeing of fibres. Howsmon and Sisson [7] had earlier visualised a range of degrees of order in the packing of chain molecules in a fibre, as illustrated in Figure 1.16. In this picture there is a continuous transition from perfectly crystalline to completely amorphous material, but it should not be assumed that such a transition is characteristic of all fibres. It is merely a hypothetical representation of what might exist.

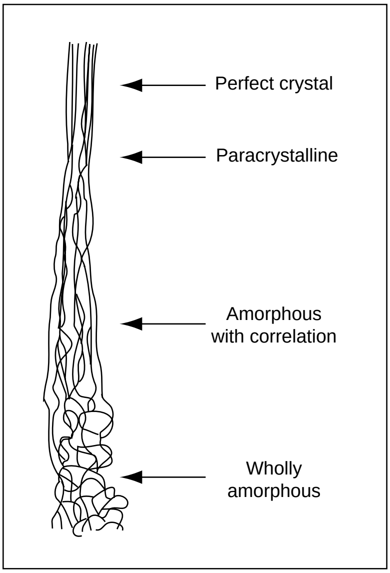


Figure 1.16 Diagram of packing of chain molecules (amorphous to crystalline). (*Source*: [7].)

In the case of cellulosic fibres the idea of fringed micelles, in which crystalline micelles are embedded in an amorphous matrix with individual chain molecules extending through several crystalline and amorphous regions, as in Figure 1.17(a), held sway for a long time. This subsequently gave way to the concept of fringed fibrils, in which the fringe molecules that constitute the non-crystalline

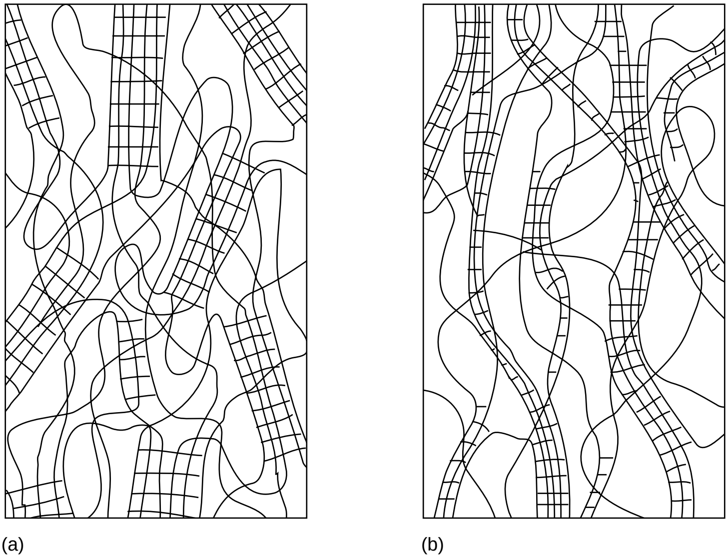


Figure 1.17 Diagram of fine structure in cellulose: (a) fringed micelles; (b) fringed fibrils. (*Source*: [44].)

regions emerge from various points along crystalline fibrils, as in Figure 1.17(b), rather than from the ends of brick-like micelles. These and other theories of fibre structure have been discussed by Hearle [96]. The fringed fibril concept is still applicable to many regenerated cellulosic fibres but the crystalline fibril concept (section 1.2.1) is usually reserved for cotton and other native fibres.

Ideally, the structure of a textile fibre should be capable of description in terms of the following five factors [75,97]: degree of order; degree of localisation of order and disorder; the length:width ratio of localised units; the size of localised units; and the degree of orientation of localised units. In practice these parameters are seldom capable of precise determination; measurements of accessibility (by chemical methods) and degree of crystallinity, orientation and crystallite size (by physical methods) are the most commonly encountered.

Physical methods of determining crystallinity

X-ray diffraction, i.r. spectroscopy and density measurements are the most important physical techniques for determining degree of crystallinity [98]. The X-ray method was pioneered by P H Hermans [99,100] and by Kast and Flaschner [101]. In essence it consists of separating the diffraction pattern of a fibre into its two components: that deriving from the crystalline and that from the non-crystalline regions of the cellulose. The original i.r. method of Mann and Marrinan [102] aimed at determining the proportion of hydroxy groups that did not exchange with deuterium oxide vapour during exposure for one hour, those that did being considered to be in the amorphous regions. This was done by comparing the spectra of the original and deuterated samples. A procedure not involving deuterium exchange has also been developed [20,103]. The density method [104] is based on the observation that the density of cellulose 'crystallites' (obtained by the vigorous acid hydrolysis of cotton) is 1.545 whereas that of amorphous cellulose (obtained by ball milling) is 1.505. The crystallinity is expressed as the ratio of the difference between the specific volumes of amorphous cellulose and the sample, and the difference between the specific volumes of amorphous and crystalline cellulose. Detailed descriptions of these physical techniques are outside the scope of this chapter.

Chemical methods of determining accessibility

Chemical methods of studying the fine structure of cellulose have been reviewed by Rowland and Bertoniere [34]. The measurement of accessibility has been popular with cellulose chemists for many years because it is simpler and less expensive than the physical methods for crystallinity. Ideally, $A = 100 - C$ where A is the percentage accessibility and C the percentage crystallinity. However, this simple relation is at best an approximation.

Essentially, the measurement of accessibility involves either measuring the equilibrium absorption of some species such as water or iodine, or measuring the rate at which cellulose is attacked by a chosen reagent. Equilibrium uptake is usually readily obtainable under convenient conditions. The rate method almost always entails distinguishing the rapid initial rate at which the accessible regions react from the slower rate characteristic of the crystalline regions. These reactions are frequently of the first order, so a semi-logarithmic time plot yields a straight line that can be extrapolated to zero time to give the 'crystallinity'. The trouble with chemical methods is that, although different reagents usually rank substrates in the same order, they give widely differing results for a given substrate. The reasons for this are fairly obvious. Firstly, if the fine structure of a fibre is relatively unaffected by the chosen reagent, the number of reaction sites accessible to the reagent must inevitably depend upon the size of the molecules. Secondly, if the fine structure can be altered by swelling or otherwise during the reaction the effects of different reagents will not be the same.

One of the most frequently used reactions for assessing accessibility has been acid hydrolysis. In one procedure, weighed samples of material are boiled with

4–6 M HCl for various times up to about 24 h [105]. Increasing quantities of material dissolve (section 1.5.2) and the proportions of undissolved residue are plotted logarithmically against time; Figure 1.18 illustrates how accessibility may be estimated. One drawback of this method is that some extra crystallisation seems to occur during the early stages of hydrolysis [106], so that the estimates of accessibility may be on the low side. It may be noted that in practice $c_o + a_o < 100$.

If all that is required is to rank substrates in order of accessibility, by far the simplest method is to compare their moisture regain values (section 1.7.1). Valentine has shown that the sorption ratio (SR), defined as the ratio of the moisture regain of the sample to that of purified cotton under standard conditions of humidity and temperature, is directly proportional to the fraction of non-crystalline material (F or F_{AM}), as measured by the i.r. method of Mann and Marrinan: SR = $2.60F_{AM}$ [98]. For many purposes this is adequate.

Nevertheless, a more detailed picture of the fine structure of cellulose can be obtained by what has been termed chemical microstructural analysis (CMA) by workers at the Southern Regional Research Center of the US Department of Agriculture, who have used it extensively [34]. The method was pioneered at the Shirley Institute [51,107,108] and entailed the methylation of cotton by a succession of treatments with diazomethane in water-saturated ether. Total hydrolysis of the products yielded the seven possible mono-, di- and trimethylglucoses and their proportions were measured by gas–liquid chromatography. Hence the relative accessibilities of the three hydroxy groups in

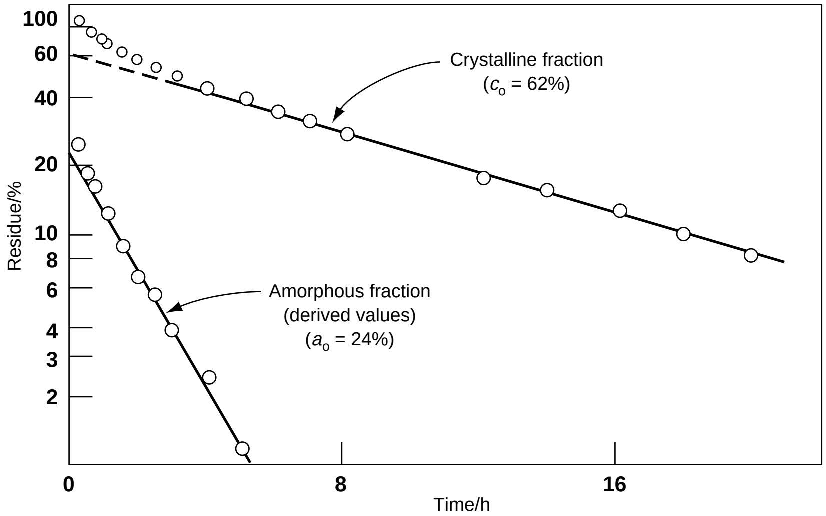


Figure 1.18 Hydrolysis of regular viscose in 4 M HCl at 100°C. Extrapolation of curves gives the amorphous (a_o) and crystalline (c_o) fractions in the untreated fibre. (*Source*: [105].)

each anhydroglucose unit were determined and conclusions were drawn about the structure of the elementary fibrils. Rowland and coworkers [34,109] did similar experiments with *N*,*N*-diethylaziridium chloride (DAC), which introduces *N*,*N*-diethylaminoethyl groups, $(C_2H_5)_2N–CH_2CH_2–$, into the cellulose, and have suggested that these methods may well provide an insight into the supramolecular structure of cellulose that is not forthcoming from physical measurements.

Orientation

In the context of fibre structure, the term 'orientation' means the average alignment of either chain molecules in non-crystalline materials or crystallites in partially crystalline materials with respect to the fibre axis. Methods of measurement will be discussed only briefly here; more detailed accounts are readily available [44,98,110,111].

The earliest, and perhaps simplest, method was to measure the optical birefringence, i.e. the difference between refractive indices for light polarised parallel and perpendicular to the fibre axis. Hermans [104] has called the ratio of this difference to the difference for a perfectly oriented specimen the optical 'orientation factor' f, and has shown that for specimens of equal density it is given by Eqn 1.2, where θ is the average angle at which molecular chains are inclined to the fibre axis:

$$f = 1 - \frac{3}{2}\sin^2\theta \qquad (1.2)$$

Polarised i.r. spectroscopy [112] has also been used to measure the orientation factor. The method depends on the absorption of radiation by a particular chemical group in the chain molecule. Only groups that behave as oscillating dipoles absorb i.r. radiation and only the component of the oscillations parallel to the electric vector is effective. Thus, if polarised radiation is used, maximum absorption will occur when the dipole vibrates parallel to the electric vector (i.e. at right angles to the plane of polarisation) and absorption should be zero perpendicular to the electric vector. It must be remembered, of course, that the vibrations of a particular group in a fully extended chain molecule are unlikely to be parallel to the axis of the chain. In practice, the ratio of the intensities of a chosen polarised i.r. absorption band parallel and perpendicular to the fibre axis is taken as a measure of the average angle between chains and the axis. Although it is quite a powerful method, Krässig [112] prefers the X-ray method, particularly for regenerated fibres, because of its simplicity and reliability.

The X-ray diffraction pattern of a perfect crystal consists of an array of sharp

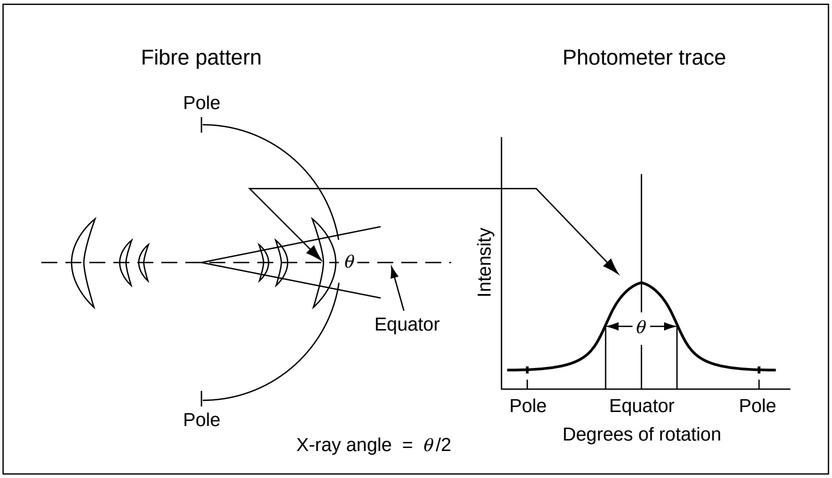


Figure 1.19 Procedure for measuring 50% X-ray angle. (*Source*: [111].)

spots, but with a fibre the reflections nearly always take the form of arcs. The lengths of the arcs are directly related to the average orientation of the crystallites with respect to the fibre axis [113]. Short arcs indicate a well-oriented material, long arcs a less well-oriented material, and complete circles (as in a powder diagram) random orientation. The commonest procedure is to select one of the equatorial arcs and to measure the angles at which the intensity is 50% of the maximum value. The arithmetic mean of these two angles is known as the '50% X-ray angle' as illustrated in Figure 1.19. From its value for two different reflections it is possible to calculate the average angle θ between the chains and the fibre axis. The X-ray orientation factor may then be obtained from Hermans' equation (Eqn 1.2).

The orientation factor of ramie (the most highly oriented natural cellulosic fibre) has been found to be 0.97, and that of regular viscose rayon 0.79, by this method [104].

Crystallite size [110,111]

Whereas the length of arcs in an X-ray fibre diagram is determined mainly by the orientation of the ordered material, their width depends on the dimensions of the crystallites. The smaller the crystallite, the broader the X-ray reflection, in accordance with Scherrer's equation [90,114] (Eqn 1.3):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1.3}$$

where D is the dimension of the crystallite perpendicular to the diffracting plane, β the broadening of the arc in radians, λ the wavelength of the X-rays and θ the Bragg angle. The correlation is by no means perfect because other factors influence the arc broadening to some extent, but this method is probably the one most often used to estimate crystallite size. It depends on the same wide-angle scattering as is used for a determination of unit-cell dimensions and can be applied to both the length and the width of crystallites. Another technique, based on low-angle scattering, has been developed, but it is difficult experimentally and its theoretical basis is somewhat uncertain.

A more direct method of estimating crystallite size is to break the material down into its crystallites and examine it in the electron microscope. This is more successful for native than regenerated cellulosic fibres. One difficulty is to be certain that the entities isolated by disintegration of the material are the same as the crystallites originally present.

Chemical methods such as chemical microstructural analysis (p.23) have been used effectively, and the length of crystallites has sometimes been identified with the levelling-off DP when the material is subjected to acid hydrolysis (section 1.5.2).

1.5 DEGRADATION OF CELLULOSE

1.5.1 Introduction

An industrially important feature of cellulosic fibres is chemical stability, enabling them to withstand degradation with its consequential loss of tensile strength under normal conditions of use. Even slight degradation during processing, however, may be accompanied by unacceptable loss of strength and other undesirable effects. The study of degradation, therefore, has important implications for satisfactory dyeing and finishing. Six different degradative agencies have been identified: acids, alkalis, oxidising agents, enzymes, heat and radiation [30]. Under certain circumstances cellulose can also be degraded mechanically, but this is never a problem in industrial processing.

Ultimately the complete degradation of cellulose yields carbon dioxide and water. However, it is the early stages of partial degradation that are important in the textile field. Only slight changes in composition may affect the physical properties of cellulose profoundly, sometimes even reducing it to powder. The water-insoluble products of the action of acids and oxidising agents are still frequently referred to by the traditional trivial names of ‘hydrocellulose’ and ‘oxycellulose’ respectively [115–117].

The constitutions of partially degraded celluloses, though difficult to determine precisely and unequivocally, have been greatly illuminated by the methods perfected (though not originated) by Clibbens and his collaborators [118]. To study the effects of a particular degrading agent, a series of progressively modified materials is prepared and characterised by measuring properties related to DP, such as tensile strength and fluidity in cuprammonium hydroxide (section 1.8.2), and to content of carboxy and carbonyl groups. Methods selected from the enormous variety available have been described in detail [119].

Except for the determination of uronic acid groups by decarboxylation with boiling 12% hydrochloric acid [120], all methods of determining carboxy groups depend on exchange between cations in solution and the solid carboxy-containing material in its free-acid form. The essential features of each method are the means adopted to ensure that the equilibrium in Scheme 1.2 is as far to the right as possible, and the analytical procedure for measuring the quantity of cations exchanged.

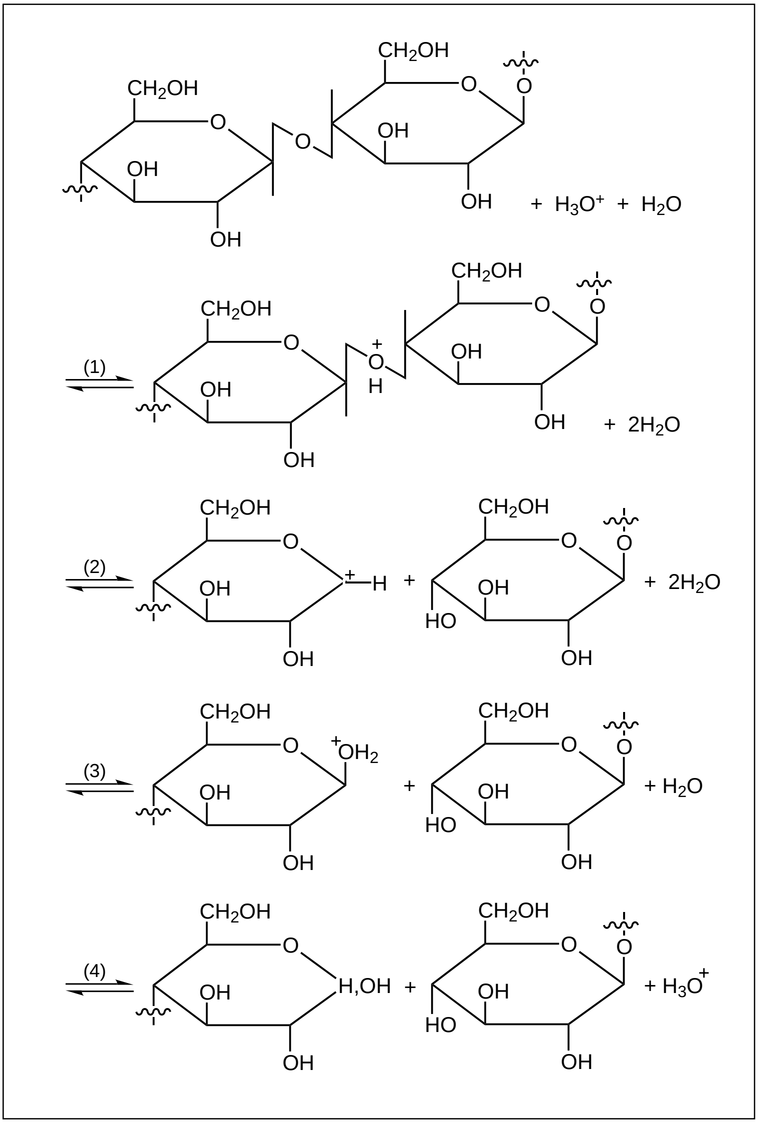
$$R_{cell}\,COOH + M^+ \rightleftharpoons R_{cell}\,COOM + H^+$$

Scheme 1.2

Several types of carbonyl-containing group may be found in chemically degraded cellulose, notably aldehyde, ketone and hemiacetal groups. For many years the only method of assessing them was the empirical measure known as the copper number. This was first introduced by Schwalbe [121] and is defined as the weight in grams of Cu(II) in alkaline solution reduced to Cu(I) at the boiling point by 100 g of dry material. The amount of Cu(II) reduced per carbonyl group varies greatly with the precise nature of the group and its position in the chain molecule. For example, the end group in a hydrocellulose reduces 22 atoms of copper [122]. Thus the copper number is a highly sensitive measure of reducing groups, even though it can seldom be related stoichiometrically to the content of such groups. It can provide valuable confirmation that a substrate is devoid of reducing groups; thus the copper number of scoured cotton is normally close to zero. Methods involving condensation reactions with hydroxylamine or sodium cyanide, or reduction to alcohol groups with sodium borohydride, have been fully described [119] and are claimed to give stoichiometric results.

1.5.2 Degradation by acids

The degradation of cellulose by aqueous acids entails acid-catalysed hydrolysis of the glycosidic linkages according to Scheme 1.3 [123,124].



Scheme 1.3

The properties of the hydrocellulose so formed depend solely on the number and distribution of glycosidic linkages broken, which vary with acid concentration, temperature and time of treatment. The identity of the acid is irrelevant and thus the tensile strength, copper number and fluidity of a hydrocellulose are uniquely related to one another, irrespective of how the hydrocellulose has been made [125]. The products of the early stages of hydrolysis are fibrous, but those with fluidities above about 44 rhes are usually powders. The rate of increase of fluidity depends on the supramolecular structure of the cellulose (Figure 1.20). Eventually the fluidity reaches a plateau, at a level depending on the nature of the starting material [126]. The degree of polymerisation calculated from one of these plateaux is often called the levelling-off degree of polymerisation (LODP).

Even when the DP has become constant, the material continues to lose weight if the acid treatment is continued. Once the readily accessible bonds have been randomly hydrolysed, further reaction occurs at chain ends in the previously inaccessible regions of the fibres (often regarded as the 'crystallites'). This slow terminal hydrolysis removes small stable fragments from chain ends and produces no noticeable effect on the average DP. It has been shown that, if the accessible regions involved in the first stage of the reaction are randomly distributed along the microfibrils of the original cellulose, an exponential distribution of crystallite lengths will result from hydrolysis and a constant particle-size distribution will be maintained as terminal degradation continues [21,127].

When cotton is treated with a dilute solution of hydrogen chloride in an aprotic solvent (e.g. benzene), the rate of hydrolysis is much more rapid than with aqueous acid of the same concentration. This is because the hydrogen

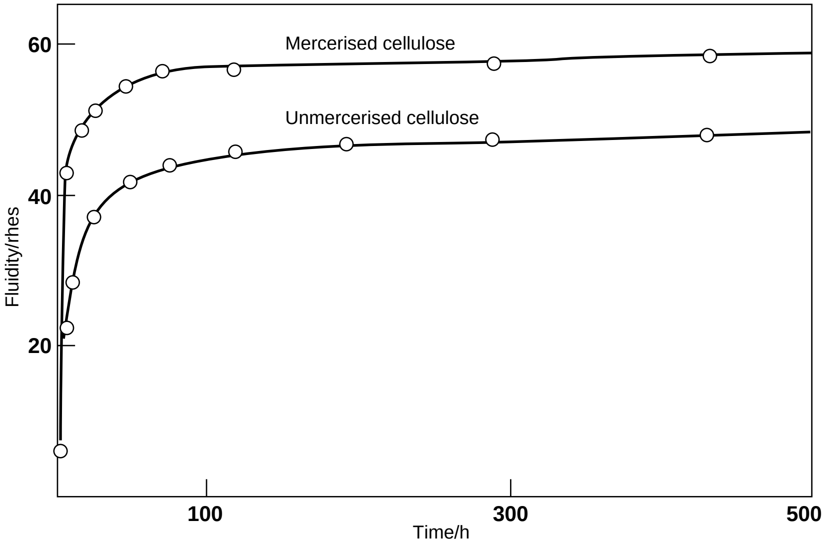


Figure 1.20 Acid hydrolysis of mercerised and unmercerised cellulose at 20°C. (*Source*: [6,p.136].)

chloride is abstracted from the solvent by the regain moisture in the cotton to give a highly concentrated aqueous solution of hydrochloric acid in close contact with the fibres [128].

For many years there was considerable controversy as to whether cellulose contained 'weak bonds', i.e. glycosidic bonds capable of being hydrolysed more rapidly than normal completely accessible 1,4-β-glucosidic linkages. Three possible causes of such acid sensitivity have been identified [21]:

(1) The presence of electron–attracting groups at points in the chain molecules where they might 'activate' nearby glycosidic bonds.
(2) The presence of occasional 'rogue' chain units (e.g. anhydroxylose units in place of anhydroglucose units).
(3) The existence of a few glycosidic bonds that are more readily hydrolysable because they are under exceptional physical stress.

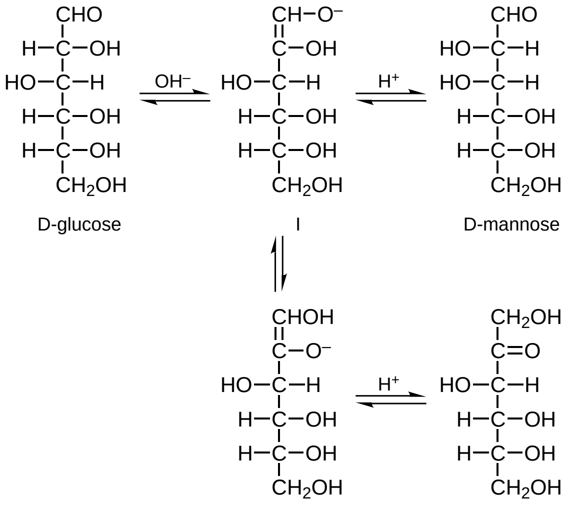
The first possibility probably applies to wood pulp, which often contains a few aldehyde groups introduced during pulping, but it does not apply to cotton. The second possibility is unlikely to apply to any reasonably pure form of cellulose; the xylose and mannose occasionally found among the soluble hydrolysis products of cellulose probably arise from non-cellulosic minor components of the starting material. The third possibility has been firmly established as applicable to native cellulose, hydrolysis rate constants 10^4 times greater than normal having been observed in the very early stages of the reaction [21,129]. The present situation has been summarised elsewhere [30,p.227].

1.5.3 Degradation by alkalis

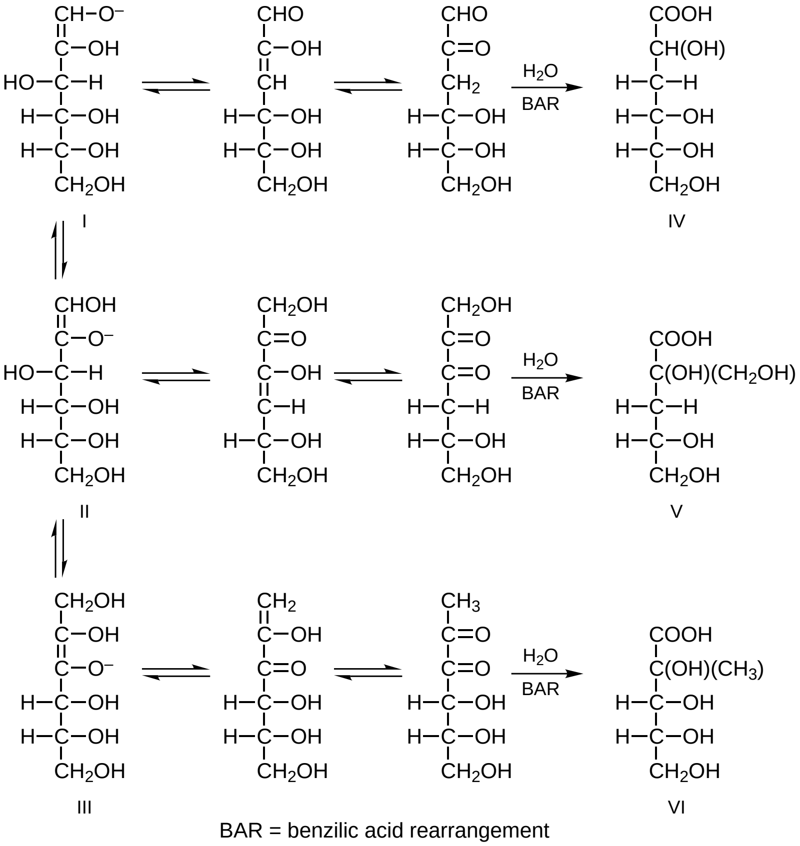
The glycosidic linkages in cellulose are not attacked by alkali at temperatures lower than about 170°C. However, the preparation of cellulosic textiles for dyeing frequently includes hot alkaline treatments that cause greater weight loss than can be accounted for by the removal of non-cellulosic substances. In the now obsolescent process of kier boiling, where temperatures as high as 140°C might be reached, weight losses of up to 4% might occur owing to dissolution of cellulosic fragments. Davidson [130] first recognised that these losses were caused by the stepwise removal of anhydroglucose units from the reducing ends of the cellulose chains, and Kenner and his collaborators later elucidated the mechanism [22,30,p.231]. They made a systematic study of the alkaline decomposition of O-substituted glucose derivatives, showing conclusively that Isbell's mechanism for the formation of deoxyaldonic acids (formerly known as saccharinic acids) by the action of alkali on glucose could be applied to the alkyl ethers of sugars and to polysaccharides [131]. The work was extended later to hydrocelluloses, which differ chemically from cellulose solely in their content of reducing end groups.

The first effect of cold dilute alkali on glucose is to convert some of it into mannose and fructose (Scheme 1.4). The formation of an equilibrium mixture of the three sugars was discovered by Lobry de Bruyn and Alberda van Ekenstein [132,133]. If the action of alkali is prolonged, more profound changes occur, leading to the production of three isomeric deoxyaldonic acids (IV, V and VI in Scheme 1.5) by elimination of the hydroxy group attached to the carbon atom next but one to that carrying the negatively charged oxygen in the intermediate ions I, II or III. The process has therefore been called 'β-hydroxycarbonyl elimination'. It is immediately followed by a benzilic acid rearrangement (so-called because of the alkaline conversion of benzil to benzilic acid and designated here as BAR) of the resulting dicarbonyl compound. When the hydroxy group has previously been alkylated, elimination of the alkoxy group occurs by the same mechanism but more rapidly. It is then known as 'β-alkoxycarbonyl elimination'.

The mechanism of the terminal alkaline degradation of cellulose can now be formulated (Scheme 1.6). The reducing end group is first converted to a fructose residue which, having a carbonyl group in the β-position with respect to the glycosidic bond, becomes detached from the end of the chain and appears in solution as 3-deoxy-2-*C*-(hydroxymethyl)pentonic acids (isosaccharinic acids, V). At the same time a new end group is exposed and then removed by the same process. This erosion of end groups, often known as the 'peeling reaction', would



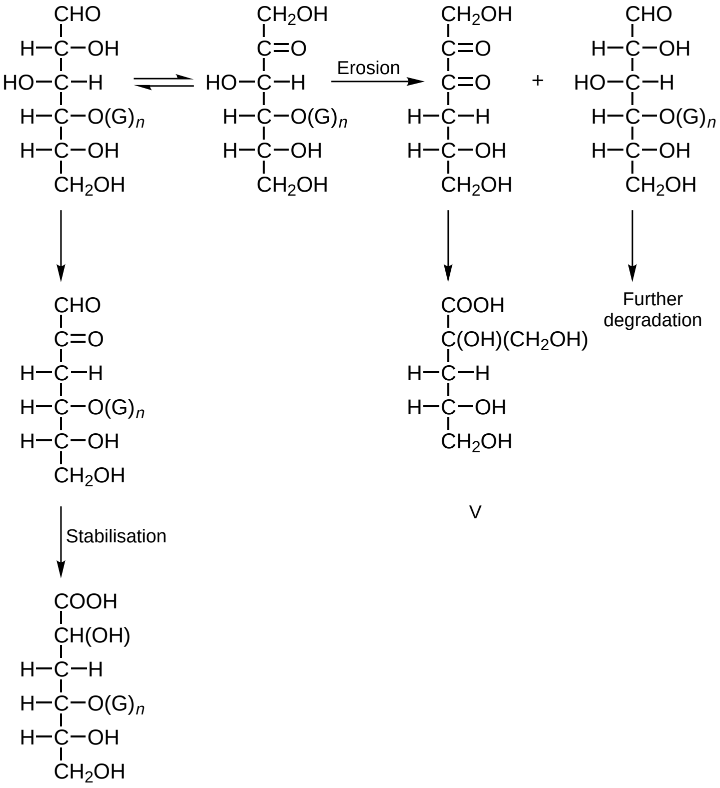
Scheme 1.4



Scheme 1.5

continue until all the material had dissolved unless some other process intervened to stop it. The fact that cellulose and hydrocelluloses show only limited weight loss on boiling with alkali means that some such 'stopping reaction' must occur. It has in fact been identified as β-hydroxycarbonyl elimination of OH from C3 in the reducing end group, converting it into a 3-deoxy-D-hexonic acid (metasaccharinic acid IV) residue still attached to the cellulose chain at C4 (VII). This end group is stable to alkali, which explains why native cellulose that has been purified by some form of alkaline treatment has acidic rather than reducing end groups.

Scheme 1.6 represents only the main reactions of cellulose with dilute alkali. Even at temperatures encountered in textile processing some other reactions occur, and above 170°C there is also considerable random chain scission [30,p.237].



VII

Scheme 1.6

1.5.4 Degradation by enzymes

The enzymic degradation of cellulose forms an essential part of the carbon cycle by which life on Earth is sustained. It is also one of the means by which, possibly in the not too distant future, cellulose may be exploited as a renewable source of industrial chemical feedstocks [35,134,135].

Biodeterioration of textiles is a serious problem and much effort has gone into methods of prevention. If damp cotton is exposed to air, mildew may gradually develop on it, accompanied by staining that is difficult or impossible to remove. Prolonged exposure also causes a serious loss of tensile strength, but little depolymerisation occurs. The tendering of cellulosic textiles by moulds and bacteria is thus easily distinguishable from that caused by acids even though both are due to the hydrolysis of glycosidic linkages [8]. The difference arises because the micro-organisms act on localised sites that are rendered soluble in water, leaving most of the cellulose unchanged.

Studies of degradation using cell-free enzyme preparations have proved difficult to interpret with certainty, although the mechanism of the process is now understood in broad outline [23,36,124,136]. Many cellulases extracted from fungi hydrolyse native cellulose only to a limited extent unless it has been rendered more accessible by some form of swelling treatment (e.g. mercerisation). Until recently certain extracts, notably those of *Trichoderma viride* and *Trichoderma koningii*, were thought to contain an 'activating' enzyme that rendered the cellulose molecules more accessible to the hydrolysing enzymes. The concept of a specific decrystallising enzyme has now been replaced by one of synergism between the component enzymes of the cellulase complex.

Unlike the undigested residue of fungal attack, cellulose that has been immersed in an active cellulase extract has a reduced DP, but for a given weight loss the DP reduction is less than would have been caused by acid hydrolysis [136]. Thus enzymolysis does not occur randomly. It is not confined to the ends of chains, however, but it does occur more readily there, removing soluble oligosaccharide fragments.

1.5.5 Oxidative degradation

Since each intermediate unit in a cellulose molecule contains three hydroxy groups, the number of possible oxidation products is considerable. End groups can also be oxidised and this may be important if primary oxidation is accompanied by chain scission, as often happens when the reaction occurs under alkaline conditions. Moreover, only a small proportion of a cellulose fibre is readily accessible to most oxidising agents, which therefore react rapidly at first and then very much more slowly. The action of most oxidising agents is non-specific and complex, and it is frequently impossible either to elucidate its mechanism or to determine precisely the constitution of the oxycelluloses produced. Nevertheless, a wealth of useful information has been obtained by the method of measuring the properties of series of oxycelluloses obtained with a variety of oxidising agents (section 1.5.1). When this method was extended to a study of periodate oxidation, where both the mechanism of the reaction and the constitution of the oxycelluloses have been satisfactorily elucidated, relationships between properties and constitution were recognised that could be used to explain the behaviour of other oxycelluloses by analogy. Only a brief account of the oxidation of cellulose will be given here as a recent comprehensive review is available [30,p.243].

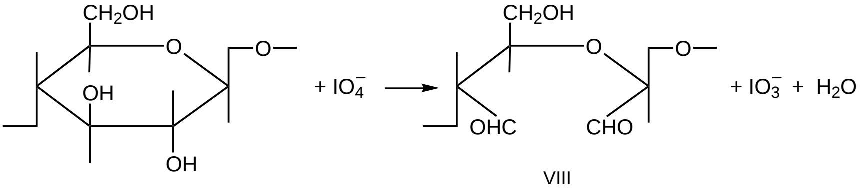
Some of the most important early work was done with sodium hypochlorite [137,138] when this was the main bleaching agent for cotton, because it was necessary to find the cause of the excessive tendering that sometimes used to occur. The work led directly to the practice of adding sodium carbonate to bleach liquors, maintaining a pH of 10–11 to minimise the formation of reducing groups. These impair both the stability of bleached cotton on storage and its resistance to damage during laundering. The rate of oxidation was found to be at a maximum at pH 7, and later work [139] showed that the ratio COOH:CHO:CO was 2:7:9 at pH 5, but 5:1:0 at pH 10.

Hydrogen peroxide is now the preferred bleaching agent for cotton. It is used in aqueous sodium hydroxide containing sodium silicate and stabilised against spontaneous decomposition catalysed by metal ions such as Fe(II) or Mn(II) by the addition of small quantities of Mg ions. As a bleaching agent it is generally regarded as 'safe', but of course if proper conditions are not maintained it can damage the cloth. Chemically, the oxidation of cellulose by alkaline peroxide and that by oxygen in the presence of alkali are similar. Carboxy groups and a few reducing groups are produced, and some depolymerisation occurs. The reaction is catalysed by transition metal ions and almost certainly involves peroxide radicals [140–142]. The oxidation of cellulose by atmospheric oxygen constitutes the process of 'ageing' to which wood pulp must be subjected to reduce its DP to a level suitable for the production of viscose (section 1.2.3). The simultaneous production of carboxy groups explains why viscose fibres contain more of these groups than purified cotton.

Another safe bleaching agent for cellulose is acidified sodium chlorite ($NaClO_2$). Only in highly concentrated solution does it cause significant oxidation, and then the active species is chlorine dioxide formed by the decomposition of chlorous acid [143]. Chlorite bleaching is declining in favour of peroxide-based methods, probably for commercial reasons.

A curious phenomenon is observed when a cellulosic fabric is suspended vertically with its lower end dipping in water. The fabric acts as a wick and, in the presence of air, a brown line develops at the height to which the water rises [144–146]. The presence of acidic and reducing groups may be detected by qualitative tests. If air is rigidly excluded no brown colour appears, but the acidic and reducing groups are still formed. Presumably, the reducing groups are formed by hydrolysis arising from increased acidity at the wet–dry boundary and then carboxy groups are formed from them in a Cannizzaro-type rearrangement. The brown colour may be due to atmospheric oxidation of the primary products. These explanations are speculative, but the effect itself sometimes has unfortunate practical consequences. For example, brown lines have been found in window curtains that have been wetted by rain from time to time over several years [147].

The oxidation of cellulose by sodium metaperiodate ($NaIO_4$) is of particular interest because it adheres closely to the mechanism that operates with all vicinal diols and it is not confined to the readily accessible regions of the fibres; once they have been oxidised, the reagent slowly penetrates the entire crystalline regions [148,149]. Thus oxycelluloses with a constitution VIII may be prepared (Scheme 1.7).

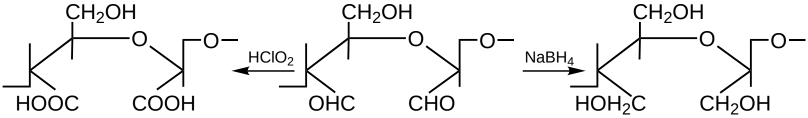


Scheme 1.7

One of the most notable features of these oxycelluloses is their extreme susceptibility to degradation by alkali, which arises from their containing a β-alkoxycarbonyl group (section 1.5.3). When the aldehyde groups are oxidised with chlorous acid to carboxyl groups [150] or reduced with sodium borohydride to primary alcohol groups [151], as shown in Scheme 1.8, stability to alkali is restored [30,p.250].

Thus the periodate oxycelluloses provide an extreme example of latent tendering (section 1.8.2). Even though little chain scission occurs during oxidation, periodate oxycelluloses have very high fluidities in cuam because of the alkalinity of the solvent. However, when their aldehyde groups are either oxidised or reduced, their fluidities fall. They never revert completely to the fluidity of the original cellulose, probably because of degradative side reactions during the periodate oxidation.

The tensile strength of cotton is reduced by periodate oxidation because of the formation of hemiacetal crosslinks between aldehyde and hydroxy groups in adjacent chain molecules (section 1.6.5) [152].



Scheme 1.8

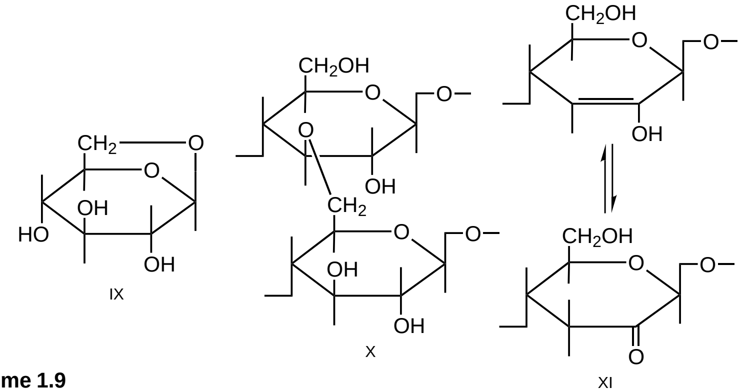
Another reagent that can penetrate cellulose crystallites is dinitrogen tetroxide (N_2O_4). Although its main effect is to produce uronic acid groups (carboxy groups at C6) it also produces both ketone and aldehyde groups [30,p.253]. Materials containing about 2% by weight of carboxy groups have been found to clot blood and then to dissolve in it slowly. They have therefore been produced as absorbable haemostatic dressings for certain post-operative conditions where other methods of arresting the flow of blood are not appropriate [153].

1.5.6 Degradation by heat

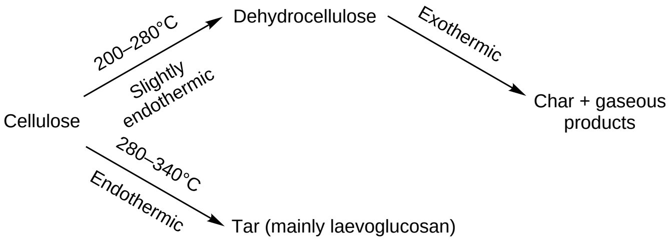
Cellulose can be heated for many hours up to about 120°C without any serious deleterious effect. In dry air at higher temperatures, however, considerable depolymerisation takes place, accompanied by the formation of carbonyl and carboxy groups in the solid material, the evolution of water, carbon monoxide, and carbon dioxide, and a loss of tensile strength [34,154,155].

The formation of aldehyde groups in cellulose renders it inherently unstable. Cotton that has been overbleached with hypochlorite under acid or neutral conditions goes yellow on storage, even in the dark at room temperature. Viscose fibres always contain a small number of reducing groups arising from the ageing of the alkali cellulose during manufacture. These groups can cause yellowing problems in the dyeing of pastel shades by a continuous thermofixation process. Periodate oxycelluloses, which have large numbers of aldehyde groups, go yellow or brown rapidly on heating to 100°C, but prior reduction of these groups with borohydride inhibits yellowing. The yellow substance can be extracted with boiling 5% sodium bicarbonate. The visible and u.v. absorbance of the extract can be correlated with the aldehyde content of the material and the yellow substance has been tentatively assigned the structure of a β-diketone [156,157].

At about 250°C pyrolysis to numerous products becomes significant, and these have been extensively studied over many years because of the fire hazard associated with cellulosic textiles [34,155,158]. The most important solid product is laevoglucosan IX (Scheme 1.9) and among the volatile products are water, hydrogen, methane and other hydrocarbons, carbon monoxide, carbon dioxide and glyoxal. In a much simplified picture, pyrolysis may be represented as occurring by two paths, namely dehydration and laevoglucosan formation (Scheme 1.10). Dehydration, which is slightly endothermic, probably leads to the formation of intra- and intermolecular ether linkages, the latter constituting a form of crosslinking (X in Scheme 1.9). The formation of unsaturated rings tautomeric with 2-keto-3-deoxyanhydroglucose units (XI in Scheme 1.9) may also occur. The complex mixture is sometimes referred to as 'dehydrocellulose'; it



Scheme 1.9



Scheme 1.10

decomposes further exothermically yielding gaseous products and a mass of carbon known as ‘char’. Many of the gaseous products are inflammable and the char glows in the presence of air, being slowly converted to carbon dioxide. The other pyrolysis pathway results in the formation of tar, the main constituent of which is laevoglucosan. This reaction is strongly endothermic and occurs to a greater extent than dehydration at higher temperatures. It is evident that the search for flame retardants for cellulose must be for reagents that will increase the amount of laevoglucosan formed at the expense of dehydration.

1.5.7 Degradation by radiation

In practice, the most important type of photochemical degradation that can affect cellulose is that caused by visible and near-u.v. radiation. This must, of necessity, be a photosensitised reaction since the radiation itself is not sufficiently energetic to disrupt the molecule. The energy needed to cleave C–C or C–O bonds in cellulose is about 330–380 kJ mol^{-1}, from which it can be calculated that, to be effective, radiation must have a wavelength less than about 340 nm

[24]. Since the visible region of the spectrum is roughly between 400 and 800 nm, it is not surprising that pure cellulose is scarcely affected by daylight. However, in the presence of oxygen and a photosensitiser considerable degradation occurs and this is enhanced by the presence of moisture. The oxycellulose formed is of the alkali-sensitive type and can be particularly objectionable in curtains or other domestic textiles. Although light exposure alone lowers the tensile strength very little, serious loss may occur on subsequent laundering. Incidentally, this is why it is often recommended that curtains should be dry cleaned.

The most important group of photosensitisers includes the yellow, orange and red vat dyes, but sulphur and basic dyes in the same colour range and certain metallic oxides, such as those of zinc and titanium, are also active. Their action is complex and has been extensively discussed [24,37]. Many years ago, Egerton [9,159–161] showed that undyed cotton threads placed as far as 8 mm away from dyed threads exposed to sunlight in a moist atmosphere were themselves degraded (Figure 1.21). Egerton concluded that some form of 'activated' oxygen

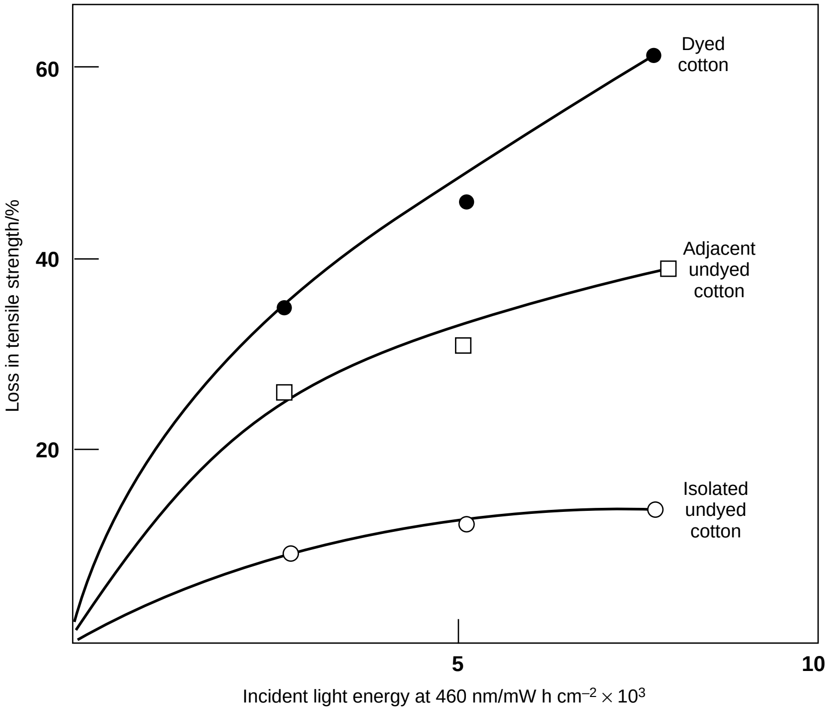


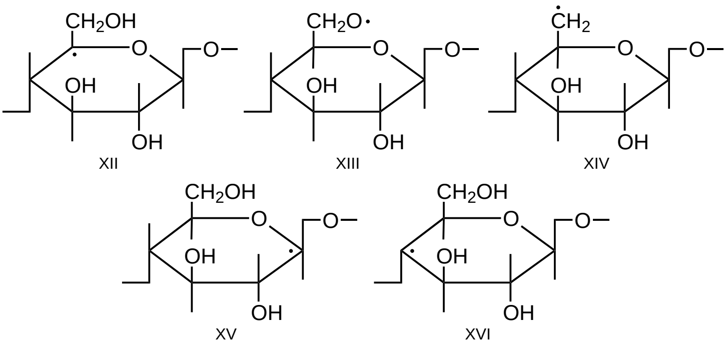
Figure 1.21 Photodegradation of cotton yarn sensitised by Cibanone Orange R (SCI CI Vat Orange 21) by sunlight in air at 100% r.h. (*Source*: [9].)

must be involved and that either this species itself or hydroxyl radicals derived from its reaction with water caused the degradation. He later [162] attributed degradation to singlet oxygen, but this has been strongly disputed [37].

The direct photolysis of cellulose is a simpler reaction than photodegradation, but it is only brought about by u.v. radiation of shorter wavelength than is encountered by textiles in normal use. For research purposes, a quartz mercury-vapour lamp giving monochromatic radiation of wavelength 253.7 nm is frequently used. In contrast to photosensitised degradation, direct photolysis is unaffected by the presence of oxygen and is inhibited by vat dyes and by water. An interesting feature is that this degradation may continue in the dark for several weeks after irradiation has ceased, at a rate that increases with storage temperature.

Some mention must be made of the effect of ‘high-energy radiation’ (also called ‘ionising radiation’) on cellulose. These terms usually refer to X-rays or γ-rays, but they also include β-rays and other high-speed electrons, α-rays and neutrons. Much work has been done with γ-radiation from cobalt-60. One effect is the formation of free radicals that are remarkably stable in the presence of moisture. Radicals have been detected by electron spin resonance (e.s.r.) spectroscopy as long as seven years after exposure of cotton to γ-rays. Since the spectrum consists of a triplet with a signal strength ratio of approximately 1:2:1, the radicals may have structures XII, XIII or XIV (Scheme 1.11), but confirmatory evidence is not available [25,37].

The e.s.r. spectrum of cellulose that has been irradiated dry consists of an intense but short-lived single line which is more easily explained as arising from the species XV or XVI (Scheme 1.11). These would be expected to lead to depolymerisation; this has been observed, together with the formation of



Scheme 1.11

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carbonyl and carboxy groups, in γ-irradiated cellulose. Small quantities of carbon monoxide and carbon dioxide are also produced.

1.6 DERIVATIVES

1.6.1 Introduction

Any macromolecular product of the reaction of cellulose with another substance may properly be described as a derivative. However, the term is usually confined to esters, ethers and similar products. The chemistry of the esters and ethers of cellulose is now outlined, including graft copolymers and crosslinked derivatives, which often fall into one or other of these classes.

The intermediate chain unit of cellulose contains three hydroxy groups capable of forming derivatives. The degree of substitution (DS) of a derivative is the fraction of hydroxy groups that have reacted, and can therefore have any value between 0 and 3. It does not define a derivative uniquely, however, because the pattern of substitution is seldom uniform. Spurlin [10] has defined the highest possible degree of uniformity as that resulting from a reaction in which every unit in the cellulose chain is equally accessible to the reagent. This definition takes no account of the differing reactivities of the three hydroxy groups. It is generally accepted that the primary alcohol group at C6 is usually much more reactive than the secondary groups at C2 and C3, but the relative rates differ from one reaction to another. Thus the reactivity ratio of primary to secondary alcohol groups is much higher for acylation with the bulky tosyl (*p*-toluenesulphonyl) group than with the small acetyl group. The overall relative reactivities of the three hydroxy groups under heterogeneous conditions are determined by the combined effects of three factors: their inherent chemical reactivity, steric effects arising from the size of the entering group, and steric effects arising from the supramolecular structure of the cellulose. In most reactions the reactivity decreases in the order C6 ≥ C2 ≥ C3. As a consequence of these differences, many different derivatives having the same average DS may exist. They may differ in distribution of substituents both within a single chain unit and along the length of the chain molecules. The properties of derivatives, especially their solubilities and their mechanical properties in the solid state, depend strongly on the distribution of substituents and on the DP, which is often reduced by degradation during derivative formation. Some depolymerisation is desirable in most commercial products, but its extent needs to be carefully controlled.

Although interest in cellulose derivatives lies mainly in their industrial applications, it must not be forgotten that they have played an important role in the establishment of the chemical structure of cellulose [30,82]. Direct acid hydrolysis is unsatisfactory for structural studies, partly because the glucose produced is often subject to further change under the conditions employed. Instead, derivatives (particularly methylcellulose) have been prepared under non-degradative conditions and subjected to either hydrolysis or methanolysis. The products of the complete hydrolysis of trimethylcellulose are 2,3,6-tri-*O*-methyl-D-glucose and one molecule of 2,3,4,6-tetra-*O*-methyl-D-glucose per non-reducing end group. Methanolysis gives the corresponding methylglucosides.

1.6.2 Esters [11,12,26,38,163,164]

Cellulose can be esterified with most inorganic and organic acids by methods analogous to those used for simple alcohols. Many of the products have practical applications, but the most important have been the acetates, nitrates and xanthates.

Cellulose nitrate is generally manufactured to a DS between 2 and 3 (11.11–14.14% N). The dinitrate esters have been used for plastics and the trinitrates for explosives; those in between are suitable for lacquers and similar products. Good solvents for dinitrated esters (11–12% N) include methanol, various alkyl acetates, methyl ethyl ketone and acetone, but at a higher DS only acetone is suitable. Although there are several ways of nitrating cellulose, aqueous mixtures of nitric and sulphuric acids are always used industrially. Here the equilibria illustrated in Scheme 1.12 are established. Nitration is effected by the nitronium ion (Scheme 1.13) and is a reversible reaction. Hence the DS achieved is governed by the composition of the nitrating bath and particularly by its water content. A typical bath composition (by weight) for a dinitrate would be HNO_3 21%, H_2SO_4 61.5%, H_2O 17.5%. The reaction is rapid (Figure 1.22), equilibrium being reached in about 10 min at a moderate temperature (20–40°C)

$$3H_3O^+ + NO_3^- + 2HSO_4^- \rightleftharpoons HNO_3 + 2H_2SO_4 + 3H_2O$$
$$\rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- + 3H_2O$$

Scheme 1.12

$$R_{cell}{\cdot}OH + NO_2^+ + H_2O \rightleftharpoons R_{cell}{\cdot}ONO_2 + H_3O^+$$

Scheme 1.13

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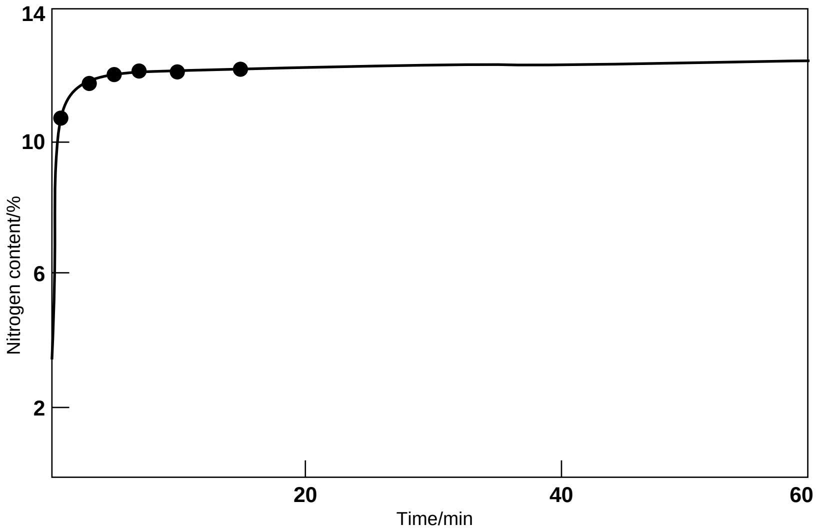


Figure 1.22 Rate of nitration of cellulose in a mixture of nitric acid (21%), sulphuric acid (61.5%) and water (17.5%). (*Source*: [11].)

to minimise depolymerisation. This unusual rapidity occurs because the nitronium ion readily penetrates the crystalline as well as the amorphous regions of the fibres and reacts rapidly with the hydroxy groups. It is thus a homogeneous process, formerly described as a 'permutoid' reaction. The initial product contains a few sulphate ester groups. These are removed by boiling with dilute acid, neutralising with sodium carbonate, and washing well with water. If this were not done, the sulphate groups would gradually hydrolyse to sulphuric acid which would catalyse the decomposition of the cellulose nitrate, under some circumstances with sufficient violence to cause an explosion. Sometimes a stabiliser (e.g. a very weak base) is added to cellulose nitrate before storage.

Cellulose acetates have a wide variety of uses, including conversion into textile fibres, transparent sheeting and moulded plastics. The dyeing of acetate and triacetate fibres is described elsewhere [165].

Acetylation may be achieved using acetic anhydride in the presence of an acid catalyst. The reaction is represented formally by Scheme 1.14, but the mechanism is more complex, involving intermediate combination of the catalyst with the cellulose. Two separate processes are used: the fibrous process and the solution process. In the former, suitable only for triacetate production, a mixture of acetic anhydride and acetic acid is used in a medium that does not dissolve cellulose acetate, e.g. an aromatic hydrocarbon or carbon tetrachloride; the catalyst is frequently perchloric acid. In laboratory investigations a mixture of

$$R_{cell}OH + (CH_3CO)_2O \longrightarrow R_{cell}OCOCH_3 + CH_3COOH$$

Scheme 1.14

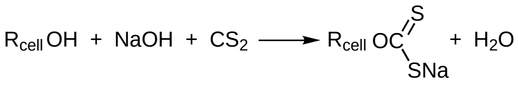
acetic anhydride and pyridine has sometimes been used to effect partial fibrous acetylation [166].

In the solution process the cellulose is treated with a mixture of acetic anhydride, acetic acid and sulphuric acid. The reaction is slow and heterogeneous. The outermost layers are acetylated first and dissolve in the acetic acid, exposing unchanged cellulose to attack and dissolution in its turn. The process continues until a solution of cellulose triacetate (the ‘primary’ acetate) in acetic acid is obtained. The reaction is exothermic and external cooling is necessary to prevent depolymerisation of the molecular chains. The product contains sulphate ester groups that must be removed by hydrolysis, water being added under carefully controlled conditions. The triacetate (DS 2.8–2.9) may then be precipitated out by the addition of more water.

The so-called secondary acetate, sometimes described as ‘diacetate’, has a DS of about 2.3 and is produced by carefully controlled hydrolysis of the triacetate at 40°C. This product is also precipitated out by copious addition of water. Secondary cellulose acetate made in this way is soluble in acetone, whereas derivatives with the same DS made by direct acetylation are not. This is a good example of the influence of the pattern of substitution on the solubility of a cellulose derivative.

Sodium cellulose xanthate [31] is the sodium salt of the O-ester of unsymmetrical dithiocarbonic acid. It is made by the action of carbon disulphide on alkali cellulose (Scheme 1.15). The ester itself is of little interest; its importance lies in its solubility in dilute sodium hydroxide. The solution is called viscose and is used for the manufacture of regenerated fibres. The DS is usually 0.5 or a little more, but for the production of polynosic fibres it may be nearly 1.0. In the regenerated-fibre industry the DS is often expressed as the γ-number, which is the number of xanthate groups per 100 anhydroglucose units ($\gamma = 100$ DS).

The technology of viscose production is too complicated to be discussed here, but two important features may be mentioned. The first is that the alkali cellulose (i.e. cellulose impregnated with 18% sodium hydroxide) must be ‘aged’



$$R_{cell}OH + NaOH + CS_2 \longrightarrow R_{cell}OC(=S)SNa + H_2O$$

Scheme 1.15

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in air at 25–30°C for at least a day, to reduce the DP to a suitable value. The second is that the viscose solution itself must be 'ripened' by storage at 15–25°C for 1–3 days, to achieve favourable conditions for regeneration. The most important chemical change during ripening is gradual decomposition of the xanthate. The degree of ripening required depends upon the particular final product.

1.6.3 Ethers [13,27,39]

Highly substituted cellulose ethers may be prepared in the laboratory by any of the methods generally applicable to polysaccharides, provided that due account is taken of the difficulty of making the material completely accessible to reagents [119,vol.3,p.274]. The DS of most commercial cellulose ethers lies between 0.5 and 2, and is commonly around 1.5. These materials are usually made by treating alkali cellulose with an alkyl halide or other alkylating agent in an autoclave at a temperature low enough to avoid degradation. Methylcellulose is made with methyl chloride (Scheme 1.16). Sodium chloroacetate is used for carboxymethylcellulose ($R_{cell}OCH_2COOH$) and ethylene oxide for hydroxyethylcellulose ($R_{cell}OCH_2CH_2OH$). The primary hydroxy group in the hydroxyethyl grouping is itself reactive and therefore gives rise to side chains of the type $-(CH_2CH_2O)_nCH_2CH_2OH$ where n is about 2 (although in theory it could be much larger). The material is therefore analogous to the graft copolymers of cellulose (section 1.6.4).

The reaction of cellulose with activated olefinic compounds in the presence of alkali also gives ethers. Cyanoethylcellulose is prepared in this way using acrylonitrile (Scheme 1.17). Vinylsulphones ($CH_2{=}CHSO_2R$), or precursors that generate them in the presence of alkali, can also be used to give sulphonylethyl ethers.

Most commercial cellulose ethers are soluble in water. Some, such as methylcellulose, are less soluble in hot water than in cold, but others, e.g.

$$R_{cell}OH + NaOH + CH_3Cl \longrightarrow R_{cell}OCH_3 + NaCl + H_2O$$

Scheme 1.16

$$R_{cell}OH + CH_2{:}CHCN \xrightarrow{NaOH} R_{cell}OCH_2CH_2CN$$

Scheme 1.17

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hydroxyethylcellulose, show normal solubility behaviour. Their numerous applications stem from their capacity to form viscous solutions and gels with water and to act as protective colloids. Their use in the food industry is widespread and carboxymethylcellulose is usually incorporated in domestic washing powders to prevent the redeposition of soil during laundering. The only commercially available ethers that are soluble in organic solvents are ethylcellulose and cyanoethylcellulose of DS 2.5 or higher. The former finds a limited use in lacquers and moulded plastics, and the latter, because of its high dielectric constant, is a useful insulator. It is sometimes used in the manufacture of electroluminescent articles.

1.6.4 Graft copolymers [167]

The possibility of modifying cellulose by grafting other polymers on to it is obvious, but extensive research on grafting has proved less commercially important than might have been hoped. Methods of grafting have usually involved homopolymeric grafts. Thus if cellulose is impregnated with a suitable vinyl monomer in the presence of a radical initiator (e.g. benzoyl peroxide, hydrogen peroxide/iron(II) sulphate, sodium persulphate or ozone), a cellulosyl radical is formed to initiate polymerisation (Scheme 1.18). Particular monomers that have been extensively studied include acrylonitrile, acrylamide, acrylic acid, methacrylic acid, vinyl acetate and styrene. This list is by no means exhaustive.

$$R_{cell}O^{\bullet} + CH_2{:}CHR \longrightarrow R_{cell}OCH_2\dot{C}HR \longrightarrow$$

Scheme 1.18

Graft polymerisation may also be initiated by means of γ-rays. Cellulose is irradiated together with the monomer to be grafted or prior to treatment with it. In either case a suitable swelling agent must also be used if a significant amount of grafting is to be achieved.

One difficulty associated with grafting of cellulosic textiles is that most methods of initiation employed also lead to degradation of one kind or another. Thus in practice a balance has to be struck between the improvement due to grafting and deterioration due to degradation.

1.6.5 Fundamentals of crosslinking

Cellulose can be crosslinked by any reagent containing at least two functional

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groups capable of reacting with hydroxy groups. Modified celluloses containing other functional groups may also form crosslinks. For example, an aldehyde group may combine with an alcohol group in a neighbouring chain to form a hemiacetal, or two carboxy groups in different chains may crosslink by forming a salt with a bivalent cation.

The mechanical and certain other properties of cellulosic fibres are profoundly affected by crosslinking, and these effects are reflected in the properties of assemblies of fibres in ways that depend on how a particular assembly is constructed. Thus the tensile properties of textile yarns and fabrics usually correspond directly with the properties of their constituent fibres because the main influence on yarn stability is interfibre friction. On the other hand the stability of paper, which is a random web of short fibres, is mainly due to hydrogen bonds between fibres. The stability of the fibres themselves, whether in a yarn, in paper or in any other assembly, is due to a combination of internal hydrogen bonding and van der Waals forces.

The introduction of covalent crosslinks into a cellulosic fibre has two important effects: it reduces the ability of the chain molecules (a) to move laterally, and (b) to extend longitudinally under stress. Evidence for the first effect is found in lower water retention (section 1.7.1), reduced swelling (section 1.9.1) and insolubility in solvents such as cuam or FeTNa (section 1.8.2). Insolubility in one of these solvents is a much-used test for the presence of crosslinking in cellulosic materials.

Evidence for the second effect is more subtle [168]. Consider an imaginary fibre with no lateral forces between chains. It would be mechanically weak because, under stress, chain molecules would slide past one another and only those long enough to span the gap between the jaws of the testing instrument would contribute to the tensile strength. The introduction of crosslinks would increase the proportion of chains spanning the jaw gap and hence increase the load required to break the fibre. After a certain point, however, the introduction of still more crosslinks would restrict the movement of adjacent chains to such an extent that the proportion of chains capable of resisting applied stress would decrease and the tensile strength would fall. This is because a chain molecule can resist stress only when it is fully extended.

In a real cellulosic fibre there are in fact very many intermolecular hydrogen bonds which, in their influence on mechanical properties, behave in the same way as other crosslinks. Their most important difference from covalent crosslinks is that they can be destroyed by water. This explains the well-known fact that the strength of cotton is increased by wetting, whereas that of regular viscose is reduced. In cotton the density of hydrogen bonding is already greater than that required to produce maximum strength. Hence, on wetting, some of the bonds are severed, lowering the crosslink density and raising the tensile strength. In viscose, however, the density of crosslinking is less than that needed for maximum strength. Hence the loss of some crosslinks causes a reduction in tensile strength. For the same reason, the dry strengths of the two materials are affected in different ways by the introduction of covalent crosslinks. For example, cotton oxidised by periodate (section 1.5.5) suffers a rapid loss of strength because the hemiacetal crosslinks formed reinforce the effect of the crosslinking hydrogen bonds already present [152,169]. With viscose, on the other hand, the introduction of hemiacetal crosslinks at first increases the tensile strength until a maximum is reached, after which further crosslinking produces a loss of strength in the same way as with cotton. A recent elegant investigation of inter-chain esterification in cotton by means of 1,2,3,4-butanetetracarboxylic acid has led to similar conclusions [170]. In this work the breaking twist angles of the fibres were determined as a measure of brittleness. As expected, crosslinking increased the brittleness of the fibres. The magnitude of the mechanical changes depends on the length, number and distribution of the crosslinks introduced.

The effect of the introduction of hemiacetal crosslinks into paper is an immediate increase in wet strength because in this case the crosslinks are predominantly between the fibres [171,172].

1.7 AFFINITY FOR WATER AND ORGANIC LIQUIDS

1.7.1 Water

The hydrophilic nature of cellulose is of great industrial importance for several reasons:

(1) Water is essential for many processes, e.g. dyeing and finishing, paper making.

(2) Cellulose cannot easily be freed from water completely; the fibres normally contain adsorbed water in quantities determined by the relative humidity and temperature of the surrounding atmosphere.

(3) The mechanical properties of cellulosic fibres vary with their moisture content.

(4) The comfort of clothing made from cellulosic fibres is closely associated with moisture absorbency.

A cursory look at its formula (Figure 1.12) might lead one to expect that cellulose would be soluble in water, as glucose is. In fact, of course, it is not. It is generally accepted that water cannot penetrate cellulose crystallites [173]. The intermolecular hydrogen bonds holding the crystallites together are no stronger than those between water and cellulosic hydroxy groups. However, the inflexibility of the chain molecules prevents these bonds from being broken successively and the chance of them all being broken simultaneously is negligible [174]. Thus the insolubility of cellulose in water is a direct consequence of the equatorial orientation of all the hexose substituents, including the glycosidic bonds. This structural feature distinguishes cellulose from all other polysaccharides. As already mentioned, alkylcellulose ethers of low DS are soluble in water. This is because the alkyl groups distort the conformation of the cellulose chains so that crystallisation is inhibited and the remaining hydroxy groups are capable of being solvated.

Adsorption of water vapour

Even in highly crystalline cellulosic fibres the crystallites are relatively small, as in the proposed crystalline fibrillar structure of cotton (Figure 1.4). Hence there are numerous free hydroxy groups in the crystallite surfaces and in whatever disordered regions exist. These are the hydroxy groups responsible for the adsorption of water vapour from the air. The moisture relations of cellulose have been extensively studied over many years and have recently been reviewed by Zeronian [40]. The main features of the sorption isotherms were established in the classical work of Urquhart and Williams, illustrated for cotton in Figure 1.23 [175]. Sorption is expressed as moisture regain, i.e. grams of water per 100 g of bone-dry cellulose. Under average conditions in the UK, say a relative humidity (r.h.) of 65% at 20°C, scoured cotton has a regain of around 7.5%, which corresponds to a moisture content of 7%. This is equivalent to about two water molecules for every three anhydroglucose units in the sample, and may seem surprising for a material that feels perfectly dry. Fully mercerised cotton and regular viscose have regains of about 11% and 13% respectively under similar conditions. Later work [176,177] has added greatly to our detailed knowledge of sorption isotherms over an extremely wide range of ambient conditions.

The sigmoidal curves in Figure 1.23 may be conveniently divided into three sections:

(1) Low humidity (0–10% r.h.) – the progressive formation of a monolayer which, when complete, has one molecule of water bonded to each accessible hydroxy group.
(2) Medium humidity (10–50% r.h.) – the formation of a multilayer of progressively increasing thickness.

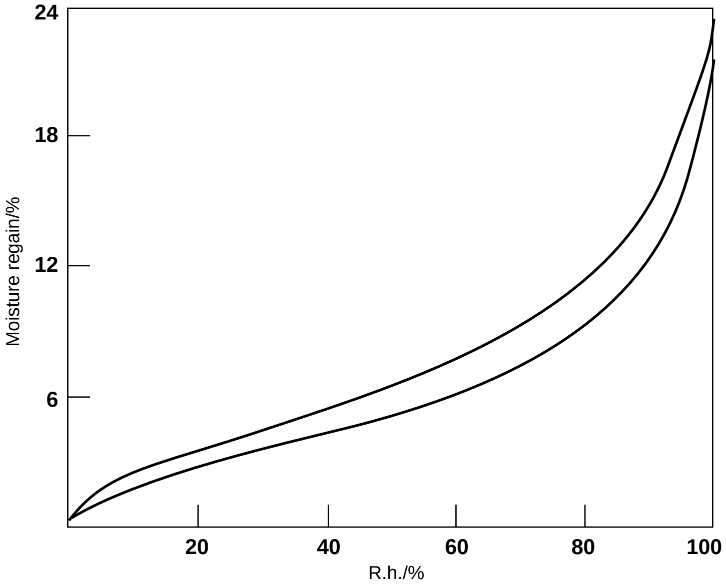


Figure 1.23 Sorption isotherms of scoured cotton at 25°C: adsorption (lower curve) and desorption (upper curve). (*Source*: [7].)

(3) High humidity (50–100% r.h.) – the further sorption of water, virtually in liquid form and gradually swelling the fibres so that more hydroxy groups become accessible.

Under most conditions the amount of adsorption decreased with increasing temperature, as expected. However, at relative humidities above about 85% there are discrepancies between the published results. Urquhart and Williams [175] found increased adsorption when the temperature was raised above 50°C, whereas Jeffries [176] did not. The difference probably lies in the methods of preparing the samples for examination. Jeffries subjected his samples to a rigorous stabilisation treatment by taking them through repeated sorption–desorption cycles at 90°C before measuring the isotherms. Urquhart and Williams used samples carefully purified by standard methods. Both sets of results are consistent with the idea that the structure of cellulose changes when exposed to high temperatures and humidities unless it has first been stabilised. It should be noted, however, that Jeffries' treatment caused some depolymerisation which may itself have contributed to stabilisation.

A notable feature of all cellulose–water isotherms is that the amount of water sorbed at a given r.h. is greater when equilibrium is approached from 100% r.h.

than when it is approached from 0% r.h. (Figure 1.23). This phenomenon is known as hysteresis. If the starting r.h. is somewhere between 0 and 100% then adsorption or desorption curves between the two extremes in Figure 1.23 are observed. This has the practical implication that the precise moisture content of a sample of cellulose depends on its previous history. The cause of hysteresis has been the subject of much speculation. Urquhart's attractively simple molecular explanation [178], that the number of hydroxy groups available to water at a given r.h. value is greater when the water has been desorbed than when it has been adsorbed, is now generally regarded as inadequate. It is difficult to reconcile with present views of fibre fine structure and with the multilayer theory of sorption [40]. In an alternative approach, Barkas [179] considered that internal stress is generated when cellulose adsorbs water from the dry state but when this stress is removed by subsequent gradual desorption, mechanical recovery of the fine structure is incomplete (because the material is plastic) so that more water is retained than had previously been adsorbed at the same r.h. value.

Water imbibition

Cellulosic fibres imbibe considerably more water when immersed in the liquid than they sorb at 100% r.h. [180]. The water can be held in several ways; in particular, a distinction is often drawn between 'free' and 'bound' water for the liquid within cell walls [40]. Outside the cell walls almost all the water is held by condensation in capillary voids within the fibrillar structure of the fibres. Much research on this subject has been carried out, but in practice the most useful method of measuring water imbibition is to weigh the amount retained after the sample has been centrifuged under standard conditions, e.g. for 30 min at 900 g. Obviously the result depends to a small extent on the conditions chosen. Cotton yarn gives a water imbibition of about 45–50%, and regular viscose about 90%, by this method. Greater retention is likely in the wet processing of fabrics, since excess liquor may be removed by less vigorous mechanical means, e.g. mangling.

1.7.2 Organic liquids

Organic liquids other than aliphatic amines (section 1.9.3) are less strongly attracted to cellulose than water [14]. Small molecules with at least some hydrogen-bonding capacity, e.g. methanol or ethanol, are adsorbed from the vapour phase but to a smaller extent than water. As the size of molecules increases, the adsorption decreases, butan-1-ol showing no adsorption. Non-polar vapours such as benzene or carbon tetrachloride are sorbed only very slightly.

Although only small quantities of non-polar liquids are imbibed by cellulose under normal conditions, they can be introduced into the structure by first swelling the material in water and then treating it successively with a series of solvents of decreasing polarity. After removal of the excess of the final solvent by pumping, the cellulose still contains an appreciable amount of the chosen non-polar solvent. Further pumping does not remove any of this residual solvent even when a high vacuum is used. Products of this type have been called ‘inclusion celluloses’ because their solvent content is not held by ordinary valency forces but is trapped in the cellulose structure in the manner of a clathrate compound. Apparently the originally swollen structure gradually collapses during the removal of the solvent by pumping. The significance of these compounds [28,181] is their higher reactivity in processes such as acetylation. They are stable only in the absence of water, which rapidly replaces the non-polar liquid. For example, if cyclohexane-inclusion cellulose is viewed under a microscope while being wetted, beads of liquid cyclohexane can be seen forming on individual fibres [181].

1.8 SOLVENTS FOR CELLULOSE

1.8.1 Introduction

For many years the only known solvents for cellulose were concentrated solutions of certain salts such as calcium thiocyanate at the boil, moderately concentrated mineral acids, e.g. 70% sulphuric acid, and cuprammonium hydroxide (cuam, Schweizer’s reagent), the latter two at room temperature [182]. Only cuam causes no depolymerisation, but to ensure this atmospheric oxygen and light must be rigidly excluded. Much effort has been expended since Schweizer’s time on the development of non-degradative solvents for cellulose [41,66].

Solvents for cellulose are required for two main purposes:

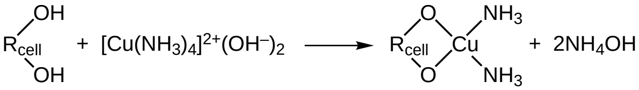
(1) For testing, e.g. for assessing properties that are dependent on DP, or for detecting crosslinking, since a solvent that normally dissolves cellulose will not dissolve crosslinked material.
(2) For making solutions from which cellulosic fibres can be regenerated.

The first successful solvents were mostly similar to cuprammonium hydroxide, but with ammonia replaced by an aliphatic diamine (usually ethylenediamine) and copper replaced by some other metal. Much more recently a wide range of non-aqueous solvents has been developed. These two classes of solvent will now be discussed briefly.

1.8.2 Metal-complex solvents

Over 60 years elapsed between Schweizer's original discovery and Traube's introduction of cupriethylenediamine as an alternative solvent for cellulose [183]. Both reagents are aqueous solutions of Cu(II) complexes. Cuprammonium hydroxide (cuam) is roughly 0.25 M in copper and has a Cu:NH_3 molar ratio of about 1:50. On the other hand, cupriethylenediamine (cuen) is usually 0.5 M in Cu(II) with a Cu:$NH_2CH_2CH_2NH_2$ molar ratio of 1:2. Cuen is the more stable of the two solvents, mainly because the amine is practically non-volatile whereas ammonia is easily lost and the cuen complex is less sensitive to light.

The copper complex in cuam is formed as shown in Scheme 1.19 [184], and that in cuen is formed in an analogous way. A series of solvents based on complexes of other metals with ethylenediamine was investigated by Jayme and coworkers during the 1950s [29]. The metals included cobalt, nickel, zinc and cadmium, the last-named being the most important in practical applications. The cadmium ethylenediamine solvent is approximately 0.45 M in cadmium and 0.35 M in sodium hydroxide with a Cd:$NH_2CH_2CH_2NH_2$ molar ratio of about 1:10; it thus contains considerably more ethylenediamine than cuen. It has the great advantage of being colourless and is usually known as cadoxen.



Scheme 1.19

Jayme and Verburg [185] also discovered a solvent for cellulose in which Fe(III) is complexed with tartrate ions. The solution is green in colour and must be 2–3 M in sodium hydroxide. It is generally designated FeTNa, except in German literature where the symbol EWNN is used. EWNN stands for Eisen-Weinsäure-Natrium, the second N indicating that the sodium is added in two stages, first as sodium hydrogen tartrate and secondly as sodium hydroxide.

The first industrial application of cuam was for the production of cupro; this has all but ceased. It has been used since the 1920s, particularly in the UK, for assessing chemical tendering in cotton and regenerated cellulosic fibres. In the British test [186], the flow time of a 0.5% (cotton) or 2% (regular viscose) solution in cuam is measured at 20°C in a special viscometer designed to exclude air. Careful temperature control is essential. The test result is expressed as the fluidity, i.e. the reciprocal of the dynamic viscosity; the unit of fluidity is the reciprocal poise, or rhe (1 rhe = 10 $m^2 N^{-1} s^{-1}$ in SI units). The conditions of the test ensure an approximately linear relation between fluidity and loss of tensile strength. In this context, fluidity values are more meaningful, since viscosity falls roughly hyperbolically with loss of strength and is an insensitive measure of tendering except for slight decreases in strength [187]. Another important feature of the fluidity measurement arises from the high alkalinity of cuam. This means that it measures any 'latent' tendering present in a material, i.e. loss of tensile strength that becomes apparent in practice only after some form of alkaline treatment, such as laundering (sections 1.5.5 and 1.5.7).

Many workers, particularly in North America, prefer cuen to cuam for assessing tendering and quality control. The TAPPI method [188] expresses the result as a viscosity, which is appropriate for its intended field of application (the paper and pulp industry). The ASTM method [189] expresses the result as intrinsic viscosity ($[\eta]$), from which the relative molecular mass M can be calculated if the constants (a and k) in the Mark–Houwink equation are known (Eqn 1.4):

$$[\eta] = kM^a \qquad (1.4)$$

Many values of these constants have been published but frequently they do not agree with one another.

Any of the solvents described may be used to test for crosslinking, but cadoxen and FeTNa are probably the most convenient. The behaviour of a fibre when wetted with a drop of solvent can be viewed under a microscope. Fibres that have no covalent crosslinks will dissolve fairly quickly; crosslinked fibres usually swell and sometimes burst, but they remain insoluble indefinitely except in rare cases where the solvent destroys the crosslink, e.g. by the hydrolysis of an ester.

1.8.3 Non-aqueous solvents

Some non-aqueous solvents for cellulose have been known for some time, e.g. liquid ammonia containing certain inorganic salts [190] and mixtures of dinitrogen tetroxide with a variety of organic liquids [191]. Only within the last 20 years, however, has the growing awareness of environmental considerations aroused interest in these media. One incentive has been the search for a less objectionable solution than viscose from which to regenerate fibres. A significant start has been made, but viscose is not likely to lose its leading position for a long time.

Although the systems under consideration are described as non-aqueous, the presence of some water is often essential for a good solvent.

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The most extensively studied system based on liquid ammonia is that in which the major constituent is ammonium thiocyanate [192,193]. A typical composition (by weight) would be 72.1% ammonium thiocyanate, 26.5% ammonia and 1.4% water. An interesting feature of solutions of cellulose in this mixture is that the ammonia can be displaced by various chemically disparate substances, e.g. γ-butyrolactone or a 1:1 mixture of morpholine and pyridine, without precipitation of the cellulose. The displacing substance must be miscible with the original solution; after its addition, ammonia is removed by pumping.

An analogous solvent is dimethylacetamide containing 10% of lithium chloride; this gives highly stable solutions of cellulose. Fibres may be regenerated from these solutions by wet spinning in water or acetonitrile. These fibres have satisfactory physical properties [194], but the process has not yet proved commercially viable.

The solvent power of certain cyclic tertiary amine oxides was reported in a series of patents from 1969 onwards [195,196]. Structural criteria for ability to dissolve cellulose were established and the crucial importance of having the right amount of water present was recognised [41]. The use of *N*-methylmorpholine-*N*-oxide (Figure 1.24) in the production of Tencel has already been described (section 1.2.3).

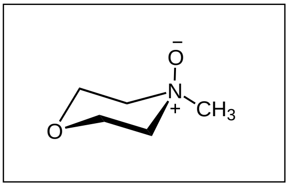


Figure 1.24 *N*-Methylmorpholine-*N*-oxide. (*Source*: [41].)

It was also in 1969 that Schweiger proposed the use of *N*,*N*-dimethylformamide (DMF, $HCON(CH_3)_2$) containing around 15% of dinitrogen tetroxide as a cellulose solvent. It appears to act by forming cellulose nitrite which then dissolves (Scheme 1.20) [197,198]. Nitrosyl chloride behaves similarly and *N*,*N*-dimethylacetamide may be used instead of DMF. Satisfactory fibres may be regenerated by spinning into aqueous DMF containing certain salts [67,199], but commercial exploitation is not yet viable.

The N_2O_4–DMF system differs from the others so far considered in that it dissolves cellulose by forming a soluble derivative. Another system in which a soluble derivative is formed is a mixture of dimethylsulphoxide (DMSO, $(CH_3)_2SO$) and paraformaldehyde (PF, $(CH_2O)_n$), [41,68,200–203]. In this case the derivative seems to be a hemiacetal formed between formaldehyde and the

$$R_{cell}OH + N_2O_4 \xrightarrow{DMF} R_{cell}ONO + HNO_3 \xrightarrow{DMF} \text{Solution}$$

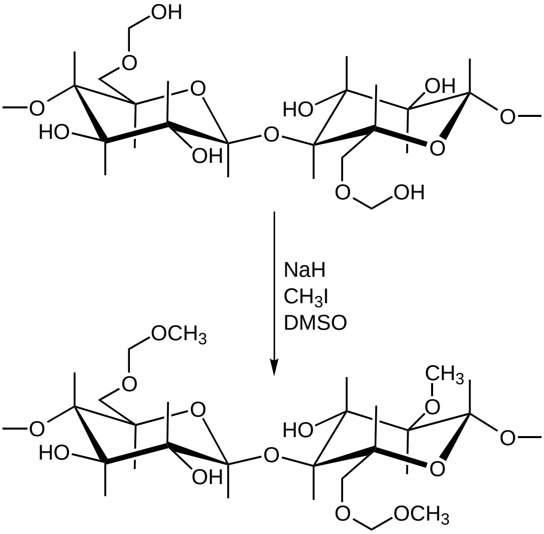
Scheme 1.20

primary alcohol groups in the cellulose (Scheme 1.21). The solution is very stable, probably because of strong solvation of the methylol groups by the highly polar DMSO. Fibres have been spun from these solutions using aqueous solutions of formaldehyde scavengers such as ammonia, various amines or sodium sulphide. For cellulose pulps with DP between 400 and 600 a solution of convenient viscosity is obtained with a composition of cellulose 6%, PF 6% and DMSO 88%. Although fibres of good quality were obtained, the process has not yet been developed on an industrial scale.

A minor, but important, use for DMSO–PF solutions of cellulose is in the preparation of unusual derivatives under homogeneous conditions [204]. For example, treatment with a mixture of methyl iodide and sodium hydride gives a mixed ether-acetal (Scheme 1.22). Some of the methylol groups are removed by sodium hydride so that the cellulosic alcohol group can be methylated; others are methylated whilst still attached to the cellulose, a stable full acetal being formed. It may be noted that solutions of cellulose in N_2O_4–DMF may also be used for the preparation of derivatives [197,198].

$$R_{cell}OH + HCHO \xrightarrow{DMSO} R_{cell}OCH_2OH \xrightarrow{DMSO} \text{Solution}$$

Scheme 1.21



Scheme 1.22

1.9 SWELLING

1.9.1 Introduction

The aqueous swelling of cellulose has already been noted. When bone-dry fibres are immersed in water their average diameter may increase by as much as 20% [205]. In practice, however, cellulose is seldom encountered in a bone-dry state and it is usual to take the water-swollen state as the basis for swelling measurements, thus restricting the term swelling to increases in size greater than those that can be effected by water alone. Degrees of swelling are expressed as percentage increases in either diameter or cross-sectional area.

Swelling always entails the breaking of hydrogen bonds between adjacent chain molecules. With water and dilute aqueous solutions this normally occurs only in accessible regions of the fibres, which often means between fibrillar surfaces. Penetration of the crystallites does not occur and the degree of swelling is always small. Some reagents, however, can penetrate the crystallites. This intrafibrillar swelling is always on a much larger scale than interfibrillar swelling.

The phenomenon was discovered by Mercer in 1844 [206,207] using such reagents as 25–30% sodium hydroxide or 62% sulphuric acid at room temperature, or 59% zinc chloride at 70°C. Cotton yarn treated in this way swells in diameter and shrinks in length, so that fabrics become denser. The process also enhances dyeability. About 40 years later Lowe [208] discovered that if cloth was stretched to its original dimensions during subsequent washing, or if it was held under tension to prevent it from shrinking during treatment, it acquired a much improved lustre and smoothness. This process became known as mercerisation and is still widely practised, almost entirely with concentrated sodium hydroxide solutions [209,210]. It is advisable to confine this term to treatments with caustic alkalis and not to extend it to swelling agents such as liquid ammonia, since the two types of reagent are quite distinct in their action (section 1.9.3).

Obviously swelling only partially disrupts the solid structure of cellulose; complete disruption would be equivalent to dissolution. A useful general picture of the process is illustrated in Figure 1.25 [211]. The swelling agent, or ‘foreign molecule’, breaks the hydrogen bonds in the crystallites, but has no effect on the van der Waals bonds which act at right angles to the hydrogen bonds. Thus the cellulose behaves as infinite sheets held intact by van der Waals forces and capable of being pushed apart by hydrogen-bond breakers to an extent determined by the size of the foreign molecule.

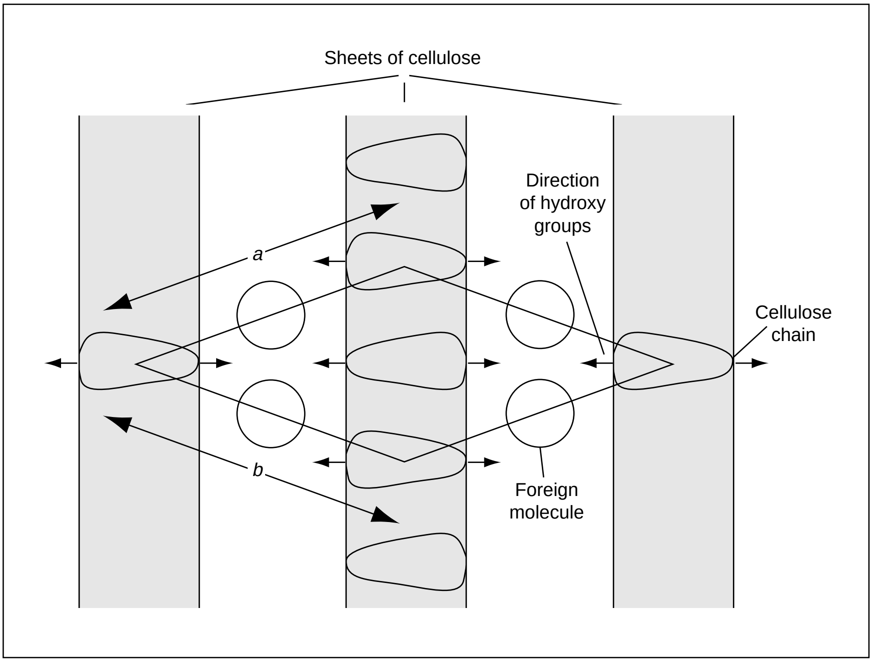


Figure 1.25 Diagram of swelling of cellulose by penetration of reagent between sheets, looking along the fibre axis. (*Source*: J O Warwicker, in *Liquid ammonia treatment of textiles*, Shirley Institute, Manchester, 1970.)

1.9.2 Aqueous alkalis

The literature on the swelling of cellulose by aqueous alkalis is extensive and sometimes confusing, but some excellent reviews are available [28,42,52]. The fundamental cause of swelling is the imbibition of water consequent upon the sorption of alkali by the cellulose.

In one early study [212] of the sorption of sodium hydroxide, curves of the type illustrated in Figure 1.26 were measured by titration of the external solution. The main features were the two plateaux in the absorption curve, which suggested that definite stoichiometric compounds were being formed. It was subsequently shown, however, that the change in the titre of the sodium hydroxide solution represented the net effect of two separate processes, namely the sorption of sodium hydroxide and a preferential imbibition of water [213]. The water uptake passed through a maximum at a concentration of sodium hydroxide of 100–200 g l^{-1} (2.5–5 M), whereas the uptake of sodium hydroxide rose steadily in a manner characteristic of adsorption. These results were fully confirmed by later investigations, but that did not dispel belief in the formation

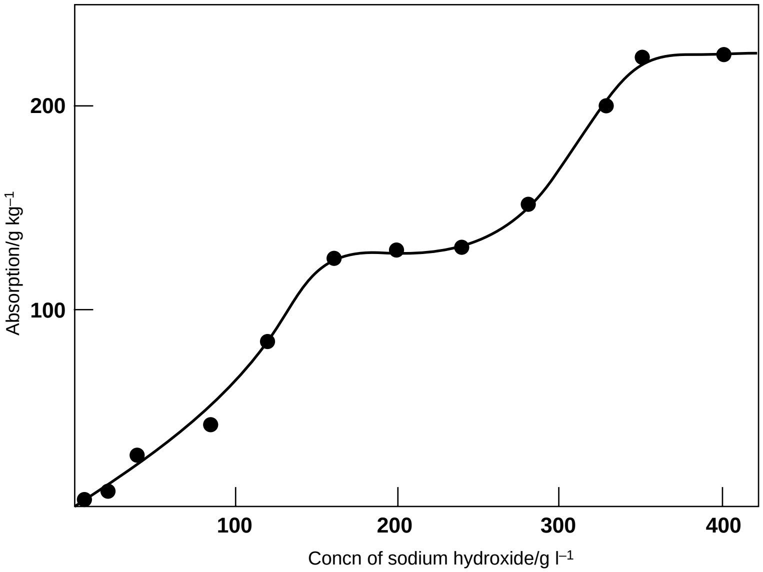


Figure 1.26 Apparent sorption of sodium hydroxide by cotton. (*Source*: [28].)

of stoichiometric compounds by some workers for many years [214,215]. The main evidence for this theory came from the X-ray diagrams of 'soda celluloses' [214], but it is now generally agreed that these were incorrectly interpreted [28]. No air-dry sample of a soda cellulose with a composition corresponding to any of the proposed formulae has ever been reported.

The degree of swelling of cotton in aqueous alkali depends on the amount of water imbibed, and this in turn depends on three factors:

(1) The nature of the cation.
(2) The concentration of the alkali.
(3) The temperature.

Early studies indicated that the essential feature distinguishing one cation from another was its degree of hydration under comparable conditions. Thus the maximum swelling at a given temperature for the series of alkali metal hydroxides was found to decrease in the order Li > Na > K > Rb > Cs, which is also the order of decreasing hydrating power [52]. Similar considerations apply to the effects of alkali concentration and temperature. Swelling, and the degree of hydration, decrease as the temperature is increased and pass through a maximum as the alkali concentration increases (Figure 1.27). The effect of temperature is also what would be expected from the fact that the sorption of alkali by cellulose

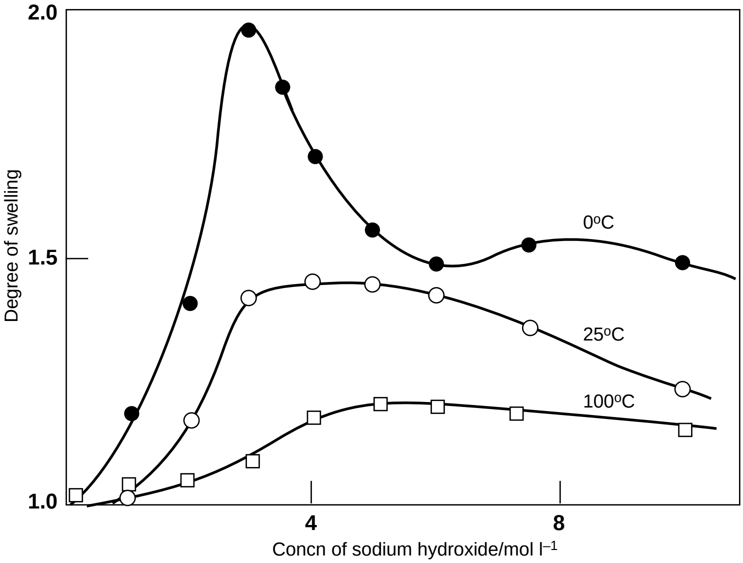


Figure 1.27 Effect of temperature on swelling of cotton by sodium hydroxide. (*Source*: [28].)

is exothermic [52]. The exceptionally sharp peak at 0°C and 3 M NaOH has been attributed to bursting of the primary wall of fibres [28].

The first quantitative theory of swelling was proposed by Neale, who applied the concept of a Donnan membrane equilibrium to the system as illustrated in Table 1.4 [216]. The membrane was the primary wall of the fibres and the non-diffusible ion the cellulosate ion $R_{cell}O^-$. The hydrogen ion concentration in the liquid phase was considered to be negligible. Donnan's equation is Eqn 1.5:

$$[Na^+]_1\,[OH^-]_1 = [Na^+]_2\,[OH^-]_2 \qquad (1.5)$$

To achieve this, water must be driven from phase 2 into phase 1 by osmosis. The approximate osmotic pressure will be given by Eqn 1.6:

$$P = RT([Na^+]_1 + [OH^-]_1 - [Na^+]_2 - [OH^-]_2) \qquad (1.6)$$

Remembering that each phase is electrically neutral and neglecting concentration changes resulting solely from the increase in volume due to swelling, Eqns 1.5 and 1.6 may be used to calculate values of P and $[NaOH]_2$ for arbitrarily chosen values of $[NaOH]_1$. In Figure 1.28 the results so obtained are compared with measured values of the amount of water taken up by a regenerated cellulosic film (used instead of cotton fibres because it was easier to handle experimentally).

The similarity between the two curves confirms in broad outline the premises of Neale's theory. It is important to appreciate its shortcomings, however, as indeed Neale himself did. The theory does not even suggest why different cations should behave differently, and concentrations have been used instead of activities in spite of the fact that in concentrated solutions the two may differ considerably.

Table 1.4 Distribution of ions immersed in sodium hydroxide

Cellulose phase (1)	Membrane	Liquid phase (2)
Cellulose $R_{cell}OH$		
Cellulosate ions $R_{cell}O^-$		
Hydrogen ions H^+		
Sodium ions Na^+		Na^+
Hydroxide ions OH^-		OH^-
Water H_2O		H_2O

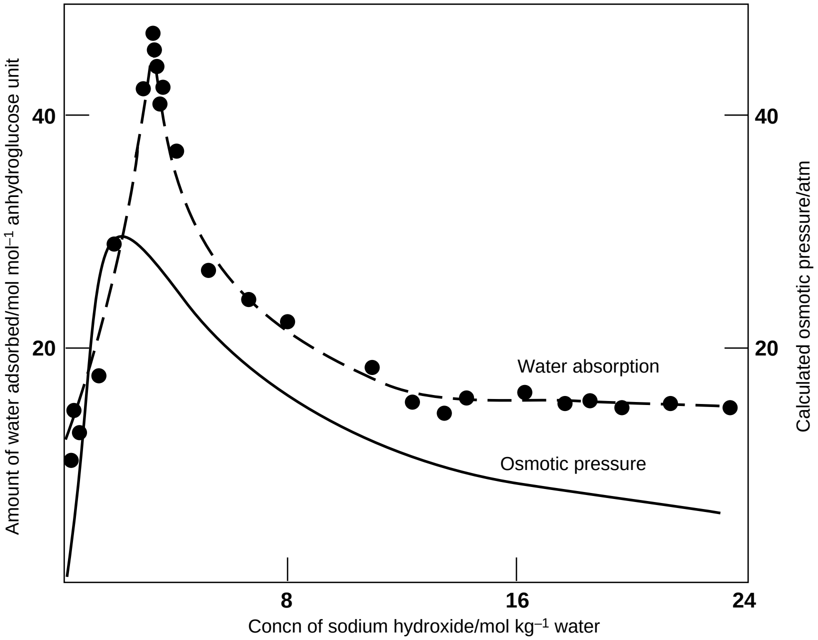


Figure 1.28 Swelling of cellulose film by sodium hydroxide: osmotic pressure (calculated); water absorption (measured). (*Source*: [6,Part 2,p.840].)

The importance of ionic hydration in swelling was emphasised by Chédin and Marsaudon [217]. They visualised the process as arising from replacement of some of the water of hydration by cellulosic hydroxy groups, as represented by Scheme 1.23. When a hydrated ion pair is adsorbed by the cellulose, three molecules of water are released and replaced by three hydroxy groups, which are unlikely to be located in the same anhydroglucose unit. The liberated water molecules occupy a greater volume than when they are associated with the ion pair, and so cause swelling [218]. Thus not only are the differences in behaviour of alkali metal hydroxides accounted for, but the theory is applicable to other aqueous systems where ionic hydration is extensive. The theory is not, of course, applicable to non-aqueous swelling agents such as DMF.

$$\mathrm{Na^+OH^-}\,n\mathrm{H_2O} + \mathrm{R_{cell}(OH)_3} \rightleftharpoons \mathrm{R_{cell}(OH)_3\ Na^+OH^-}\ (n\text{–}3)\mathrm{H_2O} + 3\mathrm{H_2O}$$

Scheme 1.23

1.9.3 Liquid ammonia and amines

When cellulose is treated with anhydrous liquid ammonia at a temperature near its boiling point (–33.4°C) a 1:1 complex with a monoclinic cell having a = 1.27, b = 1.075, c = 1.03 nm and γ = 133.5° is formed [42,219–222]. This complex is fairly stable; it loses ammonia by evaporation, slowly at room temperature but more rapidly on heating, to give cellulose III. These changes are illustrated schematically in Figure 1.29 [223], which shows that the distance between the 110 planes remains nearly constant, the distension of the lattice by the ammonia being almost entirely within these planes (compare Figures 1.14 and 1.25). If the ammonia is removed by washing with water instead of by evaporation the material reverts to cellulose I. The morphology and mechanical properties of the fibres are also affected differently by the two methods of removing ammonia.

The conversion of cellulose I to cellulose III is seldom complete and may not be permanent. Complete conversion has been achieved, however, by using liquid ammonia at 140°C under a pressure of approximately 11 700 kPa (1700 lbf in^{-2}). The product is stable to boiling water [224].

Figure 1.29 also illustrates the effect of ethylamine (b.p. 16.6°C) on the cellulose unit cell. Once again a 1:1 complex is formed, but with greater distension in the 110 planes to accommodate the larger molecule. Propylamine behaves similarly, but complexes with higher aliphatic amines and some diamines can only be obtained if the cellulose is first ‘primed’ with liquid ammonia or ethylamine [225–229]. Water does not inhibit the action of

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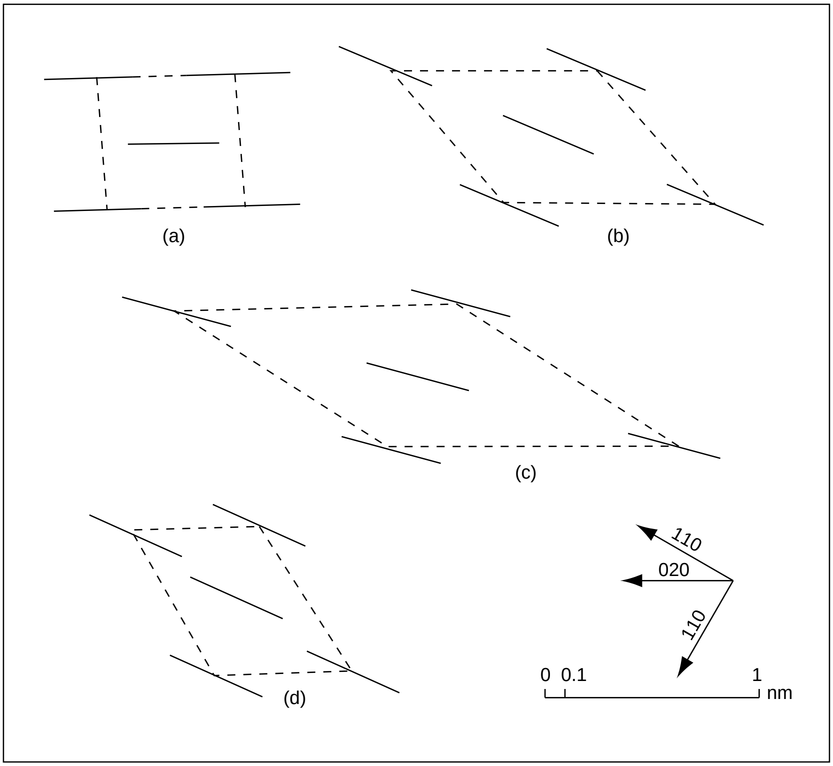

Figure 1.29 Diagram of conversion of (a) cellulose I to (b) ammonia–cellulose, (c) ethylamine–cellulose and (d) cellulose III.

ethylamine provided that the amount present is less than that required to form the monohydrate (28.6% by weight). If more water than this is present no complex is formed [230].

When ethylamine is removed from its complex with native cellulose a material of lower crystallinity and higher chemical reactivity is obtained. The product has therefore been called ‘decrystallised cellulose’ [166]. It is important to realise that decrystallisation is only partial. If the ethylamine has been removed by rapid evaporation it still gives a good cellulose I X-ray diagram. If removal has been by slow evaporation or by washing with a solvent, cellulose III is usually formed [231]. Figure 1.30 illustrates the influence of the nature of the solvent used to remove ethylamine on the chemical reactivity, here measured as the rate of acetylation by acetic anhydride in pyridine at 25°C. Washing with water gives a material of higher reactivity than the original cellulose, but washing with pyridine is even more effective. The relevant difference between the two solvents

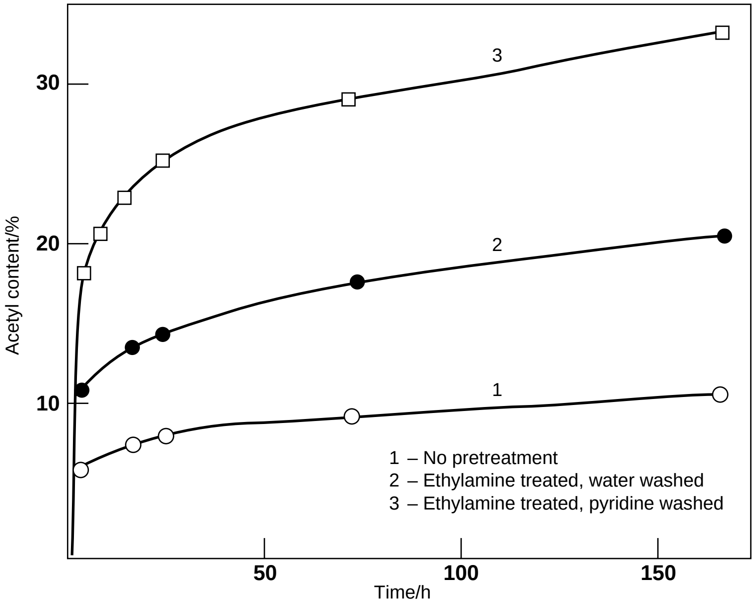

Figure 1.30 Effect of ethylamine on rate of acetylation of cotton at 25°C. (*Source*: [166].)

is that pyridine can form only one hydrogen bond per molecule whereas water can form two. Thus unlike pyridine, water molecules tend to link neighbouring chain molecules. It should be noted that the pyridine-washed product had been further washed with water and dried in the air before acetylation in order to standardise the conditions of treatment. Clearly, once the ethylamine has been washed out with pyridine, treatment with water has less effect on reducing reactivity than when it is used directly to remove the ethylamine.

In spite of early promise, ethylamine treatment of cellulose has not been exploited commercially. Liquid ammonia, however, has certainly achieved limited success [42,209,232,233]. Two different methods of removing ammonia have been proposed. In the Prograde process (J & P Coats) the ammonia is washed out with water. This was used in the 1970s instead of mercerisation for sewing threads, and to improve the handle and dyeing properties of knitgoods. In the Sanfor-Set process (so-called because the inventors, the Norwegian Textile Research Institute, appointed the Sanforized Company as their worldwide licensing agent), most of the ammonia is removed by evaporation and the final traces by means of dry steam. It is often known technically as the dry-steam process and can be applied to both woven and knitted fabrics. In contrast to mercerising, it improves the softness, flexibility and resilience of woven fabrics and reduces the amount of crosslinking agent required to produce satisfactory easy-care properties. However, its effect on dyeing is variable.

1.10 STRUCTURE OF COTTON IN RELATION TO DYEING

1.10.1 Introduction

The dyeing properties of a cotton fibre are determined by its external and internal structure. Considerable variations between different types of cotton have been found. This is illustrated in Table 1.5 which compares the colours obtained when nine different cottons were dyed separately under the same conditions with Chlorantine Fast Green 5BLL (CGY, CI Direct Green 27) [234]. The importance of uniform blending of fibres before spinning into yarn is clear.

The most obvious macrostructural feature to affect the dyeing of a fibre is its specific surface area, which is inversely related to its fineness (usually expressed as linear density). It has been known for over 50 years that the finer the fibre, the greater is the rate of dyeing [235]. The fineness of different cottons shows considerable variation. The linear density of St Vincent Sea Island cotton is about

Table 1.5 Influence of cotton type on colour after dyeing with CI Direct Green 27 [234]

Type	Staple length/mm	Colour co-ordinates			
		x	y	Y	ΔE
Pakistan Dessai	15.9	0.2369	0.2984	9.85	0
Middling American	27.0	0.2399	0.2971	9.60	1.47
Ashmouni	34.9	0.2382	0.2985	11.15	2.08
Bengal	12.7	0.2360	0.2971	10.70	1.46
Malaki	38.1	0.2359	0.2966	12.95	4.93
El Paso	30.2	0.2377	0.2967	12.05	3.50
Karnak	33.3	0.2385	0.2967	11.20	2.24
Sudan Sakel	31.8	0.2381	0.2976	11.00	1.87
Tanguis	31.8	0.2353	0.2967	10.40.	1.05

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z}$$

X, Y (lightness) and Z are tristimulus values; ΔE is the total colour difference computed on the ANLAB 40 system.

1.05 μg cm^{-1}; whereas that of the coarse Bengal variety is about 3.30 μg cm^{-1}; most American and Egyptian cottons lie between these two extremes [50].

Although dyeing, or indeed any other reaction, cannot take place within the crystalline regions of the fibre, it is not confined to the external surface. The accessible internal surfaces include the voids between microfibrils and the space between elementary fibrils, as represented by regions B and C in Figure 1.3, provided that the dye molecules are not prevented from entering by their size. One measure of the extent of these voids is the water imbibition (section 1.7.1), but perhaps a more relevant parameter for dyeing is accessibility measurement (section 1.4.3). However, these measurements suffer from the defect that the reacting molecules are mostly much smaller than those of a dye. For this reason some investigators have used the uptake of an actual dye as a measure of internal surface area. For example, Rousselle and coworkers studied the progress of the development of ordinary cotton fibres in the boll in this way [236]. They measured the uptake of CI Direct Green 26 (relative molecular mass, r.m.m. = 1350) by fibres taken from closed bolls at various times after flowering, using fibres transferred to the dyebath in the waterlogged state as well as fibres that had been dried (Table 1.6). The dyeability of fibres was drastically reduced by drying. Dye uptake decreased for both never-dried and dried fibres as the growing time (boll age) increased. Fibres harvested when the boll had been allowed to open in the cotton field, i.e. normal fibres, had the lowest uptake of all.

It might be expected that, because of their bilateral structure (section 1.2.1), cotton fibres would dye more rapidly in regions B and C than in region A (Figure 1.3), but this does not appear to have been investigated. It is clear, however, that

Table 1.6 Uptake of CI Direct Green 26 by cotton fibres at various stages of development.

State of fibre	Boll age/ days after flowering	Dye uptake/ mg g^{-1}
Closed bolls, never dried fibres	35	37.3
	42	25.1
	49	25.0
Closed bolls, dried fibres	35	2.9
	42	2.4
	49	2.2
Field-opened bolls, dried fibres		1.6

even if such differences occur they produce no overall visual effect in the dyed material.

As already mentioned, any sample of cotton is likely to contain at least some exceptionally thin-walled fibres, either ‘dead’ or ‘immature’ (section 1.2.1). These fibres lack a fully developed secondary wall and so the proportion of cellulose in the primary wall is greater than in normal fibres. The substantivity of many dyes for the primary wall is less than for the secondary, and so the dyed thin-walled fibres appear paler than the rest. Furthermore, even in those cases where there is no significant difference in dye uptake, thin-walled fibres still appear paler because the average path length of the illuminating light within them is less. If the thin-walled fibres are uniformly distributed in a yarn or fabric, differences in their dyeing properties are obscured. However, this is seldom the case. During ginning and carding they tend to form small knots of tangled fibres known as neps [62], which appear paler than the bulk of a woven fabric. The fabric may therefore appear speckled. Other types of nep are also found in cotton [237]. The most important of these are seed-coat neps which are really motes with tangled fibres attached. A mote is defined as an aborted seed [62]. Since its composition is different from that of cotton fibres, it tends to dye a different shade.

1.10.2 Effect of swelling

Mercer’s observation that swelling cotton with sodium hydroxide increases its dyeability is generally attributed to an increase in the number of accessible sites within the fibres. It is now also known, however, that even when the amounts of dye absorbed by mercerised and unmercerised cotton are identical, the mercerised sample often appears deeper [209]. This is illustrated in Figure 1.31 showing the amounts of four reactive dyes that can be saved by prior mercerisation to achieve a specific depth of colour. Even with pale shades (0.5–2% dye on weight of fabric, o.w.f.) as much as 30% less dye may be required, whilst for deep shades the saving is 50–70%. Goldthwait [238] established that the difference in apparent depth between mercerised and unmercerised dyeings varies with the actual depth of dyeing (Figure 1.32). Thus the extra dye required to achieve a match is not proportional to the depth of dyeing. Goldfinger [239] attributes the effect of mercerising on apparent depth to changes in the internal scattering of the incident light.

The conditions of mercerisation have a significant effect on dyeability [240]. In general, the higher the concentration of sodium hydroxide used, the greater the dye uptake (Table 1.7). Usually (but not always) mercerised fibres absorb

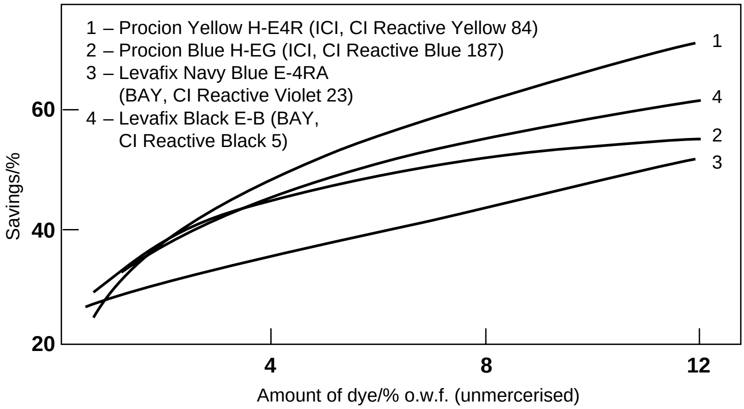

Figure 1.31 Saving of reactive dyes at equivalent visual depths on mercerised and unmercerised cotton. (*Source*: [209].)

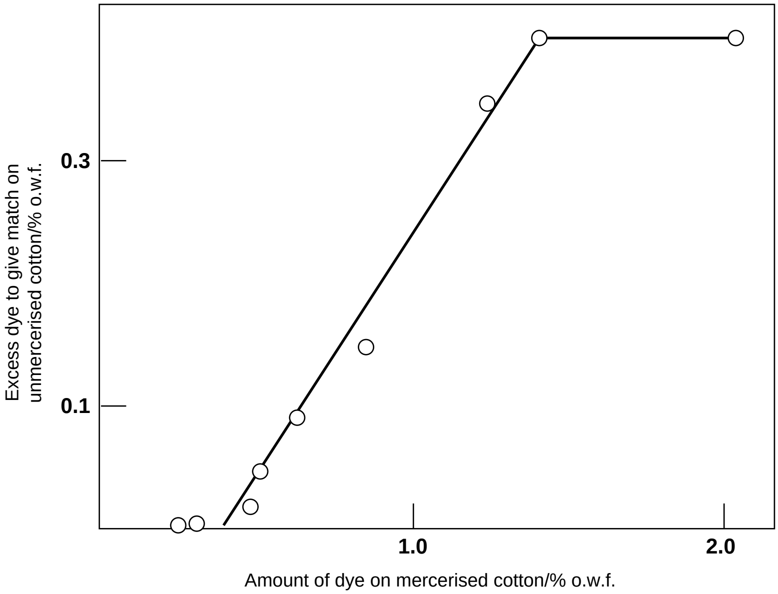

Figure 1.32 Excess of CI Direct Blue 78 required by unmercerised cotton to match a mercerised sample, plotted against dye uptake. (*Source*: [238].)

dyes better if they are not dried before dyeing (Table 1.8). Similarly, lack of tension during mercerising tends to enhance dyeability, but exceptions to this rule are known (Table 1.9) [241].

Table 1.7 Effect of concentration of mercerising liquor on absorption of CI Direct Red 2 by cotton

Sodium hydroxide concentration/%	Dye absorption/ mg g^{-1}
0	17.7
0.85	23.9
13.5	29.5
17.5	31.5
22.5	33.8
27.0	35.6
31.5	36.0

Table 1.8 Effect on dye absorption of drying after mercerising

	Absorption/mg g^{-1}	
	CI Direct Red 2	CI Direct Yellow 12
Unmercerised	8	3
Mercerised and dyed without drying	25	10
Mercerised and dyed after drying in air	16	8
Mercerised and dyed after drying at 110°C for 1 h	13	5

Table 1.9 Effect on dye absorption of tension during mercerisation

	Absorption/mg g^{-1}	
	CI Direct Red 2	CI Direct Blue 1
Unmercerised	15	1.5
Mercerised with tension	29	2.7
Mercerised without tension	35	2.4

The effect of liquid ammonia treatment on the dyeing of cotton depends on the way the ammonia is removed. Aqueous washing gives a product almost as dyeable as mercerised cotton. As with mercerising, treated yarns and fabrics appear more deeply dyed than untreated material having the same amount of dye present [233].

Successful operation of the dry-steam process depends on the fabric's containing less than 5% of ammonia on entering the steamer [233]. The improvement in fabric properties has already been mentioned, but the dyeability is often only slightly greater than that of unmercerised cotton. Some dyes, however, are absorbed as strongly as by mercerised cotton. If more than 35% of ammonia remains in the fabric entering the steamer, the product is no different from that obtained by washing with water; between 5 and 35% ammonia, intermediate properties result.

1.11 STRUCTURE OF REGENERATED CELLULOSIC FIBRES IN RELATION TO DYEING

Since the differences in fine structure between different regenerated cellulosic fibre types are much greater than between one cotton and another, precise relationships between structure and dyeability are difficult to formulate. The subject has been considered in greater detail than is possible here by Holme [75,77].

When considering dyeability it is important to distinguish between rate of dyeing and the final equilibrium, which may take a long time to reach. As with cotton, the finer the fibre, the more rapid the rate of dyeing [235,242]. Thus the time taken to reach equilibrium is greater for coarse than for fine fibres. Again as with cotton, at the same dye content there may be visual colour differences between fibres of different titre (linear density in tex) because of internal optical effects [243]. Hollow viscose fibres dye more quickly than regular viscose because of the much greater surface area of the internal channels, but the equilibrium uptake is essentially the same [70].

Although the dyeing characteristics of cotton and regenerated fibres that depend mainly on fibre fineness are similar, those dependent on fine structure show considerable differences [244]. For example, Giles [245] found that the light fastness ratings of several direct dyes (measured on an integral scale from 1 to 8 [246]) were higher on viscose than on cotton. This is illustrated in Figure 1.33. If the light fastness had been identical on the two fibres, all the points would lie on a straight line of unit slope through the origin.

An important structural feature of all regenerated fibres, but especially of regular viscose, is the difference between skin and core. The skin is more crystalline than the more readily swollen core. However, the skin crystallites are smaller than those in the core, and they are better oriented. Thus dyeing of the core is likely to be rapid once the dye liquor has reached it. In the well-known staining technique of Sisson and Morehead [247] for distinguishing skin from core in fibre cross-sections under the microscope, the dye is indeed more strongly absorbed by the core from aqueous solution. However, when the fibres are dried and then immersed in aqueous dioxan, the dye is leached out from the core only, leaving the skin deeply stained.

The direct influence of the DP of regenerated fibres on their dyeability is small [248]. The indirect influence, arising through the relationship of crystallinity and

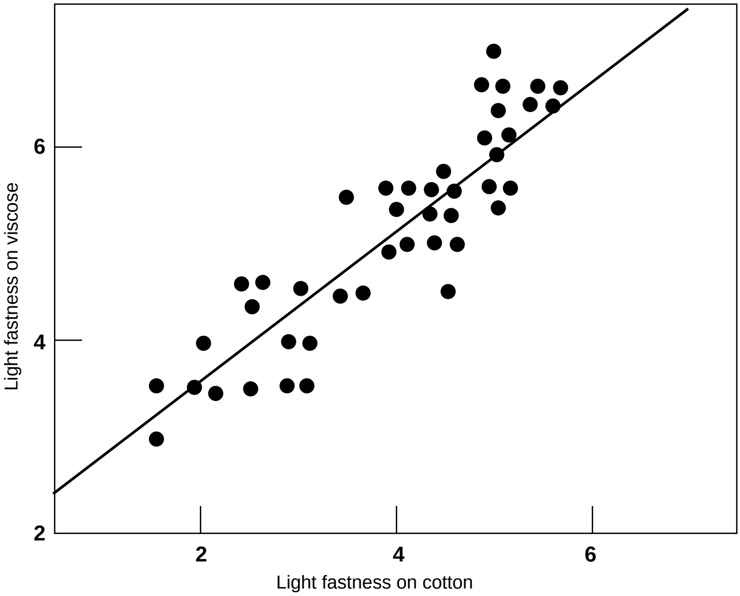

Figure 1.33 Comparison of light fastness of direct dyes on cotton and viscose. (*Source*: [245].)

orientation to DP, is greater. DP is, of course, only one among several factors that combine to determine these two properties.

That the degree of crystallinity is important in determining the dyeability of regenerated fibres is shown by the effect of steaming the fibres prior to dyeing. This is illustrated in Figure 1.34 [249]. Steaming of both regular viscose and cupro causes an increase in crystallinity which in turn leads to a decrease in dye absorption.

An equally important fibre parameter is orientation [250]. Increased orientation is accompanied by decreases in both equilibrium absorption and rate of dyeing; the latter is by far the more marked. This is probably due at least in part to an associated decrease in the volume swelling of the fibres [251]. This is illustrated in Figure 1.35, in which optical birefringence is taken as a measure of orientation, and dye absorption per unit surface area of the fibres in 15 minutes as a measure of rate of dyeing [250]. The variation of surface area with filament denier has been taken into account by multiplying the actual absorption of dye by the square root of the denier, since the surface area of a filament is inversely proportional to the square root of its denier [242]. At low birefringence values (0.015–0.025) the equilibrium dye uptake was found to decrease only slightly as the orientation increased, but the effect was greater at higher degrees of

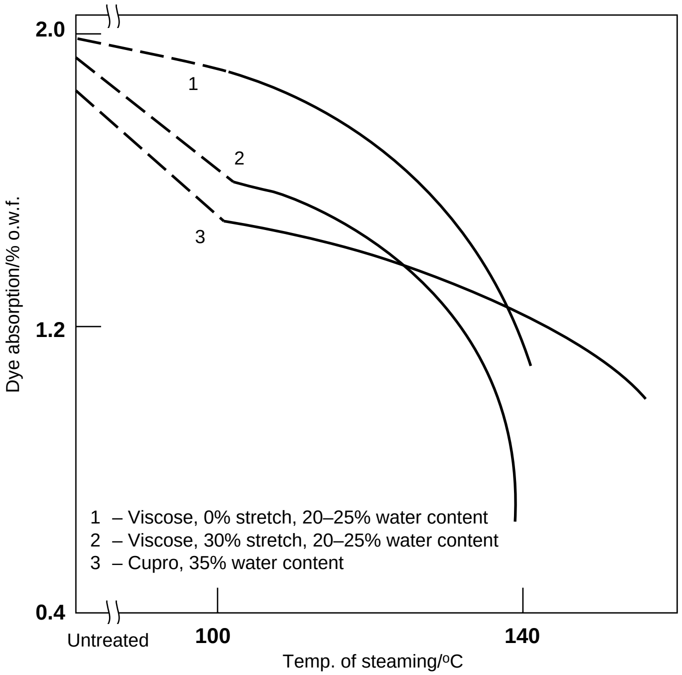

Figure 1.34 Absorption of CI Direct Blue 1 by regenerated cellulose fibres steamed for 1 h (dyeing conditions: 0.5 g dye and 5 g NaCl per litre for 2 h at 80°C. (*Source*: [249].)

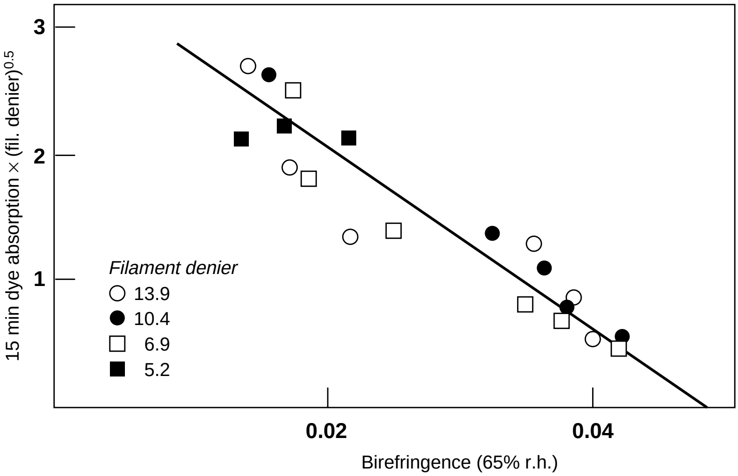

Figure 1.35 Effect of fibre orientation on uptake of CI Direct Blue 1 by viscose. (*Source*: [250].)

orientation. Thus, when the birefringence increased from 0.04 to 0.15, the equilibrium dye absorption increased from 10 to 14 μg g^{-1}[252].

So far the examples chosen to illustrate the relations between fibre structure and dyeability have been taken from studies using regular viscose. However, the same principles apply to modal fibres, which include all the old high tenacity fibres, such as high wet modulus and polynosic fibres. The most important special feature of modal fibres is their fibrillar structure, which means that they behave more like cotton than regular viscose. They usually have a high degree of lateral order; that is to say, their fibrils are uniformly distributed across a section of the fibre. As a result both the rate of dyeing and the equilibrium dye absorption are lower for modal fibres than for regular viscose. The behaviour of Tencel is anomalous in that it seems to absorb more dye than either regular viscose or cotton under comparable conditions [81], but this, of course, is a great advantage from a practical point of view.

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CHAPTER 2

Preparation

William S Hickman

2.1 INTRODUCTION

Cellulosic fibres, whether they are natural (cotton, linen, jute, ramie, sisal, etc.) or regenerated (viscose and polynosics) need some form of treatment to make them suitable for dyeing or finishing. This treatment, which removes natural or added impurities, is called preparation or pretreatment. It can be carried out on loose fibres, yarns or fabrics.

Unless the fibre is uniform in whiteness, absorbency and chemical composition (the cellulose is not chemically modified) and has low levels of impurities (waxes, lignin, electrolytes, etc.), it is unlikely that it will take up dye or finish in a uniform way or to the maximum extent possible. The prepared fabric must have 'fitness for purpose'. For example, a fabric to be given a water-repellent finish must be free from residual surfactant. Fibres used for medicinal end uses must have a low ash content.

All such requirements must be met against economic constraints relating to the costs of water, labour, plant, chemicals and energy. The first, water, is particularly important. Not only can the purity of the water affect many of the requirements but the volume and the environmental impact of effluent can, and is, adding increasingly to the cost per kilogram of textile produced. The effluent with the highest biological/chemical oxygen demand (BOD/COD) stems from pretreatment.

Successful preparation depends on four factors:

(1) The level and type of impurities present.
(2) The chemicals used in the various stages of preparation.
(3) The water supply.
(4) The type of machinery used.

These will be discussed more fully after a brief historical review [1].

The earliest methods of cotton preparation were based on boiling the fibre with potash liquor, extracted from the ashes of plants, followed by exposure to sunlight, if bleaching was required. Some of the terms still in use in the industry can be traced to such preparation. Thus a croft, which once was an open field where fabrics were exposed to light and air, is now the works where bleaching is carried out. Between alkaline boiling and crofting, fabric was rinsed and immersed in buttermilk, from which process is retained the term souring.

In the late 1700s, lime replaced potash, sulphuric acid replaced buttermilk and the methods of bleaching were revolutionised as the observations on the bleaching action of chlorine, discovered by Scheele in 1774, were developed. In the 19th century subsequent developments were related mainly to improvements in scouring techniques using lime or caustic soda. Early in this century, a detailed study was made of hypochlorite bleaching, and methods, still used today, were developed to assess the properties of the bleached fabric.

In the 1930s hydrogen peroxide and sodium chlorite bleaching processes were developed for cellulosic fibres. Hydrogen peroxide, however, had been used for fifty years prior to this to bleach wool and silk. Most developments since 1945 have been associated with these two chemicals. The most notable was the development of rapid, continuous bleaching processes with hydrogen peroxide.

2.2 IMPURITIES PRESENT IN CELLULOSIC FIBRES

Most natural fibres are not pure cellulose but contain significant amounts of other materials [1,2]. The analysis of various cotton and flax samples is summarised in Table 2.1. The pectins are polygalacturonic acids and their

Table 2.1 Impurities present in cellulosic fibres (% by weight)

	Cotton [2]			Flax [3]	
	Average	American	Egyptian	Unretted	Retted
Cellulose	88.0–96.0	91.0	90.8	56.4	64.1
Hemicellulose				15.4	16.7
Pectins	0.7–1.2	0.53	0.68	2.5	1.8
Lignin				2.5	2.0
Proteins	1.1–1.9				
Wax	0.4–1.0	0.35	0.42	1.3	1.5
Ash	0.7–1.6	0.12	0.25		

calcium, magnesium and iron salts, and the ash contains calcium, magnesium and potassium phosphates and carbonates. Not included in these figures is the vegetable debris produced by mechanical harvesting and ginning of the cotton. This includes cotton seed, leaf and calyx for cotton. The amount depends on the quality of the cotton fibres. Linters (short staple waste) used for medicinal cotton can contain up to 25% of this woody material.

In linen the vegetable debris is the residual cortex of the plant which has been left from the decorticisation process and can amount to nearly 30% of the weight of retted flax. Regenerated cellulosic fibres have much lower levels of impurities and these generally arise from the solvent used for dissolving the cellulose.

To these natural impurities are added 10–15% of size, spin finish or knitting lubricant. The spin finishes and knitting lubricants contain surfactants and mineral oils applied alone or in admixture to decrease friction on machine parts. Sizes are film-forming materials used to coat the warp yarns of woven fabrics in order to minimise yarn breakage during fabric production. Starch, usually esterified or etherified, is the most common size but polyacrylates, cellulose ethers (e.g. carboxymethylcellulose), poly(vinyl alcohol) and poly(vinyl acetate) are also used. The source from which starch is obtained, e.g. corn or rice, can affect its ease of removal. Size plasticisers such as tallow or paraffin wax are either added to the sizing liquor or applied, after the size has been dried onto the yarn, by kiss–roll coating.

Metallic ion contamination, particularly iron and copper, is of most concern during oxidative treatment as this can lead to chemical damage. This damage can manifest itself as very localised destruction of the fibre or reduced dye uptake. This form of contamination can result from the growing area where the plant absorbs the mineral matter through its roots or the wind simply blows the soil onto the fibre. It can also arise from washing off with contaminated water or heating with contaminated steam.

2.3 CHEMICALS FOR PREPARATION

Many types of chemicals are used in preparation. These include enzymes (α–amylase, cellulase), alkalis (caustic soda, soda ash and phosphates), bleach bath stabilisers (silicates, organic stabilisers), sequestrants (amino- and hydroxy-polycarboxylic acids, aminomethylphosphonates, sodium polyphosphates), oxidative bleaching agents (hydrogen peroxide, sodium chlorite and hypochlorite) and reducing agents (sodium bisulphite, hydrosulphite). To these main components are added the auxiliaries, usually surfactants, to assist in wetting, scouring and detergency. The chemistry of these products has been covered elsewhere [4], but some guidance on the characteristics and selection of such materials will be given.

2.3.1 Enzymes

Amylases degrade the components (amylose and amylopectin) of starch and starch-derived sizes very efficiently. Traditionally they are used warm (65–70°C) with a reaction time of several hours but thermostable enzymes have been developed which allow brief dwell times at temperatures up to 120°C. Common salt and calcium ions improve the degradation process. Copper and zinc ions and most anionic surfactants deactivate the enzyme. Amylases are discussed further in section 2.6.2.

Cellulase is finding increasing use as a surface modifier for denim garments and as a handle modifier for certain regenerated cellulosic fabrics. As such processes are regarded as finishing processes, they will not be discussed further. There is some interest in the use of pectinases as scouring agents and lignases as lignin removers but as yet no commercial processes have been developed. Xylanases are used for pulp delignification.

2.3.2 Wetting agents and detergents [4]

Good wetting is necessary for complete saturation and penetration of the substrate as quickly as possible. The rate of wetting is not usually so critical for batch processes but is vital to continuous processes. The exception is the processing of loose fibre where a deaerating agent is added to ensure complete, rapid penetration of the fibre mass. Commercial wetting agents are usually anionic or nonionic surfactants, or a blend of the two. The anionic products used by the textile industry are usually long-chain alkyl or aryl sulphates, sulphonates or phosphates. For most applications it is important that residues in the effluent should be biodegradable. To achieve this the alkyl groups must be linear rather than branched.

In solution the compounds dissociate, to produce a hydrophobic tail (R in Scheme 2.1) with a hydrophilic polar head. It is this combination of hydrophobic and hydrophilic parts which makes the materials surface-active. Nonionic surfactants do not dissociate in solution but have a polyoxyethylene chain which

$$\mathrm{ROSO_2ONa} \rightleftharpoons \mathrm{ROSO_2O^-} + \mathrm{Na^+}$$

Scheme 2.1

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is hydrophilic, readily forming hydrogen bonds with water molecules. Most commercial products used in textile preparation processes are ethoxylated fatty alcohols. Their general formula is shown in Figure 2.1.

$$R(OCH_2CH_2)_nOH$$

Figure 2.1 General formula of ethoxylated fatty alcohol.

The surface activity is determined by the length of the alkyl group (R) and the degree of ethoxylation (*n*). Optimum surfactant properties are found when $n = 10–15$. If *n* is lower than this the product is more hydrophobic than hydrophilic and so has low water solubility and cloud point (the temperature at which the product precipitates from solution) and tends to have good fat-emulsifying rather than wetting properties. Though both anionic and nonionic surface-active agents can have good wetting and detergency properties, it is the ability of the nonionics to improve detergency (at the cost of reduced wetting performance) as the degree of ethoxylation is decreased that makes them useful. As stated above, a low degree of ethoxylation improves fat and wax removal but reduces cloud point. To maintain detergency as the temperature is raised the cloud point is often increased by addition of an anionic product [5].

The phosphate esters can be tailor-made similarly by altering the ratio of alcohol to phosphorus pentoxide during their preparation and are finding increasing use as detergents.

The important questions about the selection and use of surfactants in preparation are the following:

(1) If an anionic wetting agent is used in a desize liquor, is it compatible with the α-amylase?
(2) Is the surfactant stable at the alkali and electrolyte concentrations used? This was of most importance in feed liquors for continuous wet-on-wet application of alkaline liquor (section 2.5.4) where the feed liquor can be five to ten times more concentrated than the application liquor, but is less critical now *all* chemicals are kept separate at this dosing stage.
(3) Is the surfactant stable to oxidation?
(4) Will the surfactant leave traces which would impair the result of subsequent processes, e.g. oil- and water-repellent finishing or printing?
(5) Is the cloud point of any nonionic surfactant exceeded? During application this would adversely affect wetting/detergency whereas during washing-off it would precipitate the surfactant onto the substrate and cause backwetting.
(6) Does the surfactant generate foam? In general, low-foaming behaviour is required and this can be temperature-dependent. In circulating-liquor

systems (jets, autoclaves), foam causes pump cavitation which leads to poor flow leading to unlevelness. On conveyor and roller-bed steamers the foam reduces traction.

(7) Is the viscosity of the product, especially on dilution, satisfactory for use in automatic dosing systems?

2.3.3 Scouring agents [4]

BASF pioneered the 'demineralisation' of cotton during scouring [6]. In this process a scouring auxiliary consisting of surfactant, a sequestering agent and a reducing agent removes iron or other metallic contamination (which can cause catalytic decomposition in subsequent bleaching) and promotes fabric absorbency by the extraction of the alkaline earth metals. The preferred surfactants were the alkylsulphates and the alkylarylsulphonates but the phosphate esters are increasingly used [7].

The reducing agent helps remove iron contamination by reducing ferric to ferrous salts, which are more readily complexed by the sequestrant. Furthermore, it has a reductive bleaching effect so that scoured cotton is less brown in colour than is usual in caustic-scoured material. Air in the fabric or in the steam causes tremendous degradation of the cellulose under hot alkaline conditions by the peeling reaction, or β-hydroxycarbonyl elimination. The mechanism will be discussed more fully later but consists of oxidation of the glucose units in such a way that a keto group is formed two atoms away from the glycoside link. This sensitises the link and causes the glucose unit to peel off. Reducing agents, for example the sulphites and hydrosulphites, are often added to scour liquors to prevent this auto-oxidation.

Scouring is usually carried out with sodium hydroxide but the addition of other alkalis (trisodium phosphate, sodium silicates and tetrasodium pyrophosphate) and solvents has also been recommended [8].

The addition of oxidants to batch processes has been recommended but the greatest benefit is gained by adding oxidant to the scouring liquor on continuous ranges to give a so-called oxidative desize.

2.3.4 Sequestrants or chelating agents [2]

Sequestrants, also called chelating agents, remove metal ions from solution. They do this by having adjacent groups (carboxylic or phosphonic acid, hydroxy, etc.) which form multidentate complexes with cations. The order in which the cations are sequestered depends on pH, but at a given pH this order will normally be the same for all sequestrants within a particular class (see below) and the relative stability of the complexes will also be the same. With a particular cation the stability of the complex and the amount bound will vary from sequestrant to sequestrant. The major classes of sequestrants are the aminopolycarboxylic acids (e.g. ethylenediaminetetraacetic acid, EDTA), hydroxypolycarboxylic acids (e.g. citric acid), aminomethylphosphonic acids (e.g. ethylenediaminetetramethylphosphonic acid, EDTMP), polycarboxylic acids (e.g. oxalic acid) and the sodium polyphosphates (e.g. sodium hexametaphosphate). The last two classes are not so important in preparation.

Most sequestrants, excepting inorganic phosphates, sequester calcium over the whole pH range [8]. The sequestration of iron varies greatly but few products sequester iron above pH 12.

2.3.5 Stabilisers

Bleaching with hydrogen peroxide is controlled by addition of a stabiliser. Commercial products are based on various combinations of magnesium salts, organic sequestrants, protein degradation products, surfactants and anionic polymers such as polysilicates and polyacrylates. Some products are designed to give stabilisation only, whereas others also combine detergent and softening actions. Many products give adequate stabilisation in batch bleaching but the selection for continuous steaming processes is much smaller.

Control of chlorite bleaching is more concerned with control of pH and the emission of chlorine dioxide to the atmosphere. Hydrogen peroxide can even be used for this last purpose.

2.3.6 Oxidative bleaching agents

Sodium hypochlorite, sodium chlorite and hydrogen peroxide are the three oxidants predominantly used for bleaching cellulosic fibres. Potassium permanganate is occasionally used for denim washing which confers a ‘stressed look’ to denim garments, and peracetic acid is being looked at as a replacement for sodium hypochlorite [9,10]. Detailed methods of use will be given later, but a brief overview of properties and problems is given here. Permanganate will not be discussed because of limited use and the environmental unacceptability of discharging manganese ions.

Sodium hypochlorite

Sodium hypochlorite (hypo or chemic) is produced by dissolving chlorine in caustic soda solution and is a yellow liquid with a specific gravity of about 1.2. The maximum commercial strength is 150 g l^{-1} of available chlorine. The solution is not very stable and so it is essential to give the chlorine content of the stock liquor a routine check. Hydrometry should not be used, as absorbed carbon dioxide rapidly changes specific gravity.

Hypo bleaches rapidly at room temperature. It is not as sensitive to heavy metals as peroxide but it does easily chlorinate any organics present. This chlorination is an advantage in bast fibre processing but is a severe disadvantage in most other circumstances. For example, it yellows grey cotton by chlorinating the pectins and proteins present. It is essential, therefore, that the cellulose be cleared of natural impurities by thorough scouring before bleaching with hypo. In practice, one or two alkaline boils may be required with intermediate washing. These will be followed by scouring and further washing prior to bleaching. Bleaching must be followed by washing and an antichlor treatment. The end result is a prolonged, labour-intensive process with relatively low chemical costs but high demand for water. Hypochlorite bleaching today is largely a batch process but has found some use in India [11,12] and Eastern Europe on continuous bleach lines as a prebleach prior to peroxide.

The chlorinated products from hypo are detected in effluent streams as adsorbable organohalogens (AOX) and chloroform. These are materials regarded increasingly as environmentally unacceptable. It is likely that hypo will disappear from use in the textile industry.

Studies have shown that hydrogen peroxide does not form AOX compounds even in the presence of salt [13].

Sodium chlorite

Sodium chlorite is usually sold as a solid (80% active solids) or as a liquid (26% active solids) with a specific gravity of 1.25. In contrast to hypo or peroxide bleaching, it is used under acidic conditions. The scouring process, required for hypochlorite, can be omitted and bleaching can be carried out on loomstate or desized materials. It bleaches seed well.

Bleaching under acidic conditions removes only small amounts of natural fats and waxes. This was an advantage for knitting yarns and knitted fabrics as it gave a softer handle. Chlorite bleaching is relatively unaffected by iron or copper contamination.

One of the bleaching agents liberated from chlorite under acidic conditions is chlorine dioxide. This corrosive gas is toxic (threshold limit value = 1 p.p.m.). Adequate fume extraction is essential, therefore, to ensure operative safety. The corrosive nature of chlorine dioxide demands exotic materials of construction such as titanium. One company used to supply special ceramic tile-lined equipment for chlorite bleaching [14].

Chlorite bleaching has little effect on oil stains but most dyes are destroyed by the process. For this reason fluorescent brightening agents are usually applied in the wash-off and few coloured-woven fabrics are bleached with this agent. It is frequently used for bleaching 100% polyester but the continuous, long-dwell J-box ranges used for bleaching knitted cotton fabrics have now been replaced by rapid, continuous peroxide bleaching.

The AOX generated by chlorite is only a tenth of the amount generated by hypochlorite [13], but even this is eight to ten times that present after bleaching with hydrogen peroxide.

Hydrogen peroxide

Hydrogen peroxide is a colourless liquid which is used, in the textile industry, as a 35 or 50% solution with specific gravity of 1.131 or 1.195 respectively. It is the most widely used bleaching agent.

Hydrogen peroxide is an extremely versatile bleaching agent, applicable over a very wide range of bleaching temperatures (ambient to 130°C) and times (minutes to days) on a wide range of machinery. Bleaching is usually carried out under alkaline conditions and this allows combination with other processes, such as scouring. Hydrogen peroxide can also be activated by agents other than the hydroxide ion, for example u.v. radiation and *O*- or *N*-acyl compounds. Irradiation generates free radicals, unsuitable for cellulose bleaching but of increasing interest in waste-water decolorisation [15,16]. The acyl compounds produce peracids, e.g. reaction of acetic anhydride (an *O*-acyl compound) with hydrogen peroxide produces peracetic acid, formula CH_3COOOH. Peracetic acid is of increasing interest as a prebleach for knitted fabrics [9] and in the washing of denim and bleaching of cotton/acrylic blends [17]. *In situ* production has been recommended, but storage of the acetic anhydride seems more inconvenient than the commercially available peracid itself.

2.3.7 Reducing agents [3]

Many coloured materials are decolorised by reducing agents such as the sulphites, bisulphites and hydrosulphites. The colourless form is sometimes insoluble in water and may be easily reoxidised to the coloured form. These reasons limit the use of reducing agents as bleaching agents. Sodium hydrosulphite (hydros) is used for the bleaching of wool but only in combination with hydrogen peroxide. Hydros is a powder that dissolves in water with difficulty and rapidly decomposes unless the solution is alkaline. Stabilised hydros has alkali added to the powder to improve solution stability.

Reducing agents are used as antichlors (chemicals that remove the last traces of chlorine from the fibre after a hypochlorite or chlorite bleach). Their use in this area is diminishing, often on environmental grounds (odour, toxicity), in favour of hydrogen peroxide.

2.4 WATER [18]

Most bleachworks were originally situated near a river which provided a copious supply of good quality water, i.e. water with low suspended solids, neutral reaction and low metallic ion content, particularly transition or heavy metal ions. The need for the following quality factors is self-evident:

(1) Any suspended solids are likely to be filtered out onto fibre, yarn or fabric.
(2) High or low pH could cause spontaneous, uncontrolled reactions to occur.
(3) Metallic ions may give rise to discoloration, stains or chemical damage (catalytic tendering) of the substrate during bleaching.

It is no longer possible to meet the original geographical requirements and water is now obtained as:

(1) surface water from rivers, canals and reservoirs;
(2) ground water from wells and bore holes;
(3) mains water from the public supply;

and as the quality can be variable it usual for the water to be:

(1) filtered, using sand filters, to remove the suspended solids;
(2) neutralised to give a pH around 7;
(3) treated, if necessary, to remove residual chlorine;
(4) softened to remove calcium and magnesium ions;
(5) treated to precipitate heavy metal ions.

During desizing, calcium ions are beneficial, whereas copper and zinc ions deactivate the enzyme; hence moderately hard water can be used but supply through copper piping should be avoided.

In scouring, calcium ions, in the presence of hydroxyl ions, produce one of the most insoluble materials, calcium hydroxide, which deposits onto fabric and machinery. In bleaching, the precipitation of calcium hydroxide can seed stabilisers, causing them to coprecipitate. The heavy metals cause rapid peroxide decomposition and chemical damage. For peroxide bleaching some water hardness is advantageous. Ideally this should be about 60 mg l^{-1} (as calcium carbonate). With water of lower hardness an addition of magnesium salts is recommended. The precipitates from alkaline scouring or bleaching liquors cause an unlevel appearance and inadequate absorbency of the substrate. Such faults can usually be corrected by souring with acid.

The bleacher is concerned not only with the quality of the water coming into the works but also with the quality of its discharge, whether this is to sewer or river. For discharge to natural waterways a consent limit for quality of effluent must generally be met. The parameters of concern to the preparation department are primarily volume of effluent, the BOD or other basis for assessing inorganic and organic chemical pollutant load, and suspended solids. Coloured effluent is becoming more of an issue. In some areas of the UK this now includes a specification of colour and this will obviously require increased cooperation between dyehouses and water treatment works. There is increasing interest in colour removal [13,19].

The efficiency of washing machines and a reduced number of washes, for example by combining stages, obviously reduce effluent volume but preparation is still the major user of water and so water reuse needs to be developed: this is likely to be an area for progress in the future. Correct selection of auxiliaries and breakdown of extracted material by oxidation, particularly starches, during processing can significantly reduce BOD/COD. Filtration, or at least settling-out in holding tanks before discharge, is increasingly being carried out to reduce suspended solids. Settlement is improved by the use of flocculants, e.g. aluminium sulphate, which will also flocculate some colouring and other organic matter.

In the UK, the formation of the National Rivers Authority and the privatisation of the water authorities are making water supply and discharge increasingly expensive as tighter and tighter specifications are set. As the preparation department uses the largest amount of water, this is an area of increasing concern.

2.5 PREPARATION MACHINERY [20]

The machinery used for preparation is, to a large extent, controlled by the physical form (loose stock, yarn or fabric) of the textile being processed and so this will be discussed first. In the sections dealing with actual machinery, brief comment only will be made as the book edited by Duckworth [20] and other reviews [21–23] deal with specific and often practical detail.

2.5.1 Form of textile

Loose stock

Loose stock is traditionally bleached in batch form on package machines or in autoclaves. Bales of fibre are mechanically opened, an essential cleaning operation, and packed into cakes. This packing is done wet with a stamping machine and the fibres are formed into packages on stainless steel rings or packed into a perforated basket. Packing densities of 250–300 g cm^{-3} are typical and limited by the strength of the container. Natural fibre in the form of short-staple waste (from ginning, carding or combing) is processed in this way.

Viscose fibres have been continuously dyed for many years but the technology was never used for natural fibres [24]. During the 1970s, however, a continuous processing unit was developed for cotton in the USA by Cotton Inc. [25]. The unit forms the fibres into a sheet called a 'batt' and this batt is processed, with minimum tension, as if it were fabric.

Yarn [26]

Yarn is processed only for certain end uses, for example sewing thread, knitting yarns, viscose muffs. This represents only 15–20% of the material that is wet-processed. The processing can be carried out either in hank form or as packages. Continuous processing of hanks is only carried out for wool yarns.

Packages are processed in either vertical or horizontal spindle machines. Such machines may be pressurised to allow wet processing to be carried out above 100°C whereas hank bleaching machines have horizontal supports and are usually operated at atmospheric pressure.

Hank processing produces a yarn with a bulky, soft handle as it is free to move and swell in the liquor. This freedom of movement does, however, result in more tangling of the yarn which makes rewinding more difficult. Hank reeling and backwinding of the processed yarn are costly and wasteful. The voluminous nature of the yarn makes it difficult to pack the batch into the machine, which leads to levelness problems, and so batch sizes are smaller than in package machines for a given volume of liquor.

Package processing, on the other hand, produces less bulky yarns and allows faster winding and backwinding with less fibre waste and bigger batch sizes per unit volume of liquor. These bigger batch sizes and the sophisticated process control found on package machines have now totally converted the processing of 100% cotton and polyester/cotton yarns to such machines. It is, therefore, cellulosic fibres and their blends, on package machines, which are primarily considered here, though similar bleach formulations can be used for such yarns in hank form.

This process control encompasses production of standard packages in terms of weight, traverse, diameter and density, constant/invariable cycle times and press packing to even out any slight variability of winding. Uniform density is essential to prevent unlevelness caused by channelling.

Knitted goods

Knitted goods have poor dimensional stability and so are deformed easily by mechanical forces. They may be prone to creasing during wet processing. Knitted goods are comfortable to wear when made into garments, owing to their high elasticity and moisture absorbency.

Preparation should not only give the required whiteness, absorbency and seed removal, but also a soft, voluminous handle and good sewability without distortion of the goods. A soft handle can be achieved by using acidic processing stages, which have no scouring action, to leave natural fats and waxes. The demand for supersoft finishes demanded application of softener. This change promoted the use of alkaline systems with the guarantee of good absorbency.

Yarns used for knitting are usually high-quality combed yarns and so contain little non-cellulosic material. The knitted structure (fabric or hosiery) is open and promotes penetration of treatment liquors and facilitates washing-off of residual chemicals and impurities.

Garments and hosiery are usually batch processed but the latter is being continuously processed in the USA. The batch machines are usually D- or Y-pocket washer extractors, though paddle machines are still used. This is a specialised area and will not be discussed further: however, the traditional bleaching agent for hosiery, hypochlorite, is being replaced by hydrogen peroxide on the environmental grounds discussed previously.

Fabric can be prepared batchwise on winch or jet, continuously processed on J-box, spiral winch or jet (Argathen, Colorado, Jemco II) and conveyor steamer, or semi-continuously prepared by cold pad–batch methods.

Woven fabrics

Fabric construction and fibre content (100% cotton/linen/viscose or polyester/cotton blends) determine whether fabrics are best processed in open-width (O) or rope (R) form. Table 2.2 summarises information from BASF but Evans also gives some ‘rules’ [27]. The more tightly woven a fabric, the more rigid it is. This

Table 2.2 Fibre composition of various fabric constructions (O, open-width; R, rope form)

Construction	Cotton	Polyester/ cotton	Viscose	Linen
Sheetings	O/R	O/R		
Tablecloths	O/R			O
Corduroy	O	O		
Furnishings	O/R		O	O
Interlinings	O/R	O	O	
Pile fabrics	O			
Ticking	O/R	O		
Shirtings	O			
Tarpaulins/tenting	O	O		
Raised goods	O		O	
Twills	O/R	O		

rigidity and the demand for wider fabrics make rope processing less easy to carry out. In new installations, batchwise or continuous rope machines are seldom considered as they severely limit flexibility of processing.

Machinery is available for continuous or batch operation for both forms. Rope processing is carried out on kiers, winches, jets and in J-boxes, whereas open-width processing is carried out on jig, beam, pad–steam ranges and open-width J-boxes. In some cases dyeing and finishing can be carried out on the same machinery but, more usually, the machines are specific to preparation.

2.5.2 Batch processing

Kiers [28,29]

Kiers came in many forms, the most popular being a cylindrical iron vessel placed vertically and holding two tons of fabric. Liquor percolates through the fabric and is pumped back, via a multitubular heater, to spray on the fabric. The machine is included here as historically it holds an important place in scouring and bleaching practice. In the Western world it has been superseded by other equipment.

Garrett in a classic paper stated that for successful use of kiers it is essential to have all air excluded from the kier and:

(1) the correct quantity of cloth in the kier;

(2) the correct loading of the kier;

(3) the correct rate of liquor circulation;
(4) the correct liquor ratio;
(5) the correct steam pressure and volume [29].

The fabric is rope washed after processing and, if bleaching is to follow scouring, the kier must be reloaded with intermediate washing. Iron vessels are unsuitable for peroxide bleaching and so the machine must be suitably passivated using silicate cement [28].

Package machines [20,26]

Package machines are usually cylindrical vessels with a domed top and bottom which are capable of being pressurised (Figure 2.2). The top, fitted with a counter-balanced hinge, forms the lid and is locked into place by a sliding ring or similar device. Treatment is carried out by pumping liquor to the base of the vessel and, after it travels through the substrate, returning to the pump through another pipe located at the bottom of the vessel.

Machine diameters go up to about 2 m with the vessel height being about the same but there are many tall units used for preparation. The machines can be supplied with a wide range of carriers for yarn or loose stock processing.

Pressurisation can be achieved using an orifice plate (a plate with a small hole

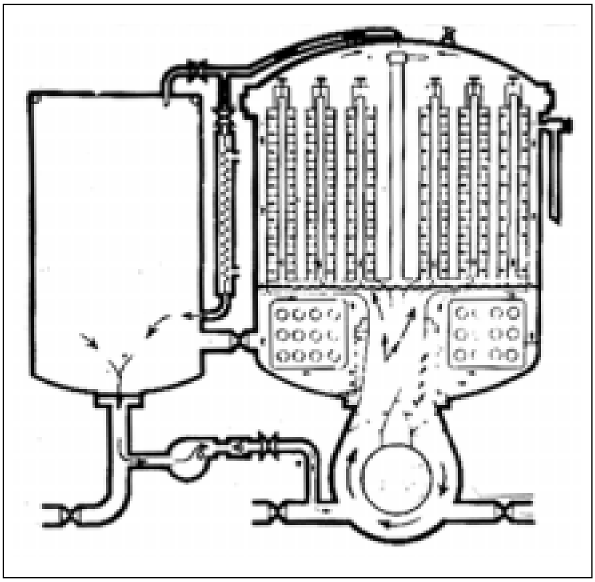

Figure 2.2 Diagram of package machine. (*Source:* [26].)

in its centre) which partially blocks the pipework to the side tank. The secondary pump attempts to deliver a greater amount of liquor to the vessel than is returned to the side tank and this creates a static pressure. Most machines are today pressurised by the air-cushion principle. Here the machine is not fully filled with liquor. When all valves are closed, the gas space above the liquor is compressed as the temperature rises. This gas space is usually fitted with control valves connected either to atmosphere or to a compressed gas supply and these valves maintain the desired pressure. This technique reduces the liquor ratio and so gives improved economy.

All machines are fitted with pressure relief valves but it is still recommended that machines used for peroxide bleaching are fitted with bursting discs.

Winch

Winch design and use has been well reviewed by Wyles [20,22]. The basic arrangement is to have several (1–40) looped ropes of fabric of equal length which are kept apart by the peg rail. Most of the fabric is plaited down into the liquor but part of the rope runs over two reels above the liquor. The smaller diameter (15 cm) circular roller mounted about 35 cm above the liquor surface is called the fly or jockey roller. The upper reel, usually elliptical in shape, is motor-driven and moves the fabric through the liquor.

Wyles deals with almost all aspects of winch operation including the use of the mid-feather (gate) to control fabric movement, the covering of the reel to improve traction and the use of drip feed buckets to add chemicals.

Jet

Developments in jet machines are well covered [20–22,30]. The main pump circulates the liquor which propels the fabric, in rope form, round the machine. The principle worked well for 100% synthetic fibre fabrics; however, the running speed and the high lift of the fabric from the liquor were unsuitable for preserving the appearance of knitted cotton fabrics. The Thies Ecosoft, one of many modern jets, has not only overcome these problems but also improved the economy of wet processing by reducing the liquor ratio, enabling the machine to process a whole gamut of fabric weights and styles from single jersey to fleece fabrics. This last point is exactly the same as the one made about open-width processing: only buy a machine if it is versatile. Such versatility is often aided by process control. An example of this is the Synchron Control of Thies, which adjusts pump speed and therefore rope speed to suit the particular stage of processing in an attempt to preserve fabric appearance [31].

Jig

The jig or jigger is one of the oldest machines for processing woven fabrics in open-width form. Fabric is transferred from one roller to the other through a small volume of liquor (Figure 2.3). All aspects of the machine are well described elsewhere [20]. The tension involved in the winding operation makes the machine unsuitable for knitgoods.

Particular problems of jig operation, as far as preparation is concerned, are the swelling and dissolution of size, which makes the fabric slippery and unstable in roll form, and the low liquor ratio which makes washing-off difficult.

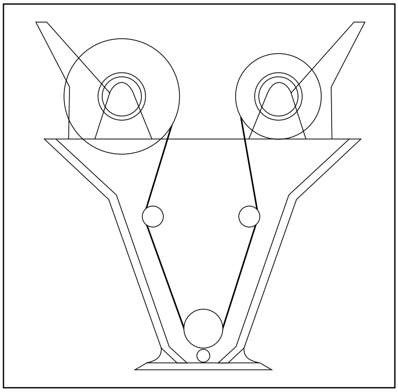

Figure 2.3 Diagram of jig dyeing machine. (*Source:* [20].)

Beam-dyeing machines

Beam-dyeing machines are, to some extent, analogous to horizontal package-dyeing machines. The carrier, or beam, is a perforated cylinder with an open end which locks on to the pump. The fabric is wound on to the beam and the beam is loaded on a cradle which runs on rails on a transporter. The beam is locked onto the pump by running the cradle from the rails on the transporter to rails inside the machine and screwing on a locking nut. The perforations on the beam that are not covered by the fabric are covered by flexible sheets of metal wrapped round the beam and held in place by large jubilee clips. The positioning of these sheaths is critical to successful beam-dyeing [20]. It is rare to beam-process cellulosic fabrics but gauze and batts of loose cotton are occasionally processed on these machines.

2.5.3 Semi-continuous processing

Semi-continuous routes entail batching fabric on to A-frames, but an element of continuity is created by refilling the A-frames. Once the process has been started there is continuous flow of fabric through applicators, washers and dryers.

Pad–roll

Pad–roll processing involves application of chemicals to open-width woven fabric and rolling the fabric onto an A-frame contained in a movable container, often referred to as a caravan. Before batching, the fabric is warmed by passage through a pre-heater.

Problems with pad–roll processing are twofold:

(1) Variable treatment from first to last end.
(2) Variability from edge to middle.

The first, variation from one end of the batch to the other (ending), is simply caused by the time difference between batching the first and last end, which can be up to 2 h. The second is caused by swelling of the fibres in hot liquors. This swelling 'squeezes' the roll on the A-frame and transfers impurities and/or chemicals from the centre to the edge (listing) leading to unlevel results.

Pad–batch

Pad–batch processing is similar to that described above except that the batch is at room temperature. This reduces the ending and listing problems but increases the treatment time by a factor of 5–10. The long dwell times allow stages (desizing, scouring, bleaching) to be combined, resulting in substantial savings [33]. The result is never as good as that obtained from hot processes but it offers adequate quality with minimal capital expenditure.

It is necessary to keep the batch wrapped in a plastic sheet to prevent it drying out. In both pad–roll and pad–batch procedures the roll must be kept turning to stop drainage occurring which would lead to irregular treatment and make the roll almost impossible to unwind. The technique was traditionally used on woven fabric but is being increasingly used for knitgoods, particularly in slit form.

2.5.4 Continuous processing [32,34,35]

All continuous application systems require:

(1) an accumulator ('marking time' machine);
(2) application of chemicals;

(3) storage of the impregnated substrate;
(4) washing-off of the treated substrate.

Accumulators are rarely discussed but are critical to continuous (i.e. non-stop) operation. The description not only covers powered accumulators but also devices such as scrays or dry J-boxes in which fabric can be stored either to facilitate the sewing together of batches of fabric or to compensate for speed differences in various sections of the machine.

The application stage implies consumption of chemicals and so a system is usually also required to replenish them.

Chemical application

Consistent, uniform application of chemicals is a major contributor to successful preparation. This, irrespective of form, involves some form of saturator. Spray application has never been used in cellulosic fibre preparation but the Raco-Yet of Ramisch Kleinewefers does apply steam and chemicals together directly to the fabric [36]. Typical saturators are shown in Figure 2.4.

The open-width saturator can be used to process woven and centre-slit knitted fabric, or in some instances fibre in sliver or batt form. The rollers and tension bars of such saturators are often essential components in promoting interchange and penetration of the application liquor. The rope saturator is used for both woven and knitted goods in rope form. The sieve-drum saturator can also be used for sliver and knitgoods, the latter in collapsed tubular form. Invariably there will be some form of pick-up control on exit from the saturator.

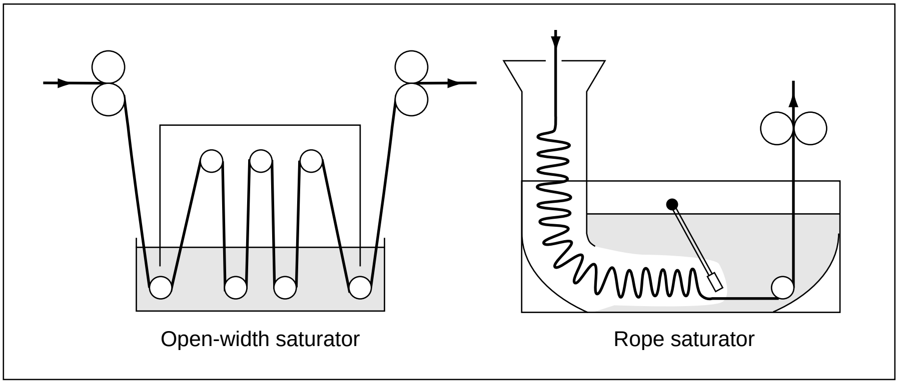

Figure 2.4 Various types of traditional saturator: (a) rope saturator; (b) open-width saturator. (*Source:* [34].)

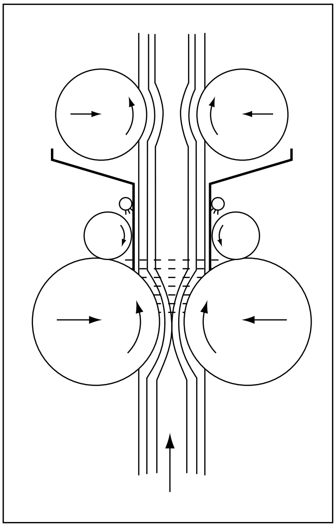

Figure 2.5 The Optimax saturator. (*Source:* [39].)

Traditionally this is a pair of squeeze rollers but the Flexnip [37,38], Optimax (Figure 2.5) [39] and Super-Sat [40] are new developments in saturator design which not only give increased control of the pick-up but add versatility to the saturator. Preparation invariably involves swelling of fibres and dissolution of impurities and so the higher the pick-up the better. Both the steam purge device and vacuum impregnation can increase this pick-up on heavyweight, dense fabrics [41]. The auxiliary suppliers also make liquor viscosity modifiers which enhance pick-up, for example, Irgapadol FE (S).

Chemical addition is made to a side-tank, usually fitted with a lint filter and circulation pump to agitate and dilute the mixture as quickly as possible. In the Raco-Yet the mixture is supplied to the spray head. The liquor taken out of the saturator is referred to as pick-up, percentage pick-up or expression. It always refers to the percentage increase in weight of the dry fabric caused by the liquor.

Storage devices [32,34,42]

Most of these are steamers but for knitted fabrics they are winch- or jet-like devices through which the fabric moves spirally. The devices used to process wool or acrylics continuously, e.g. the microwave-heated Smith Fastran unit, are seldom used for cellulosic substrates.

J-boxes

The J-box was the first fully continuous preparation range for woven fabrics (Figure 2.6). Its basic design evolved, in the USA, from the Gantt piler, formerly used for hypochlorite bleaching [1]. This was a wooden structure shaped like the letter J with rolls at the bottom of the curve to facilitate movement of fabric. Two distinct types of rope J-box were developed for bleaching woven fabrics which differ mainly in the method of fabric heating. In the Becco, or open, J-box, heating is by direct application of steam, through manifolds at various heights, to the pack of plaited fabric. With the DuPont, or enclosed, J-box, the fabric is

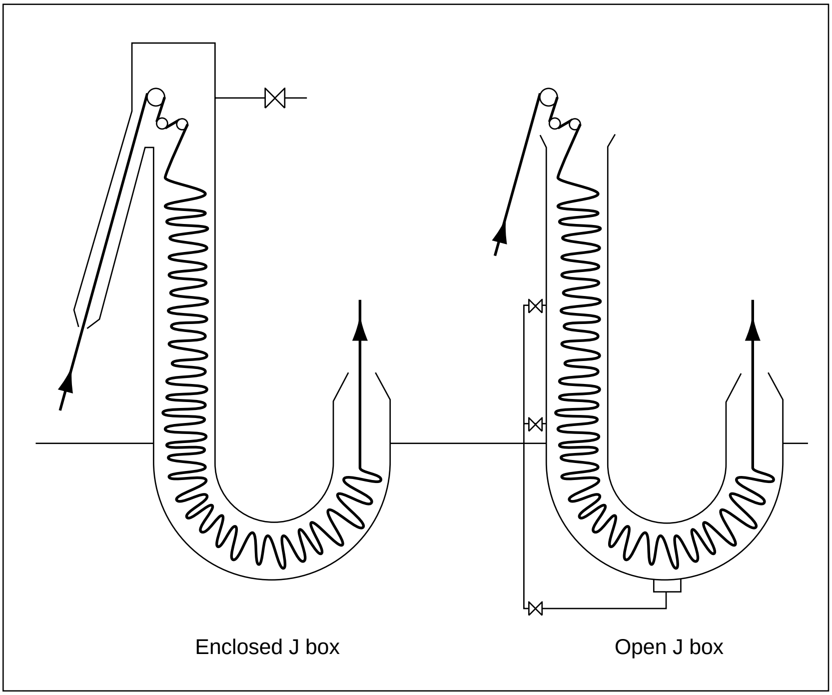

Figure 2.6 Diagrams of traditional J-Boxes: (a) enclosed J-box; (b) open J-box. (*Source:* [34].)

heated by passing through a steam atmosphere in a heater tube adjacent to the entrance of the J-box.

Some fabrics stick in the curved J and a ‘wet bottom’, formed by introducing water into a sump at the bottom of the curved section, is usually used to correct the problem. The water not only acts as a lubricant but also as an initial wash. To produce the wet bottom there is often a stand-pipe through which water flows at about 40 l min^{-1}. The stand-pipe can be swivelled to control the amount of liquor in the J-box.

Rope J-boxes hold 5–20 km of fabric for a dwell time of 1–2 h at a running speed of 100–150 m min^{-1}. This converts into a productivity of about 130 kg h^{-1}. Surface-sensitive fabrics, such as satins and sateens, and cotton/polyester blends are prone to creasing under such conditions. Heat setting of polyester/cotton prior to rope preparation reduces the problem, but such blends are best processed in open-width form.

The open-width short, or broken back, J-box (see Figure 2.6) provides a dwell time of 8–20 min and has a much smaller capacity than the rope J-box, in order to minimise the frequency and intensity of fold marks caused by the weight of fabric moving through the J-box. It is important with this equipment to ensure that the metal of the box does not become overheated. If this does occur, the selvedge areas of the fabric that have touched the sides of the box can show different dyeing properties from the rest of the material.

The FMC continuous kier evolved from the wet-bottom J-box [43]. Here the water flow is replaced by bleach liquor which is circulated, by pump, from a heel tank, at a concentration about 30–50% of the saturator concentration, to the J-box. This used to be the most popular method of bleaching tubular knitgoods in the USA but seems to be being replaced by spiral-type winch machines.

Steamers

The first open-width steamers to be used in preparation were the atmospheric tight-strand roller steamers used for continuous dyeing. Kirner, in a classic paper [44], advocated such steamers for bleaching and scouring under shock conditions. As the fabric is tightly in contact with the rollers, an increased dwell can only be achieved by reducing line speed. At the lowest line speed, the dwell time is only 1–2 min; often too short to remove seed from woven cotton fabrics.

In Europe, other designs of roller steamer were developed to try to increase the dwell time without reducing line speed. The roller-bed steamer, which consists of a flat bed of rollers driven much slower than the line, emerged as the most popular. Fabric is plaited down on to the slowly moving roller bed, which transports the fabric in a relaxed state to the exit point (Figure 2.7). It is possible to maintain a required production speed while varying the retention time in the steamer by adjusting the amount of fabric plaited on to the bed and consequently the amount of fabric in the steamer. This leads to a risk of trapping the fabric on the bed. Küsters, an innovative machinery maker, overcame this by plaiting the fabric on to a roller rather than the bed. As the roller rotates to deposit the fabric on the bed, the pile inverts [37,38].

Early machines provided dwell times of 3–5 min, but even under these conditions on the roller bed, some creases were formed on polyester/cotton fabrics. These creases are prevented by using a short tight-strand section, to allow swelling and dimensional changes to occur before plaiting down on to the bed. This combination is used in the second generation of roller-bed steamers, which are thus called Combi-steamers. Dwell times have also been extended to 10–15 min, which aids seed removal in a combined scour/bleach process. Good reviews of the development and performance of steamers have been given by Theusink of Brugman [45] and Tischbein of Babcock [46].

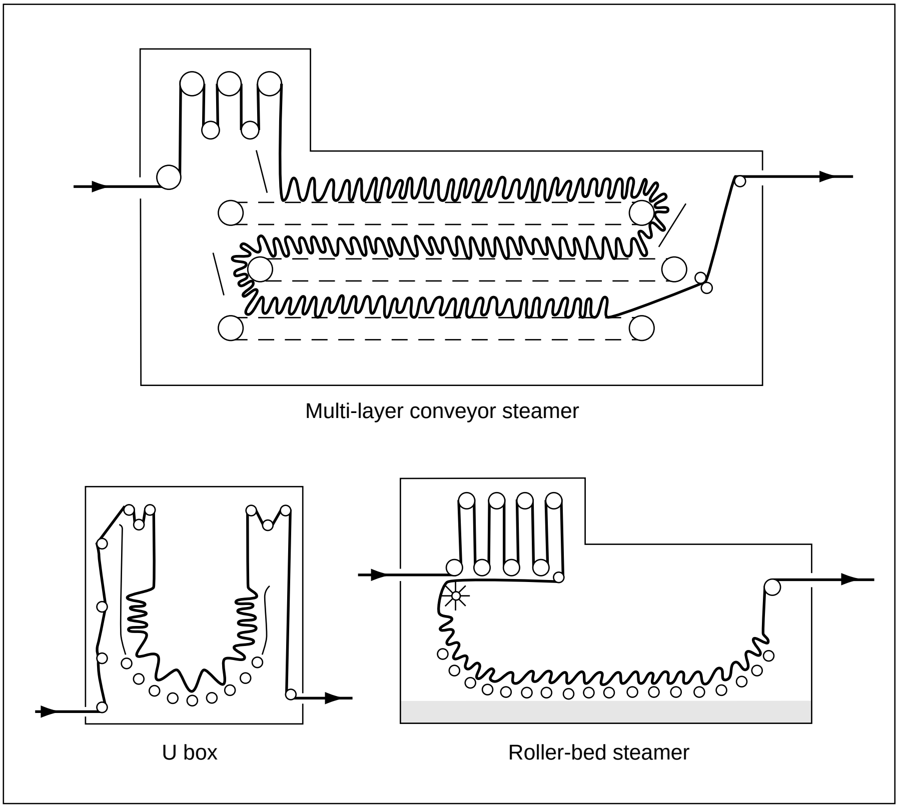

Figure 2.7 Open-width steamers for fabric preparation: (a) roller-bed steamer; (b) conveyor steamer. (*Source:* [34].)

The conveyor steamer was introduced to the USA in 1938 by Mathieson Alkali for chlorite bleaching. The impregnated fabric enters a steam-heated chamber and is plaited on to the first of three conveyor belts moving along the length of the machine (Figure 2.7). At the end of the first traverse the fabric is dropped onto a second conveyor and after another traverse onto a third conveyor. A temperature of 95°C and dwell times of 15–60 min are typical. Single-layer conveyor steamers, developed by Morrison Machinery Inc., are more popular in the USA for bleaching woven goods than roller-bed steamers. Brugman conveyors are used for bleaching linen and linen union fabrics, where the long dwell time makes them attractive, and a Fleissner conveyor is used for a multiple-strand pad–steam process for knitgoods.

In the early 1960s, James Hunter developed a commercial pressure-scouring unit in which fabric entered and left the steamer through roller seals.

Kleinewefers and Mather & Platt produced machines employing lip seals which overcame the problems of roller seals. The lip seals used a pressure tube held against a metal plate, with the fabric passing between the tube and plate without loss of vessel pressure. In the Mather & Platt machine, with its Vaporloc unit, the fabric entry and exit are side by side, and the fabric is plaited onto a roller bed. The Kleinewefers machine has entry and exit points at opposite sides of the pressure unit and is a tight-strand steamer in which expander bars are used to prevent crease formation. Normal dwell times vary in the range 1–3 min, with production speeds of about 100 m min^{-1}. Normally the capacity of the unit is 60 m which gives a dwell time of 1 min when running at 60 m min^{-1}. The machines, despite their productivity, are not very popular.

Storage at long liquor ratio

Knitgoods are often stored in the bleach liquor during continuous processing. These devices include under-liquor or immersion bleaching machines, as well as spiral winches or jets. In the spiral machines, the fabric rope is fed into the machine at one end, moves through the machine in a spiral path and is then unloaded at the other end of the machine.

The immersion or PKS bleaching process developed by Bayer [47], provides continuous bleaching under long liquor conditions (between 25:1 and 30:1). Fabric is introduced, in open-width or rope form, into the reaction box under the liquor surface and transported through the liquor to give a dwell time of about 10 min at 90–95°C. Bleach liquor is constantly recirculated and provides a transport medium for fabric in the reaction chamber. The system has high energy and chemical costs compared with most continuous processes, and these, coupled with a notoriously unstable bleach bath formulation, have limited the acceptance of this technique, but machines made by German manufacturers such as Goller, Menzel and Thies have all run satisfactorily.

In terms of spiral winches (the fabric is moved by winch reels) the machine made by Brückner, the Colorado, is probably most universally known, but the machines made by Jacumin Engineering Co. (JEMCO) called JEMCO II and III are probably best known in the USA. The Colorado is now seldom used for bleaching and is preferred for high-efficiency washing-off, so Brückner introduced the Tubolavar and Delphin as replacements.

The most popular spiral jet, especially in the USA, was the Argathen. The machines are now made and sold by Küsters, who are not only continuing to support the US market but also introducing them into Europe.

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Chemical addition to saturators [48,49]

Fabric passing continuously through a saturator not only takes liquor out of the system but also consumes chemicals. This is not a problem if dry fabric is being impregnated (wet-on-dry) as the feed liquor, usually located in a 5000 l tank in the dye kitchen, will be at exactly the same concentration as the saturator liquor and is controlled by a simple ballcock in the saturator. In this case the percentage chemical on weight of fabric (% o.w.f.) is given by Eqn 2.1:

$$\%\ \text{o.w.f.} = \text{g l}^{-1} \times \%\ \text{pick-up}/1000 \tag{2.1}$$

If the substrate is wet from the washer of a preceding stage, for example, then not only is liquor taken out of the system but water is brought into the saturator by the fabric. In theory, it is possible to measure the amount of water carried over (input) and the amount of liquor taken out (output) and so calculate the volume change in the saturator. The simple percentage pick-up in the relationship above is replaced, in this case, by percentage effective pick-up. This is the difference between the two pick-ups plus the fraction of the incoming water that has been exchanged for liquor. It is also possible to measure the concentration of chemical remaining on the substrate and to calculate the concentration of a feed liquor to replace the volume loss and compensate for the diluting effect of the incoming water [49]. In practice, the feed liquors would be chemicals at the concentrations supplied by the manufacturer, such as 46% by weight caustic soda liquor (100° Tw), and these would be metered to a mixing vessel and then added to the saturator, which has been brought back to volume by a ballcock fitted to the water supply pipe, at such a rate as to maintain chemical concentrations.

Chemical dosing can be achieved by:

(1) flow-controlled gravity feed using manually operated valves and rotameters or computer-controlled magnetic flow meters;
(2) metering pumps (e.g. Bran and Lübbe, MPL) which have pistons of various sizes and vernier-controlled delivery adjustment;
(3) measuring vessels (e.g. Texicon, ATC) which fill and empty with precalibrated volumes of feed liquors at a rate necessary to maintain saturator concentration;
(4) electrode-based systems (e.g. Polymetron, Tytronics, ATC Bleach-o-matic) which measure saturator concentration directly and then open and close valves after comparison of the measured value with the desired value.

All methods, excepting manual control, are interlocked to the main drive motor so that when the line is stopped, the chemical dosing ceases.

2.6 COTTON PREPARATION

Preparation of woven fabrics normally consists of three stages: desizing, scouring and bleaching. In most other cases, preparation is a two-stage process: scouring and bleaching. For certain end uses, an extra stage (mercerising) can be included for yarns or fabrics. Woven fabric also requires singeing, prior to desizing. In this chapter, bleaching will be dealt with under a separate section.

2.6.1 Singeing [1]

Many woven fabrics are singed to remove surface fibres. The fabric from an accumulator is passed through a brushing unit and then into a singeing machine. Various systems have been devised, for example those by Ostoff-Senge, Menzel and Parex Mather, the most usual having gas-fired burners through which the fabric passes at high speed in such a way that both sides of the fabric are singed. The fabric is passed through steam or liquor to quench any sparks. When a liquor is used it is often a desizing liquor. Singeing blends, for example polyester/cotton, can create problems by melting the thermoplastic fibre.

2.6.2 Desizing [2]

Sizing reduces the frictional properties of warp yarns by coating them with film-forming polymers. The process improves weaving productivity by increasing weft insertion speeds and decreasing yarn breakages. The size is usually applied from aqueous solution and film forms on drying. The following are typical sizing materials [5,50,51]:

(1) Natural starches from potatoes, maize (corn), rice or tapioca.
(2) Chemically modified starches (ethers or esters).
(3) Organic polymers, e.g. polyacrylates, carboxymethylcellulose, methylcellulose, polyesters or poly(vinyl alcohol).
(4) Solvent-soluble materials, e.g. copolymers of methyl methacrylate.

Starch-based sizes are normally used for 100% cotton yarn as they are economical and produce satisfactory weaving performance. Other products are also used, either alone or in combination with starches, when the higher cost can be offset against improved weaving efficiency. For example, poly(vinyl alcohol) is widely used for sizing cotton/polyester blends.

Size plasticisers, e.g. tallow or paraffin wax, may be added to the sizing mix or more usually applied after drying by kiss–roll coating.

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Most sizes are easily dissolved in water but on forming films they become much more difficult to redissolve. Singeing or heat setting can impair the water solubility even further.

Desizing is often easier in a vertical organisation, since there is complete control of the choice of size and this often leads to size recovery processes. In most cases, however, the fabric will be imported and the finisher seldom knows the source of fabric, let alone how it has been sized. This leads to trial and error desizing – an unreasonable situation now resolved by oxidative desizing (see below).

Size removal depends essentially on the following factors:

(1) Viscosity of the size in solution.
(2) Ease of dissolution of the size film on the fibre.
(3) Amount of size applied.
(4) Nature and amount of the plasticisers.
(5) Fabric construction.
(6) Method and nature of washing-off.
(7) Temperature of washing-off.

In the earliest processes the fabric was wetted and airborne organisms allowed to degrade the size (rot steeping). Acid treatments also degraded starch-based sizes and offered the further advantage of removing calcium and magnesium salts. Hydrochloric acid was preferable but all too often sulphuric acid was used on cost grounds. The concentration of acid ranged from 2% for short steeping times to 0.2% for overnight steeping. Care had to be taken to avoid any drying out as this would have damaged the cellulose itself [34]. These processes have been superseded by enzyme treatment, oxidative desizing or some form of washing-off procedure.

Enzyme desizing [2,3]

Enzyme desizing is widely practised and is highly effective for degrading starch or starch-based sizes. The enzymes used are the α-amylases and they are frequently applied in the quench box of the singer after singeing, but may be used on almost all types of batch and continuous equipment. The various preservatives (halogenated phenols) added to size mixtures to prevent mildew formation on damp fabric are toxic to enzymes, as are most anionic surfactants.

As is usual in most chemical reactions, increasing temperature of treatment promotes increasing reaction rate and decreasing treatment time. The amylases may be obtained from specialist producers such as Novo Nordisk AB or Diamalt

GmbH, but the auxiliary suppliers often have their own ranges. The enzyme may be a malt diastase, or a pancreatic or bacterial amylase. The optimum conditions for using the various types are shown in Table 2.3. The amount used depends on the activity of the product and there are at least two systems for measuring that activity. Usually the producer carries out such assays and builds the results into the application formulations. Compare the following recommendations for Aquazyme 120 L from Novo Nordisk AB (‘120’ refers to the strength of the enzyme):

Quench	10–25 g l^{-1}	J-box	20–50 g l^{-1}
Winch	2–10 g l^{-1}	Combi-steamer	20–50 g l^{-1}
Jig	5–15 g l^{-1}		

The enzymes cleave the α-1,4-glycosidic links between the glucose rings of starch. For amylose, the straight-chain fraction of starch, the fragments are glucose, maltose or oligosaccharides, all of which are soluble in boiling water. In the case of the branched amylopectin fraction, the oligosaccharide fragments may not be soluble in boiling water but are soluble in mildly alkaline solutions. The ratio of the two fractions varies from starch to starch. Rice and tapioca starches contain more amylopectin and are thus more difficult to remove than corn starch.

Starch sizes can be detected by spotting with a solution of iodine in potassium iodide and this has been converted into a quantitative test [52], but the results should be interpreted with care as oxidative damage also gives a blue colour with the reagent [53].

Table 2.3 Optimum conditions for enzyme desizing

			Effects of[a]		
	Optimum pH	Optimum temp./°C	NaCl	Ca ions	Time
Malt diastase	4.5–5.5	55–65	–	+	12–24 h
Pancreatic amylase	6.5–7.5	40–55	+	+	12–24 h
Bacterial amylase	6.5–7.5	65–75	+	+	1–4 h
Bacterial amylase	7.0–8.0	100–120	+	+	1–2 min

[a] + indicates improved desizing, – indicates no effect.

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Oxidative desizing

Oxidants have been used for many years as desizing agents. Sodium hypochlorite desizing, prior to hydrogen peroxide kier bleaching, was particularly useful. Though less effective than enzymes for degrading starches fully, it gave some improvement in colour and allowed the peroxide bleach to complete size removal.

The use of sodium bromite for desizing was developed in France [54]. It is claimed to provide a degree of bleaching with starch degradation, but has not been adopted commercially. It was highly sensitive to purity of the auxiliaries and for this reason has not been adopted.

Oxidative desizing usually refers to the addition of peroxodisulphates (persulphates) or hydrogen peroxide to alkaline scouring liquors and so this form of desizing is discussed more fully in section 2.6.3. Hydrogen peroxide was developed initially for desizing fabrics sized with poly(vinyl alcohol) where desizing at about pH 9 is recommended. With mixed sizes a higher pH can be used [55]. Oxidative desizing is increasing in popularity: not only does it remove most sizes, but time is saved by removing process stages and, with hydrogen peroxide, it gives a degree of whitening.

Hot caustic soda treatments

Starch-based sizes can be removed by hot caustic soda treatments and it is possible to combine size removal with grey mercerising [56], but this precludes recycling the mercerisation liquor.

Care must be taken when using sizes containing poly(vinyl alcohol) as caustic soda treatments can fix the size. This difficulty is overcome by using the oxidative desizing treatment. Caustic soda cannot be used to remove polyester sizes, e.g. Eastman Size WD, as hot alkaline treatment hydrolyses the polymer and leaves insoluble oligo-ester fragments on the cloth.

Hot washing with detergents

Simple aqueous washing removes some synthetic sizes. Sizes such as carboxymethylcellulose, poly(vinyl alcohol) and the polyacrylates swell when immersed in water. If this swollen size is agitated on a high-efficiency washer, complete size removal can be achieved. This is done in most countries in spite of the availability of size recovery techniques.

In the USA, most of the large vertical companies are geared to size recovery where the swollen size is squeezed off at a high-pressure nip, prior to washing, and sent to a tank for shipping back to the weaving division. For these companies the large volume of the storage tanks for the recovered size is something of an embarrassment. A particularly attractive feature of recycling is the reduction in BOD from the desizing effluents.

Solvent-soluble sizes

Several companies are active in the development of solvent-soluble sizes, which are applied and removed in non-aqueous media. Though they have the advantage of eliminating aqueous pollution, economic and technical factors have limited progress. The technology has been reviewed in [50].

2.6.3 Scouring

Section 2.2 described the impurities present in cellulosic fibres. The purpose of scouring, or treatment with hot alkaline solutions, is to remove these impurities. The nature of these impurities and the process of scouring has been well reviewed [51]. In batch systems, scouring is often called boiling off if it is carried out below 100°C.

For natural cellulosic fibres, the main effects of scouring are a 5–10% loss in weight and a dramatic improvement in wettability and absorbency. The loss in weight results from degradation of the proteins to amino acids, conversion of the alkaline earth pectates to soluble sodium salts, dissolution of the hemicelluloses and some degradation and dissolution of the cellulose. Lignins are degraded or dissolved. In the case of linen they are usually extracted as chlorinated lignins, as the scour follows a chlorination stage.

The improved absorbency results from saponification of the fatty esters and melting of the fatty alcohols and hydrocarbon waxes at scouring temperature. These are emulsified by the fatty acid soaps formed during saponification. The removal of cotton wax need not be complete but has to be reduced to a level where it cannot form a continuous film over the fibre. In batch systems, wax removal increases with temperature. Figure 2.8 shows the relationship between absorbency and scouring conditions on the J-box [57].

The alkali most generally used is sodium hydroxide but other alkalis and the other additives to the scouring liquor were discussed in section 2.3.3. The use of a reducing agent under hot alkaline conditions not only minimises oxidative damage to the cellulose but also destroys coloured impurities.

Traditionally, woven fabrics were batch scoured in kiers (kier boiled) and this process has been reviewed by Garrett [29]. Such machines are still used, for example in India and Pakistan, but have been almost universally replaced by J-boxes or Combi-steamers elsewhere. Kier boiling provided the thorough scouring which was essential before bleaching with hypochlorite but which is not so critical before bleaching with other agents.

The processes most like kier boiling are currently carried out on loose stock. These conditions are the most severe as the fibre contains the highest level of impurities, and scouring above 100°C is absolutely essential for good absorbency. Knitted fabrics are often scoured on winch or jet. In this case, the yarn is usually clean, combed fibre and so scouring can be a rapid, mild process [31]. Yarn is scoured, or more usually boiled off, on hank or package machines.

It must be noted that in any scouring process large amounts of impurities are dissolved or suspended in the scouring liquor. This is particularly important in batch processes as rapid cooling or pH change can cause deposition of the impurities on the substrate. Saturators can, in a similar way, build up large quantities of impurities and so filters on the circulation loop must be checked regularly. Antifoams are best avoided as they destabilise the liquor.

Typical formulations and conditions for batchwise and continuous processes are shown in Table 2.4 [51]. There are many references to the ‘residuals’, contaminants on scoured textiles, but the figures quoted by Bell and Stalter provide indications of the expected levels (Table 2.5) [58].

Persulphates, and recently perphosphates, are recommended for use in caustic scouring processes to increase starch degradation. The perphosphates are more

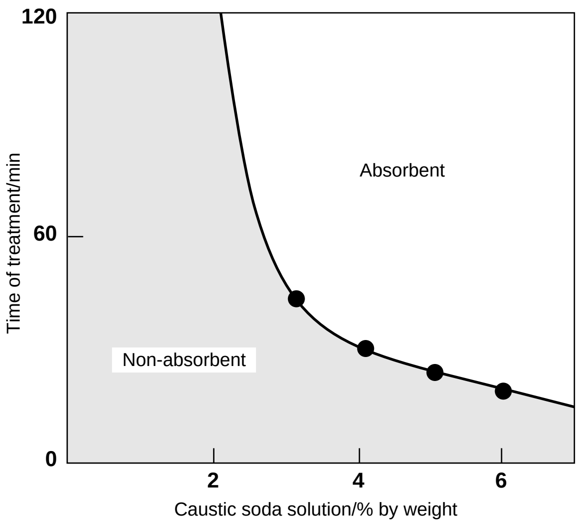

Figure 2.8 Absorbency and scouring conditions on a J-box [57].

Table 2.4 Batchwise and continuous methods of scouring

(a) Batchwise methods

	Kier	Winch or jet	Jig	Package or beam
Caustic soda (100%)/g l^{-1}	5–10	5–10	5–15	15–20
Wetting agent/g l^{-1}	0.5–1	0.1–0.2	0.5–1	0.5–1
Detergent/g l^{-1}	0.5–1			2–4
Liquor ratio	3–5:1	15–30:1	2–4:1	5–8:1
Temperature/°C	130	95–98	95–98	100–130
Time/h	4–6	1–2	2–4	3–0.5

(b) Continuous methods

	J-box conveyor pad–roll	Open-width atmospheric steamer	Pressure steamer
Caustic soda (100%)/% o.w.g.	3–6	4–10	6–10
Wetting agent/% o.w.g.	0.1–0.5	0.1–0.5	0.1–0.5
Detergent/% o.w.g.	0.5–1	0.5–1	0.5–1
Temperature/°C	100	95–98	130–140
Time/min	30–120	10–30	1–2

Table 2.5 Change of average fabric characteristics on scouring and bleaching

Characteristic	Grey	Scoured	Bleached
Whiteness/%			86.6
Whiteness (aged)/%			80.5
Whiteness retention/%			93.1
pH of aqueous extract		9.3	8.5
Fluidity/Pa s^{-1}	2.2	2.9	5.3
Absorbency/s			3.0
Non-cellulosic content/%	9.9	0.99	0.39
Oils, fat and waxes/%	0.82	0.43	0.24
Ash/%	0.99		0.18

difficult to manufacture and are not generally available in commercial quantities. Under laboratory conditions it is not always easy to show differences in size removal with and without the addition of oxidants. In practice, however, their use gives improved uniformity of preparation and size removal.

Oxidative desizing

Oxidative desizing offers the possibility of reducing the number of processing stages required for fabric preparation, an important factor in minimising energy use. The oxidant can be added to caustic scour liquors to provide combined desizing and scouring. For this system little or no silicate or organic stabiliser is included. Alternatively some stabiliser may be added to give a degree of bleaching with desizing. This useful pretreatment extends the feasibility of combined scour/bleach processes, particularly when these would otherwise give inadequate bleaching and seed removal. In the general recommendations shown in Table 2.6, the lower levels of caustic soda provide desizing only while the higher levels provide oxidative scouring.

The following should be noted:

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

Solvent scouring

If only fats and waxes were to be removed, this could possibly be achieved by treatment with organic solvent. Trichloroethylene was the first solvent used commercially, in a manner similar to that used for metal degreasing. Fabric was passed continuously through solvent vapour, which condensed on the fabric, dissolving out fats and waxes as it drained off. The system required special equipment which included solvent recovery. Even so, solvent losses contributed

Table 2.6 Recommended conditions for oxidative desizing

	Concn/% o.w.f.		
Magnesium sulphate heptahydrate	0.005	0.005	0.005
Caustic soda (100%)	2–6	2–4	9–12
Stabiliser	0–1	0–1	0–1
DTPA (40% solution)[a]	0.2	0.2	0.2
Hydrogen peroxide (35%)	5–15	5–15	5–15
or sodium persulphate	0.2–0.5	0.2–0.5	0.2–0.5
Wetting agent	0.2–0.5	0.2–0.5	0.2–0.5
Temperature/°C	100	100	120–130
Time/min	<15	15–60	1–2

[a] DTPA – Diethylenetriamine pentaacetic acid

significantly to process costs. Though fats and waxes were removed, additional wet processing was still required to remove other impurities.

The Markal (ICI) system, whilst still requiring special plant, eliminated some of the disadvantages of solvent degreasing and combined the removal of fat and wax with starch degradation. In this process, fabric was immersed in trichloroethylene containing a detergent. The fabric was then passed into a steam box in which the trichloroethylene was removed by steam distillation. Condensation followed by water–solvent separation gave good, but not perfect, solvent recovery. Immersion in organic solvent gave penetration of the detergent, which remained in the fabric after steaming. Hot-water washing followed to remove fats and waxes. These had been made, in effect, self-emulsifiable.

Introduction of an enzyme into the detergent solution gave starch degradation during steaming, allowing removal in the washing-off stage. The process provided fabric with excellent and consistent absorbency.

The disadvantages were the high costs of equipment and solvent and the effluent problems, as all the residues remained in the wash-off liquor. To overcome the problem of solvent cost, processes were introduced which used paraffin hydrocarbons emulsified with aqueous enzymes. These emulsions were padded directly onto grey fabric and, after appropriate storage for size degradation, washed off. Good absorbency was obtained, but the effluent contained the hydrocarbons in addition to wax and size.

These developments led to a better understanding about which detergents are most effective in removing fats and waxes during the pad application of desizing liquors. Whilst not strictly solvent emulsion processes, the use of these specialised auxiliary products has become common practice in many desizing and bleaching processes.

2.6.4 Mercerising [51]

Treatment with strongly alkaline solutions to improve fibre lustre, tensile strength and dye uptake is called mercerisation. The name came from Mercer's original invention based on treatment of cotton fabrics with strong caustic soda solution, without tension, to improve colour yield. It was Lowe who later found that the application of tension improved lustre. Mercerisation can be carried out either on yarn or on woven or knitted fabric. Yarn or fabric is normally impregnated with cold caustic soda 25–26% by weight solution (54–58° Tw) containing a good wetting agent. At this concentration considerable swelling of the cellulosic fibre occurs which results in shrinkage if the fabric or yarn is not held under tension.

Mercerisation may be carried out on the grey, partially or fully prepared substrate. When mercerising loomstate fabrics, penetration by concentrated caustic soda at low temperature is difficult and tends to give surface effects. Grey goods also cause fouling of the liquor by size, making caustic recovery and recycling difficult. However, it is better to impregnate certain fabrics with caustic soda while they have their maximum strength, and hence there is still a considerable call for grey mercerisation. Rösch, in his excellent series of articles on the practice of cotton fabric preparation, argues that the best position is after scouring and bleaching [59].

The weft threads of a woven fabric are kept directly under tension on a clip stenter (chain merceriser) or the fabric dimensions are controlled by a series of rollers (chainless merceriser). In adddition to these measures, the fabric is usually woven slightly wider to allow for some width loss. An important consideration in mercerisation is the rate of desorption of the caustic soda. Yarn is mercerised in hanks between two movable rollers which are used to apply tension. Knitted fabrics may be mercerised in slit or tubular form [51].

As well as the effects mentioned, mercerisation also improves fibre and fabric smoothness, coverage of dead cotton and dimensional stability. All properties are influenced by alkali concentration, temperature and dwell time in alkali prior to washing-off [56].

Usually, mercerisation is carried out using cold caustic liquors but some interest has been shown in the so-called hot mercerising process [60,61]. The basic principles are:

1. saturation with mercerising-strength caustic soda solution near to its boiling point;
2. controlled hot stretching;
3. controlled cooling;
4. traditional tension-controlled washing followed by final washing.

The advantages indicated for the process are:

1. shortening of the processing sequence providing cost savings;
2. increased efficiency and uniformity;
3. use of chain or chainless equipment with less problems related to fabric width;
4. improved lustre, tensile strength and dimensional stability since greater fabric stretching is possible;
5. increased dye uptake, though this is dependent on the extent of stretch imparted; greater than normal stretch reduces the dyeability with greater internal orientation of molecular structure;
6. good response from fabrics containing lower-grade cotton;
7. flash scouring effect obtained;
8. good desizing;
9. better fabric penetration by a hot caustic liquor than with normal mercerisation.

The main chemical and physical changes do not take place at the initial elevated temperature, but when the cooled fabrics go through the traditional section of the mercerising plant. The possibility of a combined scouring/mercerising process is of considerable potential interest, particularly as the degree of scouring, as a preliminary to peroxide bleaching, is said to equal that of a conventional caustic scour. However, since its introduction in 1977, this development has not achieved significant commercial success.

2.6.5 Liquid ammonia treatment [51,62]

Treatment of cotton with anhydrous liquid ammonia has also been developed to enhance the properties of cotton. In the original Prograde process, used on yarns, the ammonia is removed subsequently in a hot water bath. This treatment brings about an increase in tensile strength, lustre and dye substantivity. The improvements in lustre and dyeability are less than when mercerising with caustic soda, although the ammonia-treated cotton has greater resistance to thermal degradation.

In fabric processing the ammonia can be removed by dry heat. This technique gives properties quite different from the Prograde system and should not be considered to be a mercerisation process. Dye uptake may vary from a slight increase to a decrease, depending on the dye. However, the dry-heat removal does give improved crease recovery, and durable easy-care finishes can be obtained with lower resin additions. Hence the benefits are associated primarily with improved properties in resin-finished cellulosic fabrics; the ammonia treatment may follow dyeing.

2.7 BLEACHING

All natural fibres are coloured and the colouring matter confers a yellowish brown colour to the fibres. In the case of cotton, this is believed to be a condensation product of caffeic and quinic acids which is related to chlorogenic acid [63]. The purpose of bleaching is to destroy this coloured material and to confer a pure white appearance to the fibres. Bleaching should also decolorise or remove any residual impurities left by scouring. Bleaching is the linchpin of preparation and today really means bleaching with hydrogen peroxide (peroxide), since sodium hypochlorite (hypo) and sodium chlorite have both lost ground to peroxide. Hypo is increasingly unacceptable environmentally; chlorite is difficult to use (special materials of construction, extraction system for chlorine dioxide, etc.) and was caught by a change in fashion – supersoft finishing – which made a non-scouring bleaching process redundant. Chlorite bleaching plant using stoneware was still sold until quite recently [14], and both the plant and the chlorite are advocated as environmentally acceptable [64].

2.7.1 Bleaching with sodium hypochlorite [5,51]

Effect of pH

Figure 2.9 shows how the species in solution change with varying pH of a sodium hypochlorite solution. Figure 2.10 illustrates the classical fluidity results of Clibbens and Ridge which show maximum chemical damage to the cellulose occurs at pH 7 (see section 1.5.5). The bleaching effect is highly dependent on pH and can be represented by Scheme 2.2. As the curves show, reaction 1 predominates above pH 10, whilst below pH 3 reaction 3 predominates. Between pH 4 and 8 the hypochlorous acid predominates. It would appear, therefore, that it is this species that is damaging to cellulose. This is a factor which *must* be considered when washing off after hypo bleaching. The liberation

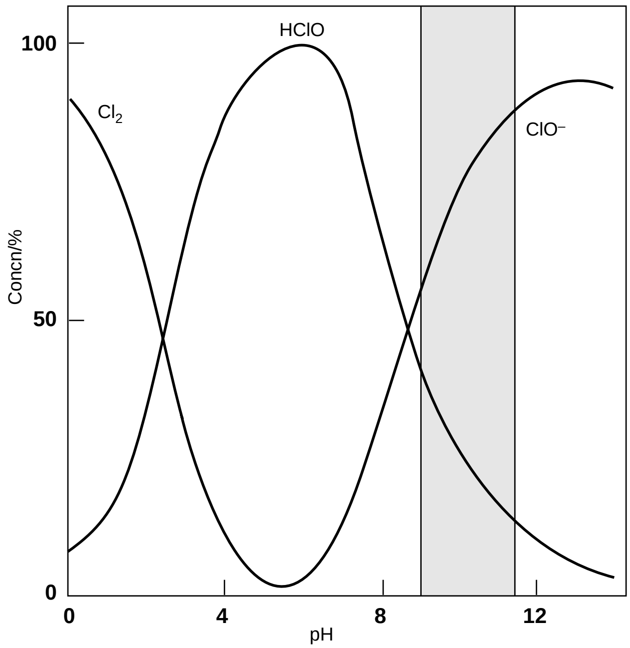

Figure 2.9 Effect of pH on the composition of sodium hypochlorite liquors. (*Source:* Agster, *Textilveredlung*, **1** (1966) 276.)

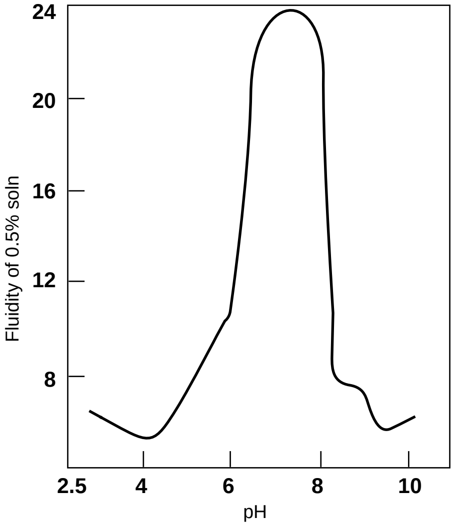

Figure 2.10 Effect of pH on degradation of cellulose by sodium hypochlorite. (*Source:* [3].)

of chlorine can be helpful (section 2.9.2) but chlorination of organic materials leads to AOX and it is for this reason that hypo will go out of use [13].

Effect of temperature and time

Increased temperature gives a higher rate of bleaching. This relationship was studied by Derry [65], who showed not only that a 6 h bleach at 20°C could be reduced to about 7 min at 60°C, but also that an increase in temperature brings a real danger of severe

$$NaOCl \longrightarrow Na^+ + OCl^- \qquad \mathbf{1}$$

$$HOCl \longrightarrow H^+ + OCl^- \qquad \mathbf{2}$$

$$HOCl + H^+ + Cl^- \longrightarrow Cl_2 + H_2O \qquad \mathbf{3}$$

Scheme 2.2

chemical damage. Bleaching is usually carried out for several hours at ambient temperature (less than 20°C).

Increasing temperature can lead to loss of active chlorine from both the storage and bleaching vessels. This situation leads to variable bleaching in many countries during the summer.

Other methods are available for accelerating the hypo bleach, including irradiation with u.v. [51] and the addition of cobalt [11] or water-soluble polyhydroxy compounds.

Effect on cellulose

Epstein and Lewin showed that hypo oxidation of cotton in the pH range 5–10 forms more carboxy groups and less aldehyde and ketone groups as the pH increases [66]. They proposed oxidation of the C_2–C_3 linkage within the glucose units which sensitises the 1,4-glycosidic linkages between units and makes their cleavage easy (β-hydroxycarbonyl elimination or peeling reaction) at any point in the chain, leading to rapid depolymerisation. This fits well with the Clibbens and Ridge results. This mechanism also suggests that the fragments (furfuraldehyde derivatives) make hypo-bleached cotton more prone to yellowing with time (see section 1.5.5).

Hypochlorite bleaching processes

Hypo liquors should always be titrated before use. Formulations are usually expressed as active or available chlorine (AC), as this gives a fixed datum. It is necessary to convert this fixed value to material as supplied before use. This is done using Eqn 2.2:

$$\text{Volume of hypo as supplied} = \frac{1000 \times \text{ desired AC in bleach bath}}{\text{AC of hypo as supplied}} \qquad (2.2)$$

This volume would be added to the bleaching vessel or a side tank containing water.

Alkali, normally soda ash, is added, predissolved in a bucket and the pH checked. It is usual to check available chlorine and pH during the course of bleaching.

The traditional process is cistern bleaching, which may be regarded as an open kier as far as liquor circulation is concerned but the process can be carried out on various batch machines [5]. Cisterns are usually cylindrical stoneware vessels but tile-lined pits were often used in their place. Typical formulations are shown in Table 2.7 [51]. A J-box in the form of an open-sided plastic piler has been used, for example in Eastern Europe and India, at higher concentrations (7–10 g l^{-1} available chlorine) as a rapid stage prior to peroxide bleaching [67].

Table 2.7 Recommended conditions for hypochlorite bleaching

	Cistern	Jig	Winch	Package machine	J-box conveyor
Available chlorine/g l^{-1}	2–4	2–4	1–2	1–2	2–5
Soda ash/g l^{-1}	2–4	2–4	1–2	1–2	2–4
Time/h	3–4	1–2	1–2	1–2	1–2

The advantages of bleaching with hypochlorite are:

(1) low chemical cost;
(2) lower (not zero) risk of catalytic damage;
(3) low energy input (heating cost).

The disadvantages of bleaching with hypochlorite are:

(1) the formation of high levels of AOX and chloroform;
(2) there is no rapid bleaching process possible;
(3) the danger of yellowing of the bleached fibre on storage;
(4) the danger of chemical damage to the cellulose (temperature and pH);
(5) the fibre must be prescoured before bleaching;
(6) degrades most dyes and fluorescent brightening agents (FBAs).

2.7.2 Bleaching with sodium chlorite

Effect of pH

The bleaching activity of sodium chlorite depends strongly on pH. Figure 2.11

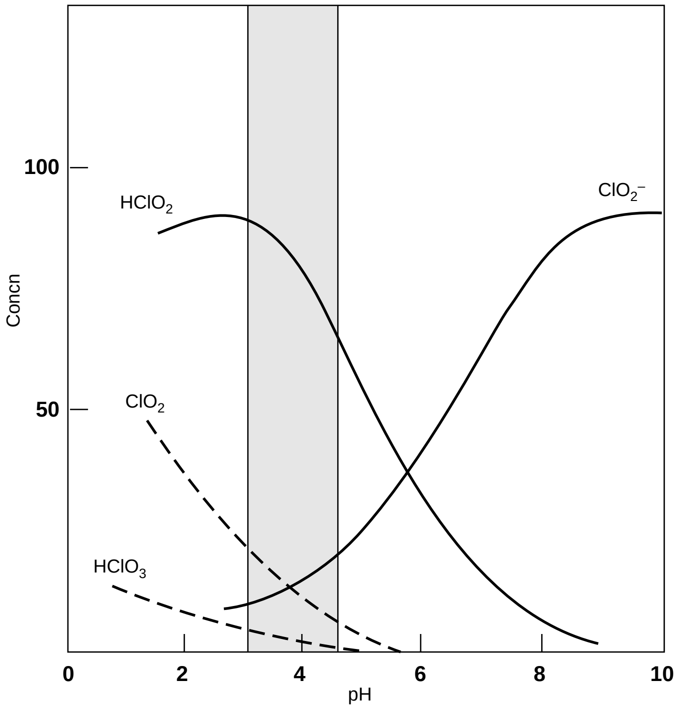

Figure 2.11 Effect of pH on the composition of sodium chlorite liquors. (*Source:* [98].)

$$5ClO_2^- + 2H^+ \longrightarrow 4ClO_2 + Cl^- + 2OH^-$$
$$3ClO_2^- \longrightarrow 2ClO_3^- + Cl^-$$
$$ClO_2^- \longrightarrow Cl^- + 2[O]$$

Scheme 2.3

shows the species in solution as the pH of a sodium chlorite solution changes. The reactions occurring in solution are highly complex and have been reviewed [2,51]. According to several authors, the chlorous acid ($HClO_2$) formed in solution by hydrolysis of the sodium salt undergoes the series of reactions in Scheme 2.3. In order to achieve the necessary concentration of chlorous acid, acid or latent acid generators (activators) must be added to the bleaching solution [68,69]. Activators include sodium chloroacetate, chloroacetamide, triethanolamine and ammonium persulphate [70]. It is also possible to activate sodium chlorite by irradiation with u.v.

Bleaching occurs most rapidly below pH 1–2, rapidly at pH 2–3 and the rate decreases as the pH increases to 8–9. Between pH 2 and 9 this rate is proportional to the concentration of chlorous acid in solution [51]. Below pH 2 the species providing the bleaching action is chlorine dioxide, a toxic, explosive, corrosive gas. In practice, a balance is usually struck between the rate of bleaching and the evolution of chlorine dioxide by controlling the bleach liquor pH. This is conveniently done on batch machinery by adjusting the pH to 3.5–4.5 with acetic or formic acid and then buffering at this pH by addition of sodium dihydrogen phosphate. The phosphate addition not only buffers the system but also improves whiteness.

When bleaching at low liquor ratio, for example on package machines or continuous ranges, the initial pH may be set higher at 4.5–6 since impurities in the substrate, especially if it is unscoured, liberate acid during bleaching, which tends to push the pH into the optimum range.

The chlorine formed (Scheme 2.3) does form some AOX but only about a tenth of that from hypo [13]. There is some discussion, however, on the source of this AOX.

Effect of temperature and time

Van't Hoff showed that, in most chemical reactions, the reaction rate doubles with each 10 degC rise in temperature. Chlorite bleaching is no exception. There are no reported detrimental effects of bleaching with sodium chlorite around 100°C, or of bleaching for more than several hours.

Sodium chlorite will bleach cellulose at ambient temperature but does need an overnight dwell. When bleaching is carried out at 100°C this dwell time is considerably reduced, for example to 1–4 h. Unlike hydrogen peroxide, no rapid (10–20 min) bleaching processes are possible.

Effect on cellulose

It is generally accepted that, under optimum bleaching conditions, sodium chlorite does not degrade cellulose. When the chlorite is in large excess or at pH above 7, however, the cotton is degraded [51].

Little is known about the functional groups formed by chlorite oxidation of cellulose. Chlorous acid at pH 3 quantitatively oxidises aldehydes or other carbonyl groups but the results are concentration-dependent. For example, if a C_1 aldehyde is oxidised, a gluconic acid ester is formed. With 0.2 mol l^{-1} chlorous acid there was no oxidation but a 1 mol l^{-1} solution gave extensive degradation after long dwell times [51]. Chlorine dioxide seems to oxidise cellulose in a similar way to chlorous acid.

The presence of carbonyl groups in cellulose pulp bleached with chlorine dioxide seems to be responsible for the yellowing and solubility in hot alkali of the pulp [51].

Chlorite bleaching processes

It is usual, though not essential, to pretreat before chlorite bleaching. The procedure depends on the machinery used, the form of the textile and the end use of the product. Woven fabrics would normally be desized and scoured whereas yarns and knitted fabrics would simply be washed off prior to bleaching to remove spinning or knitting lubricant. Loose stock would normally be required for an absorbent end use and so would need a full caustic scour before bleaching. Because of the danger from chlorine dioxide evolution, hooded machines connected to an extraction system are usually required and even then the area should be well ventilated. Typical formulations are shown in Table 2.8 [51].

Cistern bleaching is often carried out on the equipment made by Friedrichfeld GmbH. This is widely covered elsewhere and is often described as a pack system [14]. Though usually promoted for knitted fabrics, it has been used for linen and linen union woven fabrics.

On cistern, package machine, beam-dyeing machine, jet and possibly winch (in older dyehouses, chemicals would be added directly to the stuffer box of the winch machine), the bleach chemicals are made up in a sidetank adjacent to the machine or in the dye kitchen. The sidetank is about half-filled with cold water and then the sodium nitrate, buffer salts or activators, surfactants and sodium chlorite are added with stirring. Any solids should be predissolved before use. Finally, dilute acid is added and the pH checked and adjusted, if necessary. The

Table 2.8 Recommended conditions for chlorite bleaching

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

transfer pump is started and the contents of the tank transferred to the machine. The pump is then stopped and, after circulating the liquor in the machine for 5–10 min, the pH is again checked and preferably the chlorite content titrated. The temperature is raised to 85–95°C at 1–2 degC min^{-1} and held at that temperature for the appropriate time. For jig bleaching the chemicals would be added directly to the jig in the order given.

For J-box, conveyor or other pad–steam systems as well as for cold pad–batch bleaching, a similar system of tanks would be used for making up the pad liquor for the saturator. The actual concentration of this liquor will depend on whether the application is wet-on-dry or wet-on-wet.

Aftertreatment, e.g. with 2–5 g l^{-1} detergent plus 2–5 g l^{-1} soda ash at 85–95°C, on the bleaching machine, rope washer (Tensitrol or Colorado) or open soaper will often enhance whiteness and will usually improve absorbency of the substrate. An antichlor is only carried out for goods to be subsequently dyed. This can be accomplished by replacing the soda ash in the aftertreatment with sodium perborate or percarbonate but is more usually accomplished with sodium thiosulphate or oxalic acid. The reductive antichlors (hydros, sulphite or bisulphite) are seldom used as they replace one problem with another. For white goods, aftertreatment is often used to apply FBA and softener at pH 6–7.

The advantages of bleaching with sodium chlorite are:

(1) no need for severe precleaning treatments;
(2) smaller weight losses due to non-scouring action of acid bleach;
(3) soft fabric handle and good sewability due to non-removal of fats;
(4) low chemical damage;
(5) least sensitive to metallic contamination;
(6) bleaches synthetic fibres;
(7) acid process makes washing-off easier.

The disadvantages of bleaching with sodium chlorite are:

(1) a possibility of liberating the toxic gas, chlorine dioxide;
(2) the equipment is expensive because of the need for exotic construction materials;
(3) no rapid bleach process available;
(4) poor absorbency due to residual fats and waxes;
(5) expensive;
(6) incompatible with most dyes and FBAs;
(7) multichemical baths which need control.

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2.7.3 Bleaching with hydrogen peroxide

Hydrogen peroxide has achieved its dominant position as a bleaching agent because of three factors:

(1) It is environmentally innocuous (potentially it can decompose into oxygen and water).
(2) It is versatile (it can be used hot or cold, in rapid or long-dwell processes, batchwise or continuously).
(3) A variety of activation routes is available.

Hydrogen peroxide as supplied by the manufacturers is extremely stable. Typically, only a 3% loss of activity would result from storage at 40°C for 1 year [28]. On account of this innate stability, peroxide has only a slight bleaching effect on cellulose. For bleaching to occur this stability must be overcome by activation. Activators include alkalis, sulphuric acid, u.v. irradiation, hypochlorite, transition metals and *O*- and *N*-acyl compounds [71]. The usual activator for textile bleaching is alkali, usually sodium hydroxide, and the peroxide molecule undergoes heterolytic fission to the perhydroxide ion [72], as in Scheme 2.4. This nucleophile can react with organic compounds by a displacement reaction or by addition to a double bond.

$$H_2O_2 + OH^- \longrightarrow OOH^- + H_2O$$

Scheme 2.4

Reagents such as transition metals and u.v. irradiation cause homolytic fission of the peroxide into two hydroxyl radicals (•OH) and the problems created by these radicals have been reviewed [73].

It is probable that the pigments responsible for the natural colour of cotton contain a chromophoric system of conjugated double bonds. These will be attacked by a free-radical system and it has been proposed by Cates and Taher [74] that peroxide bleaching takes place by the mechanism indicated in Scheme 2.5. Such free radicals might be produced by reaction of hydrogen peroxide with an electron donor, possibly derived from a metal cation or from a perhydroxide anion. The reaction mechanism proposed is shown in Scheme 2.6.

The free radicals are believed to initiate decomposition through a chain mechanism. The decomposition within a given time interval is limited by the concentration of coloured impurities or by inhibiting metal cations. The latter appear to protect the cellulose from chemical damage by minimising the formation of molecular oxygen in the alkaline medium.

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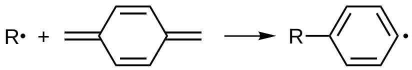

Scheme 2.5

$$\text{(a)}\quad H_2O_2 \longrightarrow H^+ + OOH^-$$

$$\text{(b)}\quad H_2O_2 + M^{2+} \longrightarrow M^{3+} + OH^- + {\cdot}OH$$

$$\text{or (c)}\quad H_2O_2 + OOH^- \longrightarrow {\cdot}OOH + OH^- + {\cdot}OH$$

$$\text{(d)}\quad H_2O_2 + {\cdot}OH \longrightarrow {\cdot}OOH + H_2O$$

$$\text{(e)}\quad {\cdot}OOH + M^{3+} \longrightarrow M^{2+} + H^+ + O_2$$

Scheme 2.6

Since these mechanisms are not fully understood, the bleacher still relies on control systems developed empirically. This control is often termed stabilisation, but this should not be confused with the use of chemicals to give the commercial product stability during storage. These compounds are effective at about pH 4.5–5, the pH at which commercial hydrogen peroxide solutions are most stable. Correct process stabilisation conditions control the rate of bleaching and ensure a residual peroxide content prior to washing-off, while making the most economic use of the chemicals. In this way the required standards of whiteness with minimum chemical damage are obtained. In effect four parameters require to be balanced: time, temperature, alkalinity and stabiliser content. Each of these factors will now be considered.

Effect of pH

Hydrogen peroxide does not have the multiplicity of species in solution as pH changes and so it is not possible to show graphs similar to those for the ‘chlorine’ bleaches. Alkalinity does have an effect and this was elegantly demonstrated by Naujoks for winch bleaching (Figure 2.12) [75] and by Rowe for pad–steam bleaching (Figure 2.13) [43].

Stabilisers

High pH and temperature lead to the decomposition of peroxide bleaching liquor and degradation of the cellulose, which are catalysed by transition metal ions [73]. The role of the stabiliser is simply to control or regulate these effects by a multiplicity of functions. For example, they act as buffers, sequestrants and dispersants as well as, in special cases, enhancing performance of the surfactants used in the bleach bath. The sequestering action inactivates metallic impurities which cause catalytic decomposition of hydrogen peroxide or precipitation of

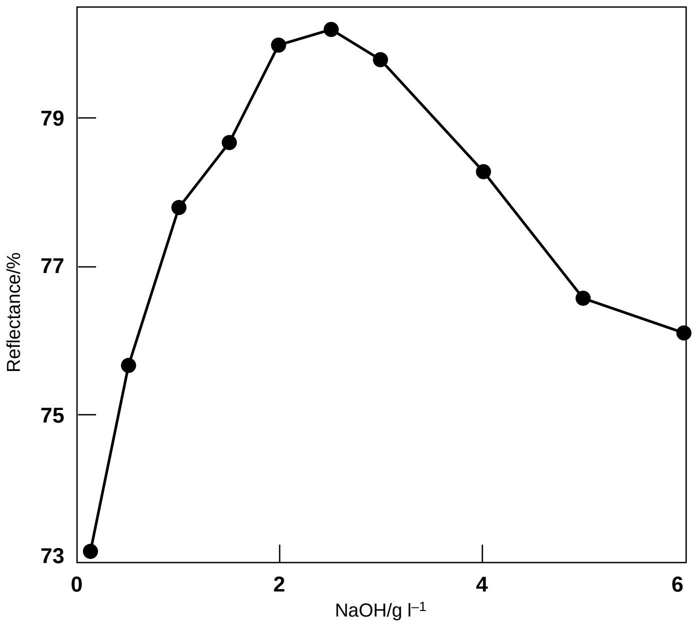

Figure 2.12 Effect of pH on whiteness for winch bleaching with hydrogen peroxide. (*Source:* [75].)

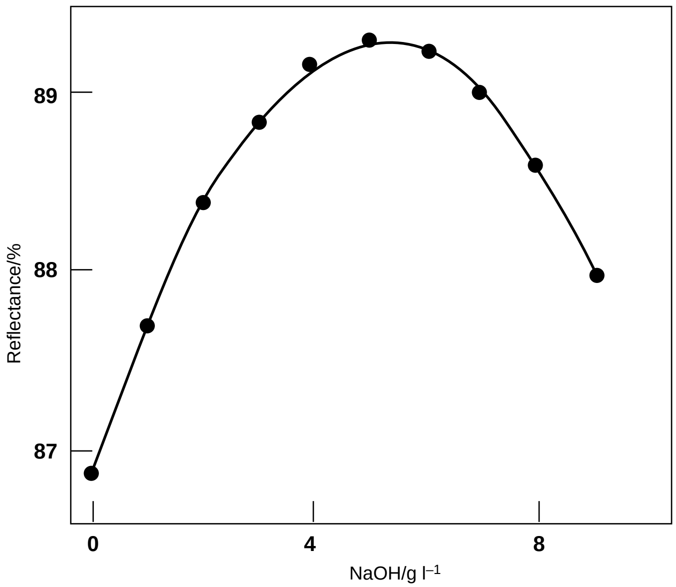

Figure 2.13 Effect of alkali concentration on J-box bleaching. (*Source:* [43].)

hydroxides or carbonates. These impurities, the most common being calcium and iron, are brought into the bleaching system by the fabric, water supply or the other chemicals used.

The stabilisers first used in bleaching cellulosic fibres with peroxide were the sodium polysilicates [71,72,76], often called water glass, which are highly effective at low cost. Sodium metasilicate (Na_2SiO_3) may be used in some applications as it can be washed out more readily than the polysilicates. The use of sodium orthosilicate (Na_4SiO_4) has been described [77] and even potassium silicates have been proposed [78]. The ratio of Na_2O to SiO_2 (Table 2.9) is often used to distinguish between the sodium silicates. In using either metasilicate or orthosilicate, more Na_2O is added than that provided by the polysilicates and so the Na_2O provided by the alkali would need to be reduced to maintain the ratio. The stabilising action of the sodium silicates and other stabilisers is improved by addition of magnesium ions. These ions may be present in the cotton being processed, or as hardness in the process water. In the case of soft water, the addition of such ions is recommended. This is usually done by adding magnesium sulphate crystals ($MgSO_4.7H_2O$) to give a water hardness equivalent to 3–4° English hardness [54].

Table 2.9 Relative Na_2O and SiO_2 content of bleach chemicals

Product	Na_2O/%	SiO_2/%
Sodium orthosilicate(Na_4SiO_4)	67.4	32.6
Sodium metasilicate ($Na_2SiO_3.5H_2O$)	29.0	28.2
Sodium silicate (sp. gr. 1.4)	8.8	29.0
Caustic soda	77.5	
Soda ash	58.0	

Over the years there has been considerable discussion on the role of silicates in peroxide bleaching, particularly on their effectiveness to control transition-metal contamination. The following mechanisms have been proposed:

(1) The silicate may form silica gel with high specific surface area or colloidal magnesium silicate by reaction with magnesium salts; either of these products can absorb metallic impurities.

(2) Silicate itself can complex with hydrogen peroxide to form unstable peroxides.

(3) Silicate may bind free radicals formed in the presence of some metallic catalysts, and whether the addition of calcium or magnesium salts supports this action depends on the nature of the metallic catalyst.
(4) Silicate not only may stabilise the peroxide but may also increase the efficiency of bleaching through the formation of peroxosilicate.

Most of the research work on the mechanism of stabilisation has been done under long liquor conditions. The proposed mechanism may not, therefore, be applicable to short liquor ratio systems. The simple explanation of magnesium silicate formation provides only a partial understanding of stabilisation. Certain auxiliaries promote its formation but prevent crystal growth and therefore precipitation [76].

When using silicates in peroxide bleaching it is important to establish the correct balance between the silica (SiO_2) content derived from the silicate and the sodium oxide (Na_2O) content derived from the alkali and the silicate. The proportions of Na_2O and SiO_2 shown in Table 2.9 may be used to calculate the total amounts in a bleaching liquor. In a typical long liquor bleaching formulation the calculation of the Na_2O:SiO_2 ratio is as shown in Table 2.10.

Substrates bleached with a silicate stabiliser must be washed off in soft, neutral, boiling water in order to prevent problems caused by insoluble silicates or silicic acid. Although sodium silicate is both effective and economical, the problems associated with silicate deposits on fabric and machinery have made alternative non-silicate or organic stabilisers attractive. These products are blends of organic materials with or without magnesium salts, and are mainly of five chemical types:
(1) Organic sequestering agents.
(2) Protein degradation products.
(3) Certain surfactants.
(4) Polymeric materials.
(5) Mixtures of any of the above.

Table 2.10 Determination of Na_2O:SiO_2 ratio for long liquor bleaching

Sodium silicate(sp. gr. 1.4)	7.0 g l^{-1} provides	2.03 g l^{-1} SiO_2	0.62 g l^{-1} Na_2O
Caustic soda	0.5 g l^{-1} provides		0.39 g l^{-1} Na_2O
Soda ash	1.8 g l^{-1} provides		1.04 g l^{-1} Na_2O
Total SiO_2 and Na_2O is		2.03 g l^{-1} SiO_2	2.05 g l^{-1} Na_2O

The above system therefore provides a 1:1 ratio of Na_2O to SiO_2.

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Stabilisers may be formulated for stabilisation alone or combined with other products to confer detergency, softness, crease-free running, etc. They are particularly useful on package machines, to minimise filtration, and jigs, where washing-off is difficult. For processing knitgoods on winch or jet the product may also include alkali, allowing addition of a single product to the bleach bath. In general, washing-off is simplified by using organic stabilisers, since citric or acetic acid can be used to neutralise residual alkali with no danger of precipitating silicates.

Originally the whiteness attained from bleaching with organic stabilisers was only considered acceptable when batch processing. Organic stabilisers were considered less suitable in pad–steam bleaching and it was believed that some silicate must be included. In recent years new products have been developed. These give similar results to silicate and are now used in continuous pad–steam processes to produce full whites without silicate addition to the saturator [79].

The degree of preparation prior to peroxide bleaching influences alkali and stabiliser concentrations used in the bleach bath. When pretreatment is limited to the oxidative removal of size the presence in the cotton of natural impurities helps the stabilisation and so the bleach liquor may need less stabiliser or more activator. Acid souring, to neutralise scouring or remove metallic contamination, can also remove natural calcium and magnesium ions from cotton and so, in this case, an increase in the magnesium sulphate addition may be necessary. Alkaline scouring may cause carry-over of alkali into the bleach bath and so the alkali in the bleach may need to be reduced or omitted altogether.

Sequestering agents are often successfully used to control the effects of small quantities of transition-metal ions during bleaching. They are less effective when the contamination is present as highly localised concentrations such as rust particles. Polyphosphates and EDTA (section 2.3.4) are reported as eliminating or reducing the catalytic degradation resulting from metal ions in baths stabilised with silicate in the presence of magnesium ions [80]. Experience indicates that is not always the case, although it is acknowledged that silicates do play a major role in controlling catalytic metals during peroxide bleaching.

In general, it is difficult to control catalytic damage from within the bleach bath and when it is suspected that it may occur, for example on Brazilian cotton contaminated with traces of manganese, an acid sour at long liquor ratio prior to bleaching is recommended. The use of milder bleaching conditions (lower temperatures, time, chemical concentrations) will always moderate the effect of metallic contamination.

Effect of temperature and time

As with sodium chlorite, bleaching rate increases with temperature. There are no reported detrimental effects of bleaching with hydrogen peroxide around 100°C or of bleaching for more than several hours provided all other things are equal, i.e. the system is well balanced (concentrations of oxidant, stabiliser and alkali are in the correct ratio) and free from heavy metal ions.

Hydrogen peroxide will bleach cellulose at ambient temperature but needs an overnight dwell. When bleaching is carried out at 100°C this dwell time is considerably reduced (e.g. to 3–20 min): this ability to bleach in such short times at high temperature is unique to hydrogen peroxide and makes rapid bleaching processes possible.

Effect on cellulose

The main functional groups formed by cellulose oxidised by hydrogen peroxide are ketone groups, i.e. there are very few aldehyde or carboxy groups. These ketone groups do not promote yellowing or β-hydroxycarbonyl elimination (the peeling reaction) [51]. Unlike hypochlorite it does not rapidly depolymerise the cellulose but slowly oxidises terminal anhydroglucose units in almost a 'wet' combustion. There are no large organic fragments formed which can cause yellowing, so the stability of the white is good.

Peroxide bleaching processes

As with chlorite bleaching, pretreatment prior to bleaching is usual but not essential. The nature of the pretreatment depends on the machinery used, the form of the textile and the end use of the substrate. Woven fabrics would normally be desized and scoured whereas yarn and knitted fabrics would simply be washed off prior to bleaching to remove spinning or knitting lubricant. Loose stock would normally be required for an absorbent end use and so would need a full caustic scour before bleaching.

Because of the diversity of application conditions it is convenient to divide the processes into batchwise and continuous.

Batchwise processes

Typical formulations are given in Table 2.11 [51]. The bleach chemicals are made up in a sidetank. This is about half-filled with cold water and then the

Table 2.11 Recommended conditions for batch peroxide bleaching

	Kier/ % o.w.f.	Jig/ % o.w.f.	Winch or jet/g l^{-1}	Package machine/g l^{-1}
Magnesium sulphate heptahydrate			0.1	0.1
Wetting agent			0.5–2	0.5–2
Sodium silicate (79°Tw)	2–3	3–5	7	2–7
Organic stabiliser		1–1.5	1–2	0.5–2
Caustic soda (100%)	0.6–1.4	0.25–0.8	5–15	5–15
Hydrogen peroxide (35%)	3–5	2–5	5–15	5–15
Liquor ratio	4:1	3:1	15–20:1	8–10:1
Temperature/°C	95	95	95	90
Time/h	1–2	1–2	1–2	1–2

magnesium sulphate crystals (magnesium chloride should not be used because of the corrosive effect of chloride ions on stainless steel), organic materials (surfactants, stabilisers), sodium silicate and caustic soda are added with stirring. It must be remembered that the specific gravities of both sodium silicate (79° Tw) and caustic soda (70 or 100° Tw) are much greater that 1 and these liquors sink to the bottom of the tank. Stirring is, therefore, an absolute necessity. Any solids should be predissolved. Finally, hydrogen peroxide is added and if required the concentrations of alkali and peroxide are determined by titration. This check of concentrations is essential for package machines that use air-cushion pressurisation. The transfer pump is started and the contents of the tank transferred to the machine, before the temperature is raised to 85–95°C at 1–2 degC min^{-1} and held at that temperature for 1–2 h. For jig bleaching the chemicals would be added directly to the jig in the order given.

For kier bleaching, the transfer pump supplies the piler and when the kier is about half full, the steam to the kier heater is opened to give a temperature of 40–50°C and loading is completed. The temperature is raised to 65–70°C over 30 min and the kier is rested for 30 min at this temperature to expel air. After raising to 80°C and resting again, the lid is closed and the temperature raised and held for 1–2 h at 95°C.

On package machines with stock tanks, the spent bleach liquor can be pumped up and regenerated by bringing back almost to volume and again titrating (titre T_1). If the original liquor made up had titre T_0, then chemicals are added in the ratio defined by Eqn 2.3:

$$\text{Chemical addition (kg or l)} = \text{original addition} \times \frac{(T_0 - T_1)}{T_0} \quad (2.3)$$

On a jig, water is normally used in the first few ends to bed in the fabric but can also be used for precleaning at the boil with detergent, enzyme, etc. At the bleaching step, all of the bleach chemicals, except peroxide, are added and the temperature raised to boil. To prevent variation from one end of the batch to the other (ending), the peroxide is drip fed over two to four ends. To moderate activation of the peroxide over the first end the peroxide should be added below 50°C. Washing-off is notoriously difficult on jigs, and overflow rinsing or soda ash scaling should be considered as solutions to problems at wash-off. In the latter, 2% soda ash on weight of good is added to the first wash liquor, the temperature raised above 80°C and the fabric run for a further two ends. This process not only gives an alkaline scour but also activates any residual peroxide which enhances the final whiteness of the fabric.

Continuous processes [35]

Continuous hydrogen peroxide bleaching of woven fabric in rope form was introduced in the late 1930s by the American peroxide producers Becco and DuPont. Many machine developments have been made since that time [35], and now most woven and, increasingly, knitted fabrics are bleached with hydrogen peroxide by continuous methods either in rope or open-width form. The main justification for installing a continuous range is productivity.

Most knitted fabrics are scoured and bleached in a single stage on spiral rope processing machines such as the Küsters KRP, Jemco or Ashby Industries machines, but most woven fabrics are pad–steam processed continuously in three stages: desizing, scouring and bleaching. As the washing stages of such a route consume 75% of the energy, much attention has been given to combining process stages to reduce energy demand and minimise capital investment in plant. The scope for combining stages depends on grey fabric quality and the standard of preparation required, particularly seed removal. With a good balance between stabilisation, alkalinity, peroxide concentration, time and temperature [81], it is often possible to reduce the stages from three to two, or even one. The most usual limitation is inadequate seed removal in the absence of an alkaline pretreatment. Oxidative desizing with hydrogen peroxide or a persulphate can minimise the need for separate hot alkaline scouring [82].

In such pad–steam bleaching processes, sodium silicate was considered, until recently, the only effective stabiliser. Organic stabilisers have been developed to an extent that silicate can be eliminated entirely from many bleaching processes and considerably reduced for others [83]. The alternative method for minimising silicate deposition onto cloth and machinery is the use of the so-called silicate dispersants. It is strange that many of these dispersants also act as stabilisers.

Magnesium salts, beneficial in long liquor bleaching, are of less importance in the saturator liquor of a pad–steam range [84], but they can improve the bleached result, once the fabric is in the steamer, by enhancing the performance of the stabiliser. In long liquors, mixtures of caustic soda and soda ash are often useful as the Na_2O content can be increased without significantly raising the pH. Under pad–steam conditions no advantage is gained by using soda ash. In fact it may well be deleterious as soda ash promotes saturator liquor decomposition.

In pad–steam bleaching, steam quality is of paramount importance. It should contain neither air nor rust particles. When fabric is maintained at a high temperature for more than a few minutes the steam used for heating in the scouring and bleaching stages must not contain more than 3 degC superheat. Poorly conditioned steam can lead to tendering of the fabric. High-pressure steam over 304 kPa (3 atm) must not be fed directly to steam spray pipes even if these are in the ‘wet bottom’ of the steamer. The steam should be reduced to a pressure of 101 kPa (1 atm or 15 lbf in^{-2} gauge) using a suitable reducing valve and then conducted through a desuperheater, fitted with suitable baffles and cooling jacket, and from which any condensate can be led to drain. The line should also be fitted with suitable filters, such as those made by Spirax Sarco, fitted with replaceable cartridges.

Chemical requirements depend on fabric quality and pretreatment. The recommendations in Table 2.12 are for 100% cotton fabrics that have been caustic scoured or peroxide desized prior to bleaching [34]. Where no such pretreatment has been given it is usually necessary to increase amounts of alkali and hydrogen peroxide by 50%. The silicate may be partially or wholly replaced by an organic stabiliser.

Semi-continuous processes

The pad–batch process consists of padding the grey fabric with a strong solution of alkali and hydrogen peroxide and storing, in batch form, for 2–24 h depending on storage temperature. The pad–roll processes have declined due to their innate variability (section 2.5.3), but in recent years interest in cold bleaching has increased as it provides a low-energy preparation route with low capital investment, applicable to both woven and knitted fabrics. Cloth can be impregnated with the bleach solution on standard stainless steel pad mangles (or

Table 2.12 Recommended conditions for continuous peroxide bleaching

	J-box conveyor woven or rope form	Roller-bed steamer	Pressure steamer	Jemco machine	J-box knitgoods [42]
Magnesium sulphate heptahydrate/g l^{-1}	0.1	0.1	0.1	0.1	0.1
Wetting agent/g l^{-1}	2–5	2–5	2–5	0.5	5
Sodium silicate (79° Tw)/g l^{-1} or organic stabiliser	5–10	10–20	5–10	1.5	10
Caustic soda (100%)/g l^{-1}	2–5	5–15	2–5	4	5
Hydrogen peroxide (35%)/g l^{-1}	15–30	45–60	30–45	2	45
Liquor ratio	1:1	1:1	1:1	10:1	1:1
Temperature/°C	95–98	95–98	120–140	95–100	95–98
Time/min	60–120	10–30	1–2	40–60	60–90

even jigs) but for regular production by this method an efficient open-width saturator is recommended, simply because high pick-up is difficult to achieve on grey cloth.

Cold pad–batch bleaching requires:

(1) control of pad bath concentration and temperature, preferably 25–35°C;
(2) greater than 80% liquor pick-up;
(3) fabric storage without uneven drainage or surface drying;
(4) washing-off at a minimum of 95°C.

A good wetting agent is essential to ensure good penetration of grey fabric by the bleaching liquor, and a good detergent is also necessary to aid fat and wax removal and development of good absorbency.

A formulation for cold pad–patch bleaching is [33]:

(1) sodium silicate (79° Tw) 8–12 g l^{-1}
(2) organic stabiliser 6–10 g l^{-1}
(3) caustic soda (100%) 8–15 g l^{-1}
(4) hydrogen peroxide (35%) 40–50 g l^{-1}.

Persulphates can also be added, at up to 5 g l^{-1}, to the cold pad bleaching formulation. These aid the desizing action during bleaching.

After impregnation the fabric is batched, covered with a plastic sheet to prevent drying and left for a period of 15–24 h. The fabric is then washed off at

95°C in an open soaper or jig (two ends) through a solution of 1% soda ash, to which can be added soap, detergent or sequestering agent. This alkaline treatment makes a significant improvement to fabric absorbency and increases brightness by 1–2%, compared with washing-off in water only.

The advantages of bleaching with hydrogen peroxide are:

(1) no need for severe precleaning processes;
(2) no need for exotic materials of construction, but iron and copper must not be used;
(3) environmentally acceptable; no AOX even in the presence of salt;
(4) decomposition products are oxygen and water;
(5) excellent storage stability;
(6) compatible with most dyes and FBAs;
(7) gives versatile processing (batch/continuous, hot/cold, rapid/long dwell, most fibre types);
(8) produces a stable white fibre with good absorbency;
(9) allows route shortening by combining stages (desize with scour, scour with bleach and desize with scour and bleach).

The disadvantages of bleaching with peroxide are:

(1) some water is always transported;
(2) sensitivity to metallic impurities;
(3) multichemical baths which need control;
(4) comparatively expensive.

2.8 PREPARATION OF REGENERATED CELLULOSIC FIBRES

Wood pulp from certain trees can be dissolved in a solvent and can be regenerated as a fibre by extrusion of the cellulose solution into a precipitation medium. The most common solvents are caustic soda/carbon disulphide and cuprammonium hydroxide, both of which are aqueous solutions, and *N*-methylmorpholine-*N*-oxide which is an organic solvent. In the case of the aqueous solutions, the precipitation is carried out in an aqueous acid bath containing certain additives. The *N*-methylmorpholine-*N*-oxide solution is dry spun. The additives in the wet spinning bath control the nature of the product, such as normal viscose or high wet modulus (HWM) fibres [85]. Regenerated fibres are sensitive to alkali, and impurities in the precipitation bath or solvent make them prone to oxidative damage. The degree of polymerisation and resistance to alkali increase on going from normal viscose, via HWM to solvent-spun viscose. They are less variable in composition than cotton or linen and their impurities are more easily removed.

2.8.1 Desizing

Fabrics made from these fibres are desized in exactly the same way as for cotton. Care should be exercised with oxidative desizing in terms of both alkali and oxidant concentrations, which should be no more than half of those used for cotton. Most warps contain starch-based sizes and so enzyme desizing is customary. However, carboxymethylcellulose is sometimes used, and a cold swelling process followed by hot washing with a detergent is adequate in this case.

2.8.2 Scouring [79]

Soap and soda scouring is usually carried out for yarn, knitted and woven fabrics and typical processes are shown in Table 2.13. Anionic surfactants have generally replaced the true soaps as they are much easier to wash out than either soaps or nonionic detergents. The first box of the open soaper contains these additions, sequestrant is added to the second and 2 g l^{-1} anionic detergent added to the third. The remaining boxes are simply hot and cold rinses. On the J-box, the low-temperature steam is provide by an air-aspirator.

Table 2.13 Recommended conditions for scouring of regenerated cellulosic fabrics

	Winch or jet	Jig	Open soaper	J-box
Anionic detergent/g l^{-1}	1	2	5	10
Soda ash/g l^{-1}	1	2	2	10
Temperature/°C	95	95	95	80
Time/min	30	30		30

2.8.3 Mercerising

Regenerated cellulosic fibres dissolve in caustic liquor at about 6.5% by weight (15° Tw). At concentrations above and below this critical level there is much less effect. If high concentrations are used, however, it is impossible when rinsing to avoid the critical region and so causticisation rather than mercerisation is carried out on the fibres using 1.5–5% by weight caustic soda (3–12° Tw). The addition of salt reduces the risks even further. As the fibres swell less in hot caustic liquors, there is some advantage in using elevated temperatures.

2.8.4 Bleaching [86,87]

Most regenerated fibres are used as staple and bleached in fabric form (Table 2.14). Bleaching is only required for fluorescent whites and pastel shades. Any of the three oxidative bleaches can be used.

Peracetic acid bleaching requires 3 g l^{-1} peracetic acid (Proxitane 4002, Solvay Interox) for 60 min at 65°C and pH 7 in the presence of sodium hexametaphosphate [28,51].

For winch bleaching the following chlorite bleach is recommended for 45–90 min at 90–95°C [87]:

(1)	sodium chlorite (80%)	0.5–1.5 g l^{-1}
(2)	bleaching auxiliary HV	0.5–1.0 g l^{-1}
(3)	sodium nitrate	1.0–2.0 g l^{-1}
(4)	sodium acetate	2.0 g l^{-1}
(5)	acetic acid	to pH 4.0

Bleaching processes for normal and HWM fibres have been compared [88].

Table 2.14 Recommended conditions for bleaching of regenerated cellulosic fabrics

	Winch or jet	Jig	Roller-bed steamer	J-box
Sequestrant/g l^{-1}	1	1	0.5	2
Caustic soda (100%)/g l^{-1}	0.5–1	0.5–1	3	
Sodium silicate (79° Tw)/g l^{-1}			5	5
Organic stabiliser/g l^{-1}	1–2	1–2	8	
Hydrogen peroxide (35%)/g l^{-1}	5	10	10–15	8.5
Temperature/°C	80	80	100	80
Time/min	60	60	4–5	45

2.9 PREPARATION OF BAST FIBRES [85,89]

Linen, jute, ramie and hemp are all bast fibres, forming bundles in the bast layer of plant stems. Ramie has a low content of impurities compared with the other fibres and can be processed much like cotton.

The other fibres, however, have large quantities of non-cellulosic components and are usually a medium brown colour. The impurities include hemicelluloses and pectins (and their salts) together with lignin, which is responsible for the

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brown colour. In the processing of flax it is the fibre bundles that exhibit the properties associated with linen fabrics; each fibre consists of cells cemented together by the hemicelluloses. If the cells are large, as in the case of flax, this intercellular cement can be removed without undue loss in strength, although the weight loss is substantial. In jute and hemp the cells are small and removal of the hemicelluloses causes substantial weakening of the fibre. It is usual to remove the lignin from flax but not from jute [90], which makes the latter sensitive to photo-yellowing. In all cases the greater the whiteness of fibre or fabric, the greater the weight loss.

2.9.1 Jute [89]

The Indian Jute Industries Research Association has described a combined hypochlorite/peroxide bleach consisting of treatment at 10:1 liquor ratio with 0.25% o.w.f. available chlorine for 30 min at pH 10.5, then treatment with the following recipe for 60 min at 70°C [90,91]:

(1)	hydrogen peroxide	0.25%
(2)	trisodium phosphate	0.25%
(3)	sodium metasilicate	1.0%.

2.9.2 Linen [92]

Linen is the fibre obtained from the flax plant. Unbleached linen varies widely in colour because of climatic differences during growth and variable extraction (retting) of the fibre from the plant stalk by biological attack. Flax may be retted under water or on the ground, where a darker, heterogeneous fibre that is more difficult to bleach tends to be produced. Control of retting is important. An under-retted flax often has a reddish hue while a fully retted flax is almost grey in colour. Over-retting is accompanied by degradation of the cellulose. The retting process creates massive BOD/COD loads and there is a constant search for a viable chemical method confined to tanks, where the process would be more reproducible and reduction of the effluent load would be much easier. A good overview of linen wet processing is given by Sloan [92]. Linen may be processed during wet spinning (rove) or more conventionally as yarn or fabric.

The preparation of linen is a compromise between the whiteness level required (often defined in quarter steps, to full white) and the weight loss that can be tolerated. The presence of woody matter (sprit) that the mechanical operations (scutching and combing) have failed to remove may be desirable in certain products or tolerated for low weight loss. In such cases, careful dye selection is necessary to give uniform coverage. High whiteness demands multiple processing and there is a danger of separating the fibre bundles (called cottonising). The risk of cottonisation is minimised by repeated mild treatments rather than one severe stage. The interplay of process stages, whiteness and weight loss has been well described by BASF [93].

Traditionally the route for producing the best white was:

(1) Chlorination of the lignin, preferably with gaseous chlorine but possibly with acid hypochlorite at long liquor ratio (the solubility of chlorine in water is low).
(2) Dissolution of the chlorinated lignin and hemicelluloses in alkali. This alkaline extraction stage carries some risk; the pectins are dissolved out but the heavy metal ions forming salts with them are released to impair later peroxide bleaching.
(3) Improvement of the whiteness by bleaching, probably with sodium chlorite and hydrogen peroxide in sequence.

With the AOX problem such routes are no longer possible but Dierkes describes combined sodium chlorite and hydrogen peroxide processes [94].

2.10 MONITORING THE PROCESS LIQUORS [49]

Whatever the preparation stage, chemicals are measured or weighed and then dissolved in water to make up the treatment liquor. During the treatment these chemicals will be consumed and, in continuous systems, it will be necessary to make further additions to maintain the concentrations in the bath. In batch processes measuring the amount of chemical consumption may also be necessary to obtain a repeatable result, for example from hypochlorite bleaching, or to be able to regenerate the bath for further use. In all cases, even with sophisticated automatic control, manual titration of the liquor must be carried out. This stems not only from the fact that automated control is not infallible – computers fail and valves stick – but also from the need to give the operative a pride in what he or she is doing. The reagent used in the titration, the titrant, is always standard solution, i.e. a solution of known molarity.

Like process liquors, the impregnated or bleached substrate can also be titrated. Information about residual peroxide, for example, can often give useful data for improving the process. In this case, a known weight of substrate is immersed in the liquor in which the titration is carried out.

2.10.1 Titration of alkali

A suitable volume of liquor, V ml (usually 10 ml), is placed in a beaker or flask and one drop of indicator, preferably bromothymol blue but, in highly coloured scour liquors, phenolphthalein, is added. Then 0.1 mol l^{-1} hydrochloric acid is added until the indicator changes colour.

From the appropriate equations, the following equivalences can be stated:
Caustic soda: 1 ml of 0.1 mol l^{-1} acid = $1000 \times 0.004/V$ g l^{-1} NaOH (100%)
Soda ash: 1 ml of 0.1 mol l^{-1} acid = $1000 \times 0.0053/V$ g l^{-1} Na_2CO_3

In the case of the substrate, it is difficult to extract all the alkali and so it is often better to back-titrate, i.e. neutralise with an excess of standard acid and then titrate the unreacted acid with standard alkali. In this case the concentration of alkali on the fabric, expressed as percentage on weight of fabric (W) is given by Eqn 2.4:

$$\text{Concentration} = f \times \text{titre} \times 100/W \qquad (2.4)$$

where f is 0.004 (NaOH) or 0.0053 (Na_2CO_3).

2.10.2 Titration of oxidising agents

In theory, any reducing agent can be used to titrate any oxidant. The method chosen here is iodometry where the oxidant liberates iodine from a potassium iodide solution and the iodine is titrated with standard sodium thiosulphate, as this technique is applicable to all three bleaching agents.

The general procedure is to pipette V ml (usually 10 ml) of the liquor into a flask or beaker and add 20 ml of 150 g l^{-1} potassium iodide solution and 50 ml 10% sulphuric acid. The flask is then kept in the dark for 5–10 min to allow the reaction to occur. The iodine is then titrated with standard (usually 0.1 mol l^{-1}) sodium thiosulphate (thio). X in Eqns 2.5–2.7 is the percentage strength of the oxidant, e.g. 35% for peroxide:

$$\begin{aligned} H_2O_2: 1\ \text{ml standard thio} &= 0.0017 \times \frac{1000 \times 100}{V \times X} \\ &= \text{g l}^{-1}\ H_2O_2\ X\% \qquad (2.5) \end{aligned}$$

$$\begin{aligned} NaClO_2: 1\ \text{ml standard thio} &= 0.00226 \times \frac{1000 \times 100}{V \times X} \\ &= \text{g l}^{-1}\ NaClO_2\ X\% \qquad (2.6) \end{aligned}$$

$$\text{NaOCl: 1 ml standard thio} = 0.0035 \times \frac{1000}{V}$$
$$= \text{g l}^{-1} \text{ available chlorine} \qquad (2.7)$$

When titrating a substrate, it must be removed from the acid before liberating the iodine, as the iodine would be absorbed by the substrate and thus become inaccessible for titration. The concentration of oxidant is defined by Eqn 2.4, where *f* is 0.0017, 0.00226 or 0.0035 as appropriate.

In the case of peroxide, concentrations are usually monitored by titration with potassium permanganate and the procedure is to pipette *V* ml (usually 2 ml) of the liquor into a flask or beaker containing 100 ml dilute (10%) sulphuric acid solution and titrate immediately with 0.1 mol l^{-1} potassium permanganate. If the titre is *A* ml, then Eqns 2.8–2.11 hold:

$$A/V \times 4.86 = \text{g l}^{-1}\ \text{H}_2\text{O}_2\ 35\% \qquad (2.8)$$

$$A/V \times 4.28 = \text{ml l}^{-1}\ \text{H}_2\text{O}_2\ 35\% \qquad (2.9)$$

$$A/V \times 3.4 = \text{g l}^{-1}\ \text{H}_2\text{O}_2\ 50\% \qquad (2.10)$$

$$A/V \times 2.86 = \text{ml l}^{-1}\ \text{H}_2\text{O}_2\ 50\% \qquad (2.11)$$

2.11 MONITORING THE RESULTS [49,95,96]

A well-prepared substrate should have:

(1) a high, uniform whiteness which is stable on storage;
(2) a high, uniform absorbency for aqueous solutions;
(3) low chemical damage.

There are national standards for measuring these values in most Western countries [95,96].

2.11.1 Whiteness

The whiteness of the substrate may be assessed by comparing it visually with a standard, or determined instrumentally using a reflectance photometer. The photometer is calibrated at 8, 16 or 32 wavelengths using a white standard (magnesium oxide, barium sulphate). An ideal standard would give 100%

reflectance at all wavelengths. In order to assess the whiteness of a non-fluorescent cellulosic fibre or blend, the amount of light reflected in the blue region of the visible spectrum is usually measured. Whiteness of a fabric is normally assessed on multiple layers (usually between four and eight) so that the background support does not affect the reflectance. Unbleached 100% woven cotton fabrics usually have a reflectance at 460 nm of about 55%. This increases to 83–85% for fully bleached fabric. Lower reflectance, say 78–82%, is generally acceptable as a preparation for subsequent dyeing.

Yarn is measured by winding the sample on to a former, and loose stock is measured in a cell with an optical glass window. The glass is also an absorber or internal reflector of the incident light and so true reflectance is reduced by 10–12%.

There are no fully acceptable instruments for assessing samples whitened with FBAs. Ciba-Geigy and Bayer have considerable experience in this area, as have instrument suppliers such as Instrumental Colour Systems or other Datacolor Group members. Perspex plates, which absorb u.v., may be used to assess the bleached ground.

2.11.2 Absorbency [95]

Various methods are available for testing fibre, fabric or yarn absorbency. Tests based on the time for water to be absorbed by the sample, or for a sample to sink in water, are frequently used. Well-prepared substrates should absorb a drop of water or sink in less than 1 s. In the case of fibre, a representative sample is packed into a light wire cage and the sinking time measured. The weight of water absorbed may also be measured. Yarn absorbency can be, but is rarely, assessed by the Draves test in which the sinking time of a hank is measured under standard conditions.

Fabric absorbency is usually assessed using water drop absorbency times. To differentiate between samples of good absorbency, the water drop may be replaced by a drop of 50% sugar solution which increases the absorbency time by a factor of ten. The LINRA wipe tester is a more sophisticated test apparatus for fabric. In this test drops of dye solution are applied to the test paper, which is drawn under a piece of fabric. The fabric is held so that a constant load is applied. Highly absorbent fabrics rapidly absorb the dye and very short streaks are shown on the paper. Poor fabric absorbency is shown up by long dye streaks being spread on the test paper. As with the drop absorbency test, the sensitivity of the test can be modified by using dye solutions of differing viscosity. In Europe, a simple capillary rise test may be used. In this test, a thin strip of test material is suspended vertically above a solution, usually of a blue acid wool dye, with the lower edge just touching the liquor surface. The height to which the solution rises by capillary action is noted after a set time, e.g. 5 min, or alternatively the time to reach a fixed height is determined.

2.11.3 Chemical damage

The degree of polymerisation of a polymer is directly proportional to the viscosity of its solution, providing all solutions are at the same concentration. In parts of Europe and the USA, this describes the basis of a test for damage in which the viscosity of a standard solution is assessed using a U-viscometer. In the UK, the reciprocal viscosity, or fluidity (*F*), is the basis of BS 2610, in which cuprammonium hydroxide is the solvent for the cellulosic fibre and the fluidity is measured from the flow time in special Shirley X-type viscometers. The fluidity test is more sensitive for detecting chemical damage than loss in tensile strength.

In this test a weighed sample of the cellulose, finely chopped to give fibres 1–2 mm in length, is dissolved in standard cuprammonium hydroxide in a standard capillary viscometer. The quantity of cellulose is sufficient to give a 0.5% solution for cotton or a 2% solution for regenerated cellulose. The viscometer must be filled completely to exclude air and covered to prevent exposure to light, whilst controlled agitation is given over 16 h. The viscometer and contents are then brought to 20°C in a thermostatically controlled bath and the rate of flow through the capillary measured. Standard viscometers are marked so that this flow measurement is simply a timing between two points. As each viscometer is precalibrated, fluidity is then determined, from the data provided, by dividing a viscometer constant by the time recorded. This gives a direct calculation of fluidity in terms of pascals per second (Pa s^{-1}).

The principle of the test is that during dissolution no further breakdown of the cellulose molecular chain structure will occur. Long-chain material, i.e. with low damage, will provide a highly viscous solution, hence low fluidity. Unbleached cotton shows a fluidity of about two. As a general guide, bleached cotton with a fluidity of five or less is accepted commercially. Above a value of ten, chemical damage shows up as a loss in tensile strength.

For regenerated cellulosic fibres, using the 2.0% solution, the high wet modulus products give similar fluidity levels to cotton, but the standard viscose has an unbleached fluidity of about ten.

In some countries, particularly those in Western Europe, cupriethylenediamine (cuen) rather than cuprammonium hydroxide (cuam) is used. It is also more general to express the results as a degree of polymerisation (DP) value. A high DP represents undamaged and a low DP damaged cellulose. The relationship between the two systems is given by Eqn 2.12 [71,72]:

$$DP = 2032 \frac{\log 74.35 + F}{F} - 573 \qquad (2.12)$$

A useful adaptation of the fluidity measurement is the so-called rapid fluidity test devised by the British Textile Technology Group (the Shirley Institute). For this test, 0.125 g of cotton is dissolved in 50 ml cuprammonium hydroxide in a wide-mouthed polypropylene bottle. Six drops of 50% pyrogallol solution are added and agitation aided by addition of 12 stainless steel ball bearings, 6 mm in diameter. The bottle is mounted on a shaker and the cotton dissolves within 30 min. The solution is centrifuged and the supernatant liquor is transferred to a standard viscometer. The measured fluidity is converted to actual fluidity, using a conversion scale.

This method can be used for blends of cellulosic fibres with polyester or nylon, provided the composition of the blend is known. In such cases the weight of fabric taken is that which contains 0.125 g cotton. After agitation the cellulosic fibres can be separated by centrifuging. Whilst not absolutely accurate, the technique is suitable for process control and certainly indicates any serious overbleaching situations. BS 2610 describes a modified method for linen.

Viscometric methods assume that the small samples taken for testing are representative of the fabric as a whole. This is usually so and it is reasonable, therefore, to use such methods to assess scouring and/or bleaching performance. Such methods are not suited to detecting localised hydrolytic or oxidative damage to cellulose (it is difficult to distinguish between the two).

Physical testing, for example tensile strength, bursting strength and abrasion resistance measurement, can be used but the results are influenced by both fabric structure and chemical damage. Tear strength is also influenced by residual, natural lubricants. Details of such tests are not given here but can be found along with many others in the British Standards Handbook No. 11 [95].

Staining tests are often useful in this area. Oxidised cellulose usually has a higher concentration of carboxy groups than the unbleached control. These resist staining with CI Direct Blue 1, or give enhanced uptake of CI Basic Blue 9 [97].

A most useful and simple test is the Harrison test for oxycellulose. The reagent is an alkaline silver nitrate solution that produces brown to black deposits of silver on the substrate where there are reducing groups (alcohols oxidised to aldehydes). Two solutions are prepared. One contains 80 g l^{-1} silver nitrate (A) and the other 200 g l^{-1} sodium hydroxide and 200 g l^{-1} sodium thiosulphate (B).

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For each gram of fabric to be tested, 2 ml of B is added to 20 ml distilled water, followed by 1 ml of A added slowly with stirring. The prepared test solution is then brought to the boil and the sample immersed. Boiling is continued, with stirring, for 5 min. Freshly cut edges can sometimes give a positive result and, when trying to distinguish mechanical (abrasion) damage from chemical damage, it is usual to slice the sample with scissors. The solution can be tested by preparing an oxidatively damaged control. This is done by spotting hypo on desized and scoured fabric and drying it in with a hot iron.

Spot tests are also useful for detecting pectins (Ruthenium Red test), lignin (Phloroglucinol test), NO_x (Salzmann's reagent), heavy metal contamination and size identification on grey fabric [97]. Iron, for example, can be detected with an acidified solution of potassium thiocyanate or ferrocyanide. The latter is preferred as it is less sensitive to atmospheric contamination and the blue colour produced is insoluble in water. Size often interferes with this test and so the substrate, if fabric, should be carefully desized before testing. Copper may be detected by spotting with sodium diethyldithiocarbamate solution, but many other ions interfere and the result must be assessed carefully. When testing for copper it is advisable to spot the suspect area first with dilute nitric acid, then neutralise with dilute ammonia before spotting with the reagent. Details of these and other spot tests have been published [97].

Size identification usually involves potassium iodide solution with or without the addition of boric acid. The scheme shown in Figure 2.14, one of many such, has been suggested by Fornelli [52].

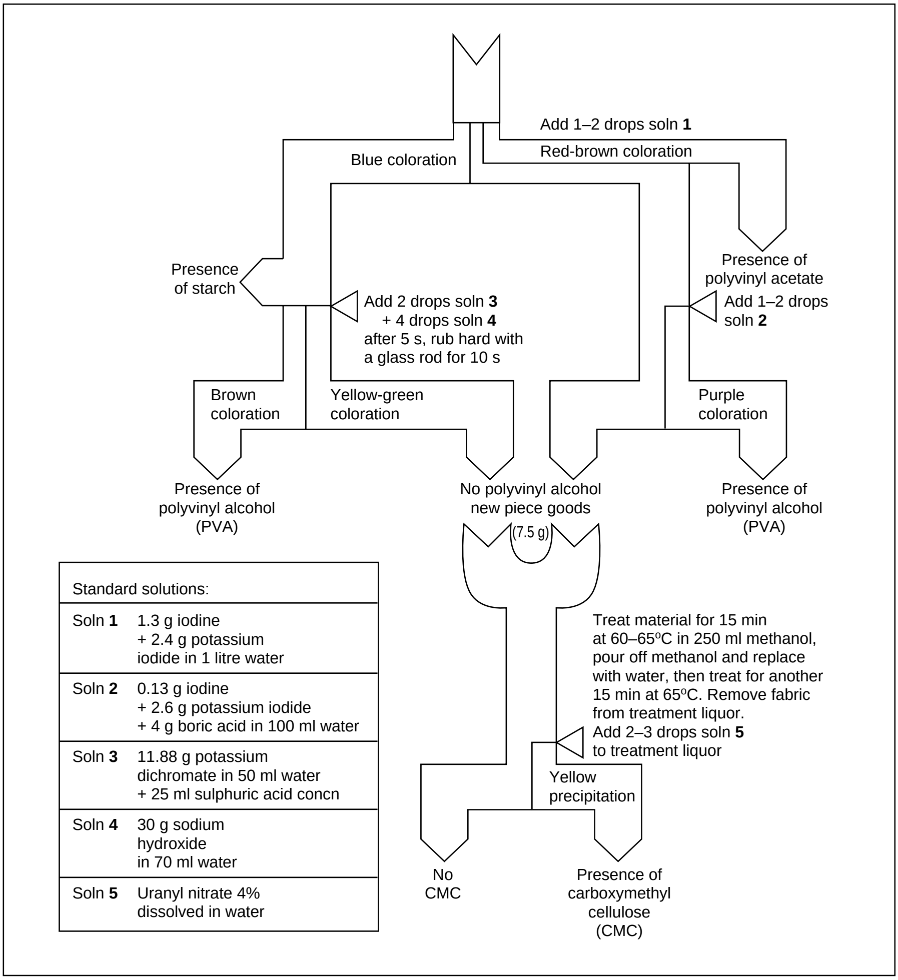
2.11.4 Analysis of residues [58]

Other materials, both inorganic and organic, may be present on the substrate before or after preparation. Their detection and estimation is usually carried out by ashing or extraction. Extraction methods may be used quantitatively on the untreated substrate but often they are not recommended on prepared goods as the experimental error (fibre loss, regain) is often of similar magnitude to the result. Furthermore, heat is always applied and there is always a danger that this will alter residues, or make them volatile.

Standards usually exist for the extraction methods established in each particular country.

Aqueous extracts

A tared sample is Soxhlet-extracted with demineralised water, preferably in an extraction thimble to prevent fibre loss, and reweighed after suitable drying and



Standard solutions:	
Soln **1**	1.3 g iodine + 2.4 g potassium iodide in 1 litre water
Soln **2**	0.13 g iodine + 2.6 g potassium iodide + 4 g boric acid in 100 ml water
Soln **3**	11.88 g potassium dichromate in 50 ml water + 25 ml sulphuric acid concn
Soln **4**	30 g sodium hydroxide in 70 ml water
Soln **5**	Uranyl nitrate 4% dissolved in water

Figure 2.14 Scheme for size identification. (*Source:* [52].)

conditioning. The extract is used for measuring fibre pH. In this case, the extraction flask is sealed with a suitable stopper before cooling and the result is only valid on a flask without ingress of air. Some residual water-soluble sizes may be removed, and detected with suitable reagents. The weight loss can be used as a direct measure of water-soluble material or as a measure of washing efficiency. Careful removal of the water (vacuum distillation, rotary evaporation) leaves a residue that can be examined by i.r. spectrometry. Nettles has provided a useful catalogue of the spectra for such materials but their interpretation is best left to a skilled, regular user of such techniques [5].

Solvent extracts

Fats and waxes are usually determined by solvent extraction of tared samples in a Soxhlet extractor. The solvents are usually chloroform for cotton and petroleum ether for polyester/cotton blends but occasionally dichloromethane is used. Careful evaporation of the solvent leaves a residue that can be examined with an infra-red spectrometer [5].

Ash content

Ashing provides a measure of the inorganic residues left by careful combustion of the substrate. The amount of residue can often give indication of the presence of silicate residues, calcium salts, etc. For more specific analysis, the ash must be examined spectroscopically. Emission spectroscopy was popular for element identification: particular elements would then be quantitatively determined using atomic absorption spectrometry (a.a.). In well-equipped analytical laboratories, the initial screening is done by X-ray fluorescence (x.r.f.) and the quantitative determination is then carried out with an induction-coupled plasma spectrometer (i.c.p.). This has lowered the detection limit from parts per million to parts per billion. X.r.f. can also be carried out on the substrate itself and small areas can be investigated with an ion probe, enabling localised concentrations of cations to be identified and quantified from their X-ray spectra. The technique is weak for elements lighter than sodium.

2.12 FINAL COMMENTS

The references in this review have been chosen to be freely accessible, where possible in English, via the British Library, for example. This is not always possible as the sources in German are very rich in this area and the textbooks by Rath [98], Peter and Rouette [99], and the annuals *Deutscher Färberkalender* [7,45,94] and *Internationales Lexicon* [100] must be mentioned. The last-named started out as a dictionary but has been updated with supplements as knowledge develops. Chapters 1B [98] and 7 [99] of the textbooks are particularly relevant. In quoting references from *Melliand Textilberichte* and *Textil Praxis* International E numbers and roman numerals indicate an English translation is available. *The American cotton handbook* [101] and Volumes 1 and 4 of the *Handbook of fibre science and technology* [51,85] are of interest, notably chapters A3, A4, B1 and B2 [51].

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CHAPTER 3

Dyeing with direct dyes

John Shore

3.1 INTRODUCTION

Direct dyes are defined as anionic dyes with substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte. Their most attractive feature is the essential simplicity of the dyeing process, but a separate aftertreatment to enhance wet fastness has been necessary for most direct dyeings since the end of the last century [1]. The two most significant non-textile outlets for direct dyes are the batchwise dyeing of leather and the continuous coloration of paper.

The standard of wet fastness, particularly to washing, of direct dyeings, even when given a conventional cationic aftertreatment, does not meet the more demanding end uses in cellulosic apparel and furnishing materials. Consequently, direct dyes have been replaced to a great extent by reactive dyes, which have better wet fastness and exceptional brightness in many hues.

Nevertheless, there are still many applications in the textile industry for goods dyed with direct dyes, particularly where a high standard of wet fastness is not required. Resin finishing after dyeing produces a notable improvement in wet fastness, especially on regenerated cellulosic fabrics. The development of specialised aftertreating agents and crosslinking reactants for use with selected direct dyes of high light fastness has reached new levels of sophistication, enabling direct dyes to compete more effectively with reactive dyes in meeting severe wet fastness requirements [2–4].

Direct dyes are used in low-priced viscose or blended curtain fabrics, furnishings and carpets, where good light fastness and moderate fastness to washing are usually adequate. Cheap cotton dressing gowns and bedspreads that may be washed infrequently, viscose ribbons and linings, flannelettes and winceyettes for baby-wear, as well as dischargeable ground shades for low-quality prints are often dyed with direct dyes. They may also be used in cellulosic or blended fabrics for casual wear and rainwear, provided that an appropriate durable press or water-repellent finish is given.

3.2 STRUCTURE AND PROPERTIES OF DIRECT DYES FOR CELLULOSE

More than 75% of all direct dyes are unmetallised azo structures and these are represented in every hue sector [5]. In contrast to all other application ranges, the great majority of them are disazo or polyazo types, the former predominating in the brighter yellow to blue sectors and the latter in the duller greens, brown, greys and blacks. The copper-complex direct dyes are mostly duller violets, navy blues and blacks derived from the disazo and polyazo subclasses, mainly used in maroon, brown, grey, navy and black recipes. Stilbene and thiazole dyes, the only non-azo chromogens in the yellow to red sector, bear certain similarities to the disazo and polyazo structures. The dioxazine and phthalocyanine chromogens are represented in bright blue direct dyes of high light fastness.

3.2.1 Chemical classification

Approximately 50% of all direct dyes are disazo structures, a typical example being the symmetrical dianisidine derivative CI Direct Blue 1 (Figure 3.1).

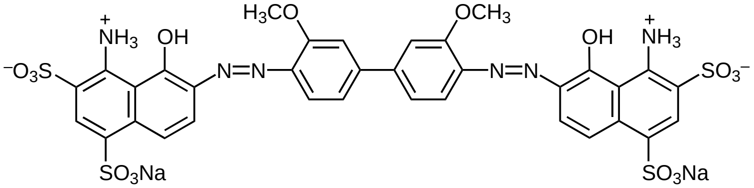

Figure 3.1

A major application for copper complexes is in the prior metallisation or aftertreatment of direct dyes containing at least one *o*,*o*′-dihydroxyazo or *o*-methoxy-*o*′-hydroxyazo chromophoric system. The best-known example is CI Direct Blue 76, a greenish blue copper complex (Figure 3.2) derived from CI Direct Blue 1 by metallisation with cuprammonium sulphate in the presence of an alkanolamine.

Triazine ring structures are used in the manufacture of certain azo dyes, particularly those containing two separate chromophoric systems. In the resulting product each chromogen contributes its own absorption characteristics; by combining yellow and blue chromogens, green dyes are formed that are much brighter than conventional polyazo dyes. A typical example is CI Direct Green 28 (Figure 3.3) in which cyanuric chloride is used to link a non-substantive anthraquinone derivative to a substantive phenylazosalicylic acid intermediate.

The characteristic chromophore of azophenylthiazole direct dyes is the thiazole ring itself, normally forming part of a 2-phenylbenzothiazole grouping. Most are yellow direct dyes such as CI Direct Yellow 59 (Figure 3.4), which contains two of the thiazole rings that enhance their substantivity for cellulose.

Stilbene direct dyes are mainly yellow, orange or brown. They are mixtures of indeterminate constitution resembling polyazo direct dyes in their application properties. They result from the alkaline self-condensation of 4-nitrotoluene-2-sulphonic acid or its initial condensation product. The characteristic chromophores are azo- or azoxy-stilbene groupings and these dyes are mostly non-dischargeable. Azostilbene dyes of more precise constitution are prepared by tetrazotisation and coupling of 4,4′-diamino-2,2′-stilbenedisulphonic acid, such as CI Direct Yellow 12 (Figure 3.5).

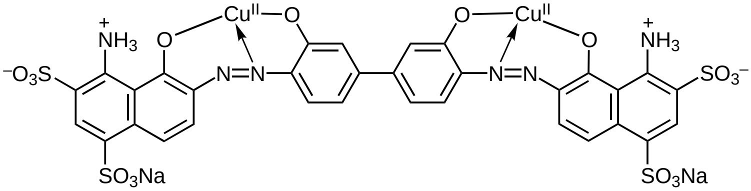

Figure 3.2

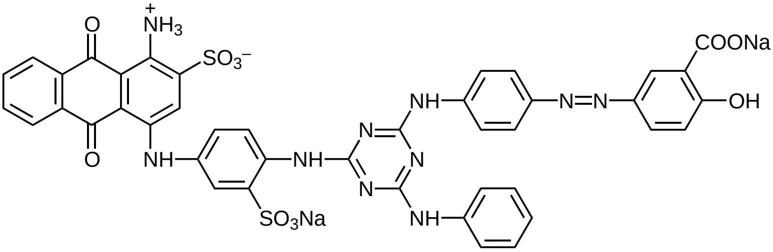

Figure 3.3

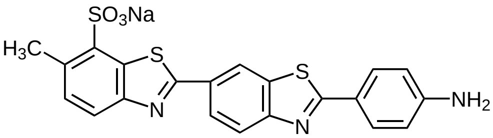

Figure 3.4

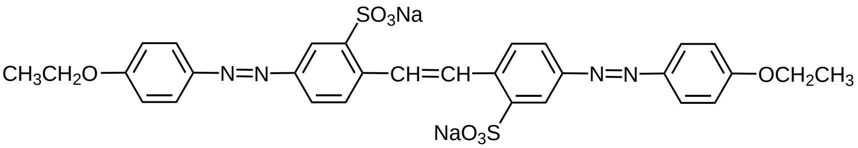

Figure 3.5

The triphenodioxazine ring system is the basis of some important blue direct dyes such as CI Direct Blue 106 (Figure 3.6). The tendency in recent years for the technically excellent but less cost-effective anthraquinone reactive dyes to be replaced by alternative bright blue derivatives of phthalocyanine, triphenodioxazine and formazan chromogens has a spin-off effect in yielding non-reactive precursors that are directly applicable as direct dyes.

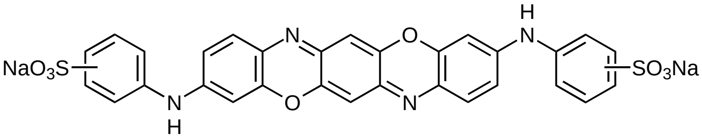

Figure 3.6

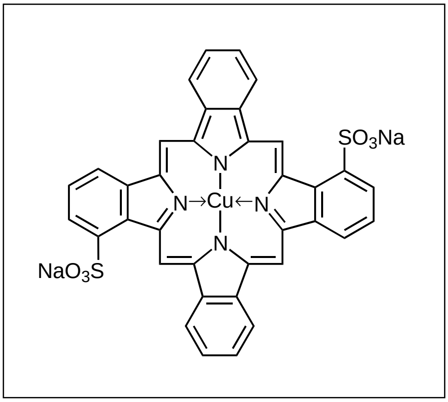

Figure 3.7

Phthalocyanine direct dyes are water-soluble sodium salts of sulphonated copper phthalocyanine, e.g. the disulphonate with sulpho groups in the 3-positions (Figure 3.7). They have poor absorption properties so that deep dyeings are virtually unobtainable. Dyeing has to be done at about 95°C in order to facilitate absorption and this precludes their application in low-temperature dyeing processes such as pad dyeing. Problems of poor reproducibility are encountered in exhaust dyeing. They give brilliant turquoise blue colours of high light fastness but poor wet fastness unless resin finished. They are applicable to paper where wet fastness is not as significant as on cotton and viscose.

3.2.2 Replacements for benzidine-derived dyes

Congo red (CI Direct Red 28), the first direct dye marketed, was produced from benzidine and naphthionic acid (Figure 3.8). It soon lost its importance for dyeing cotton because of its extreme sensitivity to acids, and was later used mainly as an acid indicator. Many direct dyes of former importance made from benzidine have been withdrawn from manufacture on account of the occurrence of carcinoma of the bladder in operatives, which is known to be caused by benzidine and certain derivatives. Epidemiological studies carried out in the early 1950s revealed this increased incidence of bladder cancer after exposure to benzidine, but it was not until the 1970s that the major dyemakers agreed to phase out the manufacture of benzidine-derived dyes. An analytical study of more than 40 direct dyes requiring the use of benzidine in their manufacture demonstrated that all contained 2 mg kg^{-1} benzidine or more as an impurity and three of them contained as much as 50–70 mg kg^{-1} [6].

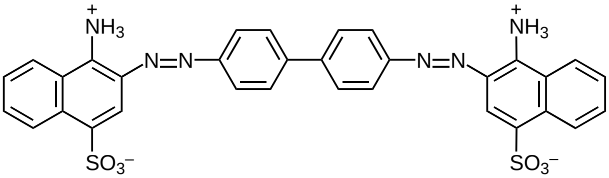

Figure 3.8

An intensive search was undertaken into alternatives produced from less hazardous intermediates [7], principally the following:

(1) The substitution of existing benzidine derivatives by analogous dyes in which benzidine is replaced by a structurally similar but less hazardous diamine such as *o*- or *m*-tolidine, or dianisidine; however, these diamines are also suspected of having carcinogenic activity and are controlled substances.

(2) The use of new diamines, including 4,4′-diaminobenzanilide, 4,4′-diaminodiphenylbenzaldehyde, 4,4′-diaminodiphenyl ether, 4,4′-diaminodiphenylsulphone and 1,5-diaminonaphthalenes.

Apart from the brighter symmetrical disazo direct dyes such as Congo red, many traditional brown or black polyazo dyes for application to cellulosic fibres and leather, such as CI Direct Black 38 (Figure 3.9), relied on the extremely versatile intermediate benzidine. The two diazonium groups can be coupled selectively in a stepwise manner to produce many useful products.

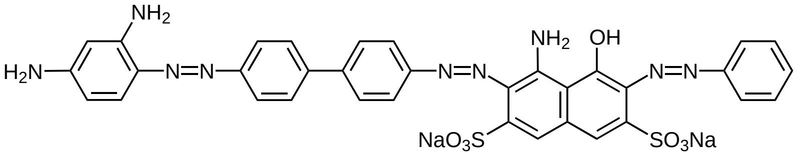

Figure 3.9

However, benzidine was found to be carcinogenic and its withdrawal by the major dyestuff manufacturers has led to the discontinuance of dyes such as Black 38 in favour of products such as CI Direct Black 166 (Figure 3.10) in which 4,4′-diaminobenzanilide is used as a replacement.

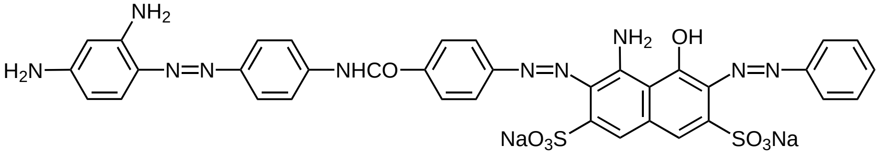

Figure 3.10

Another novel intermediate synthesised for this purpose is 7-amino-3-(4′-aminophenyl)quinoline that has been used to prepare various disazo and trisazo derivatives. The differential reactivity of this tetrazonium salt is helpful in this regard, the diazonium cation on the phenyl ring being the more reactive, but unfortunately the novel dyes are deficient in tinctorial power and light fastness [8].

A more general objective has been to identify and utilise precursor intermediates that have been shown to be non-genotoxic. Increasing use is being made of the published results of the mutagenicity and carcinogenicity testing of azo dyes and their intermediates in this field. It is clearly helpful in the design of non-carcinogenic azo dyes to ensure that the intermediates are non-mutagenic and to take into account the potential genotoxicity of the metabolites resulting from the reductive cleavage of the azo linkages. Following this approach, the replacement of benzidine by 5,5′-diamino-2,2′-bipyridine in four well-known carcinogenic azo structures was examined. It was shown that this novel component was much less genotoxic than benzidine itself and the derived dyes were also less genotoxic than their older analogues made from benzidine [9].

The effect on mutagenicity caused by incorporating an alkoxy substituent into the structure of a water-soluble disazo dye was investigated. The results indicated that, although bulky alkoxy groups were useful in lowering the mutagenicity of certain analogues of CI Direct Black 17, the decrease observed was less than that noted for a series of monoazo disperse dyes [10].

3.2.3 Reactant-fixable direct dyes

One of the most significant breakthroughs in the field of direct dyes in recent years has been the introduction by Sandoz of Indosol SF dyes and a series of Indosol fixing agents for use with them [2–4,11–15]. The original range of Indosol SF dyes comprised twelve members, all copper complexes selected from the existing Solar range for good light fastness when aftertreated with the preferred agents. Few of these dye structures have been disclosed but CI Direct Violet 66 (Figure 3.11), marketed as Indosol Violet SF-B, gives an indication of the molecular characteristics represented.

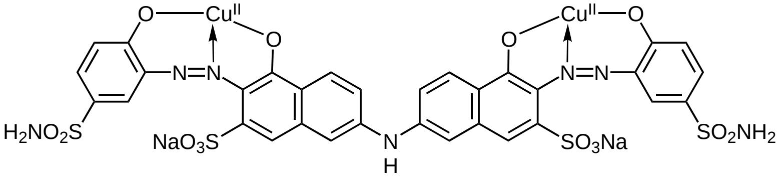

Figure 3.11

The original range of Indosol SF dyes was strong in the blue and grey sectors but somewhat deficient in the yellow to violet series. Novel reactive yellow and red dyes were later introduced to supplement the range, slightly blurring the distinction between the reactive and reactant-fixable classes. The specific aftertreating agents used with Indosol SF dyes and their methods of application to cellulosic fibres and blends are discussed later (section 3.7.7).

3.2.4 Photochromism of direct dyeings

Certain direct dyes, principally sulphonated copper phthalocyanines, exhibit a photochromic change on cellulosic fibres, the hue changing from bright turquoise to violet or reddish blue on prolonged exposure to sunlight or u.v. radiation. The hue reverts gradually to the original turquoise when the illuminant is withdrawn. This effect is accentuated by the presence of dye-fixing agents or crease-resist finishes, particularly if the dyed material is stored in an acidic condition. The type of crease-resist finish plays a significant part, the order of decreasing effect being: urea–formaldehyde > cyclic alkyleneurea reactants > melamine–formaldehyde.

The degree of photochromic change is related to the intensity of the u.v. radiation and the ambient humidity. The drier the atmosphere, the slower the reversion to the original turquoise in the absence of the illuminant. Thus products that lower the moisture regain, e.g. crease-resist finishes, greatly increase the tendency to show photochromic change.

The photochromic behaviour of copper phthalocyanine direct dyes appears to follow a redox mechanism. When dyeings of this type on cellulosic fibres are subjected to a vatting procedure with sodium hydroxide and sodium dithionite at 60°C, the hue changes rapidly from turquoise blue to violet. The dyeing reverts to its original hue on rinsing in water followed by air oxidation, thus producing similar changes to those taking place on illumination. It is interesting to note that the unsulphonated copper phthalocyanine pigments do not exhibit this redox behaviour.

3.2.5 Aggregation of direct dyes in solution

Dyes often exist in aqueous solution as aggregates of several ions or molecules rather than as individual molecules. It is not necessary to assume that all component molecules in a dye aggregate are in the same state of ionisation. Dye aggregates should be envisaged as relatively amorphous in composition with zones of more or less polar character distributed within them, although there will still be a tendency for the individual molecules to become oriented with their ionised groupings towards the aqueous phase.

Aggregation is promoted by a high ratio of relative molecular mass to ionic group content, that is, by a high value for the equivalent mass per sulphonic acid substituent in the case of sulphonated anionic dyes. Multisulphonated dye anions may be stabilised as dimers in which the two components adopt a planar arrangement with the sulpho groups located if possible at opposite ends of the dimer. Dimers are formed before larger aggregates, growing further by accretion of more dye anions to form lamellar micelles in which the dye units are stacked like cards in a pack [16]. Planar chromophores, especially the sulphonated phthalocyanines, are particularly prone to such stacking.

Most measurements of aggregation number (the average number of molecules/ions per aggregate) have been carried out on solutions of direct dyes, since these dyes aggregate more readily than most of the other classes of water-soluble dyes. Regrettably, aggregation numbers determined for the same dye under the same conditions using different methods of measurement are seldom consistent. Most investigators agree, however, that such solutions contain a mixture of aggregates of various sizes in dynamic equilibrium. Individual ions, dimers or trimers are removed by adsorption onto the fibre surface during dyeing and larger aggregates break down to maintain a similar overall distribution of aggregate sizes. The extent of aggregation of a direct dye decreases with increasing temperature and increases with increasing concentration of added electrolyte or of the dye itself. Although many direct dyes are highly aggregated at room temperature, the degree of aggregation is often negligible under normal dyeing conditions at the boil even in the presence of an electrolyte [17].

Although quantitative agreement between the aggregation numbers obtained using different techniques of measurement is poor, meaningful conclusions can be drawn from them regarding the relative tendencies to aggregate of different dye structures. Under given conditions of temperature and electrolyte concentration, CI Direct Orange 26 (Figure 3.12) is much more highly aggregated than CI Direct Yellow 12 (Figure 3.5). Both are disulphonated disazo dyes, but presumably the two phenolic groups and especially the urea residue in the former dye provide much greater scope for intermolecular hydrogen bonding than the etherified phenolic groups in the latter.

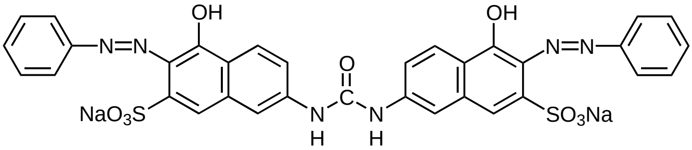

Figure 3.12

CI Direct Red 28 (Figure 3.8) is highly aggregated, no doubt because of electrostatic intermolecular attraction between matching pairs of protonated primary amino groups and sulphonate anions of the naphthionic acid residues. CI Direct Blue 1 (Figure 3.1) is considerably less aggregated because the charges on the protonated amino groups are satisfied by intramolecular association with their neighbouring sulphonate groups, and the dye anion thus has a net negative charge of two.

3.2.6 Decomposition of direct dyes during dyeing

If a direct dyeing is unduly prolonged, either to improve the levelness or to attain an exact colour match to standard, decomposition of a minor proportion of the dye present may occur. The rate of decomposition is normally much more rapid in the dyebath phase then on the fibre and the onset of degradation can sometimes be observed as a change in colour of the exhaust liquor. Many direct dyes show instability of this nature if applied at temperatures above the boil. A frequent cause of the problem is reduction of the azo linkages; the decomposition may be accelerated in the presence of viscose, which has a reducing action under alkaline dyeing conditions [18]. Buffering to pH 6 with ammonium sulphate confers a stabilising influence when dyes of lower stability have to be used on viscose. Mild oxidants such as sodium *m*-nitrobenzenesulphonate are occasionally useful, and more powerful inorganic oxidants, such as potassium chlorate or dichromate, can be most effective if used with care. An alternative approach is to use sodium perborate but it is necessary to exclude copper, which would cause catalytic degradation of cellulose, and the dyes used must be unaffected by sodium perborate.

Direct dyes with exposed azo groups free from electron-withdrawing *o*-substituents are particularly prone to reductive decomposition, CI Direct Yellow 12 (Figure 3.5) being a typical example. Some dyes with protonated *o*-aminoazo groups, such as CI Direct Red 28 (Figure 3.8), are also reduction-sensitive [19]. In the relatively unstable trisazo structure of CI Direct Green 33 (Figure 3.13), the most vulnerable of the three azo groups is the unprotected central linkage.

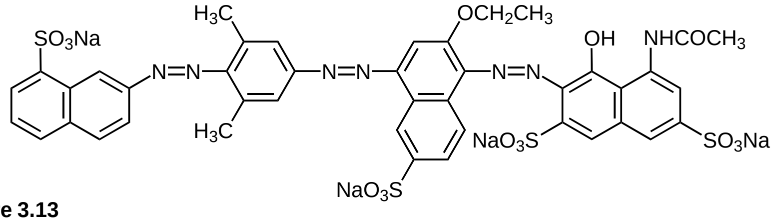

Figure 3.13

Dyes containing azo groups protected from electrophilic attack by *o*,*o*′-substituents, especially *o*-sulphonate groups, are generally relatively resistant to reductive breakdown during dyeing. Azothiazole dyes such as CI Direct Yellow 59 (Figure 3.4) and especially copper-complex structures such as CI Direct Violet 66 (Figure 3.11), in which both azo groups are fully protected as the metal complex, show excellent stability in high-temperature conditions [20]. Direct dyes of the diphenylurea type, such as CI Direct Orange 26 (Figure 3.12), are particularly prone to decomposition in high-temperature dyeing because molecular breakdown can occur by hydrolysis [21] as well as by the reductive mechanism under alkaline conditions. Thus the ureido linkage may be broken by hydrolysis to give monoazo dye fragments, or the azo groups can be reduced and naphthylamine breakdown products formed.

3.2.7 Dischargeability of direct dyeings

As already noted, more than 75% of all direct dyes are unmetallised azo structures and without aftertreatment may show good dischargeability. They are suitable for dyeing fabrics that are to be printed with a white or coloured discharge; the lack of wet fastness is a disadvantage for many end uses but this can be overcome by subjecting the discharge print to a resin-finishing process.

Diazotised and developed direct dyeings (section 3.7.1) generally exhibit very good dischargeability, providing excess developer is removed. With fabrics intended for discharge printing, residual sodium nitrite and acid must be removed after diazotisation, or undesirable by-products may be formed during coupling. During discharge printing the reducing agent (sodium formaldehyde-sulphoxylate) reduces the azo groups in the correctly developed dyes but not in the by-products, resulting in an unsatisfactory discharge.

Premetallised direct dyeings and those aftertreated with copper salts are generally less readily dischargeable than those dyeings that do not contain copper. This is a limiting factor in their use as dyed grounds for discharge printing. The maximum discharge effect is obtained by dyeing, discharging and then after-coppering, but difficulties due to inadequate wet fastness arise when washing-off the uncoppered discharge print. Printers generally prefer to after-copper the dyeing before discharge printing.

Non-azo direct dyes, including stilbene derivatives, sulphonated copper phthalocyanines and triphenodioxazine dyes, are not suitable as grounds for discharge printing.

3.3 DYE STRUCTURE AND DYEABILITY OF CELLULOSIC FIBRES

The degree of sulphonation is decisive for the dissolution of direct dyes in water and the tendency of such dyes to form aggregates (section 3.2.5). In general, the lower the equivalent mass (i.e. the ratio of relative molecular mass to ionic group content), the higher will be the aqueous solubility of the dye. Exceptions from this simple rule can arise, however, if a direct dye structure contains protonated amino groups (as in Figures 3.1 or 3.8, for example). As already noted, the converse of this general trend is that dye molecules of higher equivalent mass tend to aggregate more readily because of the greater opportunity for hydrophobic interaction. Such dyes in the presence of a cellulosic substrate will tend to escape more readily from the aqueous dyebath by adsorption onto the fibre surface. It is reasonable to assume that the dye molecules will become adsorbed as far as possible in such a way that the hydrophilic sulphonate ionic groups are directed outwards towards the aqueous phase.

3.3.1 Dye structure and substantivity for cellulose

Just as addition of electrolyte to a solution of direct dye tends to lower the electrostatic repulsion between the negatively charged dye anions and promote aggregation, the effect of the presence of an inorganic salt when dyeing cellulose is to overcome the long-range forces of repulsion between the dye anions and the negatively charged fibre surface. The closer approach then allows hydrogen bonding and other short-range attractive forces to operate between the dye molecules and the glucoside units of the fibrous polymer.

Hydrogen bonding between the hydroxy groups of cellulose and centres of electronegativity (nitrogen, oxygen and sulphur atoms) in the dye molecule, especially those substituted with hydrogen atoms (as in =N–NH–, $-NH_2$, –CONH–, –OH and –SH), is widely acknowledged to contribute to adsorption and retention of the dye molecules. Stereochemical studies have demonstrated that hydrogen bonding is possible for almost any cellulosic hydroxy group in the amorphous regions of the fibre. The more hydrogen bonds that a dye can form with the glucosidic polymer, the more readily it can compete with and rupture the fibre–fibre hydrogen bonds in order to penetrate more deeply into the amorphous structure of the polymer.

Many direct dyes with high affinity for cellulose are disazo or trisazo structures in which the azo groups are located in *para* positions relative to one another, so that the longest conjugated chain through the azo-linked aryl nuclei tends to be as near linear as practicable. This is facilitated in dyes derived from intermediates contributing a 1,4-phenylene or -naphthylene (Figure 3.13), 4,4′-biphenylene (Figure 3.1 or 3.8) or 2,6-naphthylene (Figure 3.12) residue. A methine group oriented *para* to an azo group through an intervening aryl nucleus (Figure 3.5) boosts substantivity even more than does an amide group in a similar position [22].

The significance of conjugation as a contributor to the substantivity of dyes for cellulose is not always easy to distinguish from the effect of the degree of linearity of the molecule. The molecules of almost all direct dyes possess flexible chains of aryl nuclei linked by azo or other groups. Such structures can readily adopt a near-linear spatial conformation, as far as the angular constraints of the participating bonds will allow. Hence azo groups attached to central naphthylene residues are frequently oriented in 1,4- or 2,6-positions relative to one another and typical central diamines give linear dyes on tetrazotisation.

The ability to adopt an extended configuration has long been recognised [23] to be a desirable feature of substantive dyes. A further refinement of the concept that linear conjugated aryl–azo–aryl–azo–aryl sequences and analogous systems represented the preferred design for highly substantive molecules was the stipulation that the aryl nuclei must be able to adopt a coplanar conformation [24]. This favours the adsorption of one dye molecule on to another during the formation of laminar aggregates, as well as the multi-point adsorption of a dye molecule on to two or more glucoside units of a polymer segment via hydrogen bonding.

3.3.2 Ability of direct dyes to cover neps in cotton fabrics

Pale flecks in dyed cotton fabrics can be caused by immature or dead cotton. Clumps or neps of immature fibres tend to exhibit poor dyeability and the flattening of such neps may form small, highly reflective flecks. Poor dye penetration may leave undyed areas if the neps of loosely attached immature fibres change position after dyeing. The dyeability of immature cotton can be improved by mercerisation but the lack of secondary cell wall development in dead cotton makes such treatment ineffective [25].

Direct dyes vary considerably in their ability to cover dead or immature cotton, but by careful selection a sufficient range can be found suitable for this purpose. Cotton fabrics containing both immature fibre neps and process neps composed of damaged mature fibres were given various mercerising treatments. After dyeing with ten direct dyes, fully mercerised fabrics showed a 95% increase in visible coverage of neps, but causticised fabrics only an 85% increase in coverage. After liquid ammonia treatment, significant improvement in nep coverage occurred with only five of the ten dyes [26].

The differences between direct dyes in their behaviour towards nep coverage are most evident with those neps composed of immature fibres with some secondary wall development [27]. Direct dyes containing more than one amino or amide group in their structure were found most likely to achieve relatively good coverage of neps [28]. Although good coverage bears no obvious relationship to molecular size or shape, aggregation and migration properties of direct dyes do appear to be related to nep coverage [27].

3.3.3 Effect of mercerisation and liquid ammonia treatment on direct dyeing

Comprehensive reviews of caustic soda mercerisation and its effect on direct dye uptake are available [29,30] and several studies of possible mechanisms have been published. Scoured-only or scoured and bleached cotton yarns were slack mercerised, restretched and then dyed with a disazo direct blue at 70°C. The exhaustion and rate of dyeing of the mercerised yarns were appreciably higher than those of the scoured yarns but these differences decreased as the degree of restretching was increased. A hypochlorite bleach after scouring also decreased the difference in dye uptake between scoured and mercerised yarns [31].

The relationship between fibre porosity and direct dye uptake was examined by preswelling with caustic soda or zinc chloride, followed by measurement of pore size distribution and porosity. Average dye savings of 30% were demonstrated by treatment of cotton fabrics with 20% sodium hydroxide solution for 1 min at 20°C, washing, neutralisation and dyeing with three typical direct dyes. The improved colour yield was attributed partly to increased dye uptake and partly to the optical effect of fibre swelling and internal light scattering influenced by the change in total pore volume [32].

Dyeings of CI Direct Red 81 (Figure 3.14) and Blue 1 (Figure 3.1) on bleached cotton fabrics that had been mercerised in various ways also provided evidence that the dye saving is related to the reduction in diffuse light scattering and depends on the method of pretreatment given. The reduced light scattering occurs at the interface between the fibre secondary wall and the cell lumen [33].

Scoured and mercerised samples of cotton were compared with viscose staple and grey cotton for steam sorption and water retention to characterise their physical structure. Sorption measurements with sugars and dextrans of graduated sizes were used to determine changes in pore structure caused by mercerising. By correlating the pore structure with the uptake of CI Direct Blue 1 (Figure 3.1), it was deduced that transition pores in the cellulosic fibres with a diameter of about 20–60 nm are responsible for dye sorption [34]. Characteristics of the pore structure of cotton and viscose in the water-swollen state enables new volume terms to be determined for calculation of thermodynamic substantivity [35]. Substantivity parameters for CI Direct Blue 1

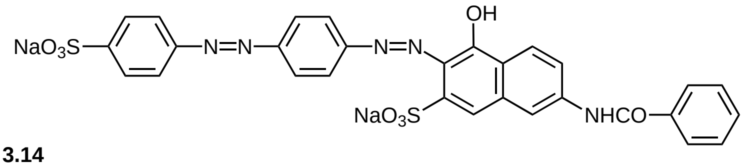

Figure 3.14

on cotton under various application conditions after hot mercerising at 60 and 90°C have been given [36].

Warm mercerisation of grey cotton fabrics at temperatures below 50°C resulted in little difference in adsorption of a symmetrical disazo direct blue, although treatment above 50°C did produce a measurable increase [37]. Grey or bleached cotton and cotton/polynosic knitted fabrics showed decreased uptake of direct dyes with increase in mercerising temperature up to 80°C, but higher fabric tension tended to enhance dye uptake. Shade variations between the centre and selvedges of dyed knitgoods may be attributable to differences in tension during mercerisation [38].

Liquid ammonia pretreatment is a highly effective and well-controlled alternative to caustic soda mercerisation, but the high capital cost of the necessary equipment for recovery and reuse of the ammonia as well as the application step limits the adoption of this sophisticated approach more widely. Bleached cotton fabrics treated by these two processes were examined for changes in morphology by X-ray analysis, fibre cross-section and measurements of the sorption of iodine, steam and CI Direct Blue 1 (Figure 3.1). Marked differences between the two treatments were found and liquid ammonia swelling does not always result in a stable fibre structure [39]. High-quality cotton shirting subjected to liquid ammonia treatment followed by durable-press finishing showed good easy-care properties with only modest strength loss. Changes in dyeing behaviour and morphology during this sequence were investigated [40] using the direct dyes of markedly different molecular sizes that are recommended for the red–green test to indicate immaturity in raw cotton: CI Direct Red 81 (Figure 3.14) and Green 26 (Figure 3.15).

In a further study by the same group of workers, treatment with liquid ammonia followed by caustic soda was compared to treatment with ammonia alone [41]. The changes in fibre structure were examined by X-ray analysis for crystalline fraction and type of lattice, as well as sorption measurements using the disazo dye CI Direct Blue 1.

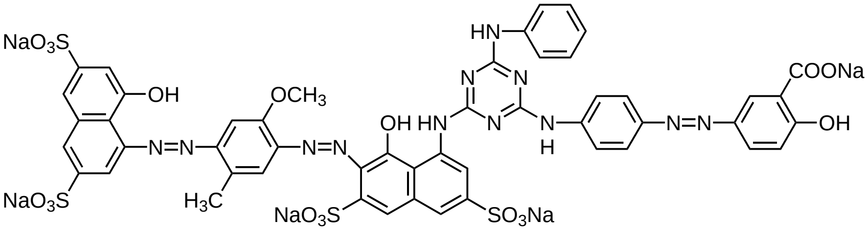

Figure 3.15

3.3.4 Diagnostic dyeing tests to assess effects of preparation

Many latent faults in textile materials only become visible during the dyeing process. The sensitivity of dyes to inherent variations in properties of untreated or processed textiles can be applied in the development of diagnostic dyeing or staining tests to define the nature and extent of such differences [42]. One of the long-established stain tests is based on the violet colour obtained by spotting iodine onto cotton containing residual starch size. Durable violet scales produced with direct and vat dyes or printed pigments can be used to quantify the degree of staining produced by the iodine, which fades rather quickly on storage [43].

Several possible dyeing tests are available to assess the maturity of cotton samples and their response to alkaline pre-treatments. The red–green test at the boil using a mixture of direct dyes of different molecular sizes, disazo CI Direct Red 81 (Figure 3.14) and the tetrasulphonated CI Direct Green 26 (Figure 3.15), has been mentioned already. Another sensitive test of this kind is based on a mixture of the monosulphonated CI Acid Red 151 (Figure 3.16) and the tetrasulphonated CI Direct Blue 10 (Figure 3.17). Untreated cotton is stained red but an increase in concentration of alkali in the causticising or mercerising process results in progressively bluer staining [44].

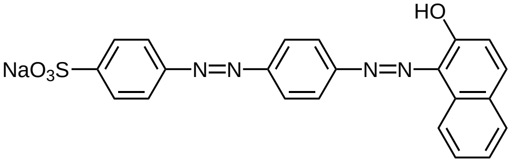

Figure 3.16

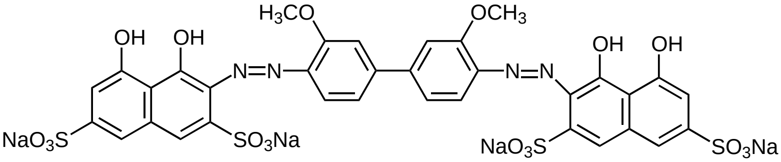

Figure 3.17

3.3.5 Dyeing properties of viscose and bast fibres

When different cellulosic fibres are dyed from dyebaths containing the same amount of a direct dye, the depth attained on each fibre may differ considerably. The visual differences observed are due partly to the effect of the rate of dyeing, since practical dyeing is seldom carried to equilibrium, and partly to an optical effect arising from different fibre thicknesses. The apparent depth of dyeings produced with the same percentage of dye on filament viscose varies with the linear density of the filament. This is an optical effect, finer filaments appearing lighter in depth due to the greater degree of surface reflection. In order to achieve equal apparent depth on viscose filaments differing only in their linear density, the dye concentration must be inversely proportional to the square root of the linear density.

In addition to these effects, however, there remains a substantial difference between the amounts of dye absorbed by the various cellulosic fibres at equilibrium. Since the basic chemical structure is the same for all cellulosic fibres, the energetics of dyeing equilibrium should also be the same. The differences that do exist between the fibre types are in the total micellar surface available for dye adsorption and in the electrical charge on the fibres. In the manufacture of viscose, dissolution of the natural cellulose produces intense swelling and leads to a much greater micellar surface in the finished viscose than in the original cellulose. At the same time oxidative degradation occurs, leading to an increased number of carboxy groups in the viscose.

Developments in evaluation of the effects of conventional mercerisation and liquid ammonia treatments on the dyeability of cotton with direct dyes have been paralleled by corresponding studies of the implications of these treatments for other cellulosic fibres. High wet modulus and polynosic modal fibres in 50:50 blends with cotton have been compared for their response to alkaline bleaching, causticisation and mercerisation processes, in terms of the effects on physical properties and dye uptake [45].

Liquid ammonia swelling can be used to enhance the uptake of direct dyes by viscose, either by dyeing from liquid ammonia as the application medium [46–48] or by pretreatment before conventional aqueous dyeing [49]. The increase in internal surface of viscose film when dyeing from liquid ammonia permits the deposition of dye aggregates of smaller average size than in the case of aqueous dyeing. Liquid ammonia pretreatment of high wet modulus and conventional viscose fibres followed by a water quench produces higher colour yield and uptake of dye than ammonia treatment followed by evaporation in air, although the latter gives better levelling at the dyeing stage.

Linen fabrics and blends of cotton with linen and with ramie were scoured, bleached, dyed with direct dyes and resin-finished. Liquid ammonia treatment was given in most cases, in order to determine at which stage this swelling process was most effective. The dyeability and finish performance were invariably enhanced by liquid ammonia pretreatment but the stage that showed optimum improvement was dependent on the fabric type and the improvement sought [50]. The effects of caustic soda mercerisation, either slack or with tension, on the direct dye uptake and colour yield of ramie, linen and cotton yarns were investigated. Treated and untreated ramie exhibited lower dyebath exhaustion than cotton or linen, but for a given dye content the visual depth of the dyeing on ramie was greater [51].

3.3.6 Cationic pretreatment of cellulosic textiles to enhance dyeability

During the 1980s there was a notable revival of interest in techniques for deliberately enhancing the dyeability of cellulose with reactive or direct dyes by pretreatment with a greater variety of cationic products, usually based on nitrogen. Three main approaches were adopted:

(1) Vinyl grafting.
(2) Reaction with cationic reactant molecules.
(3) Application of cationic polymers.

To date, however, none of these treatments has achieved significant commercial success.

Grafting reactions with cellulose by free-radical polymerisation of olefinic monomers have been explored for many years but the development of modified cotton fibres with enhanced dyeability via this route has attracted particular interest recently [52–55]. Thus a redox system consisting of iron(II) ions, thiourea dioxide and hydrogen peroxide was selected for the emulsion polymerisation of combined glycidyl methacrylate/cotton cellulose in the presence of direct dyes containing labile hydrogen atoms. The treated fabric showed appreciable colour depth with fastness comparable to cotton dyed with reactive dyes, together with a considerably improved dimensional stability [52].

Diethylaminoethylated cotton can be prepared by reacting cotton with the tertiary amine 2-chloroethyldiethylamine in the presence of alkali at 95°C. The uptake of direct or reactive dyes by the modified substrate was much higher than on untreated or alkali-treated controls. The diethylaminoethyl substituents acted as a built-in catalyst, capable of initiating fixation of the reactive dye even in the absence of alkali [53]. A more effective approach to the aminisation of cotton fabric involved padding with caustic soda solution, followed by immersion in an acetone solution of epichlorohydrin and triethanolamine. The etherifying agent for cellulose hydroxy groups was assumed to be the reactive tertiary amine formed by the initial condensation between the starting materials [54].

Many of the attempts to fix quaternary nitrogen compounds to cellulose via ether linkages have depended on the use of epoxy derivatives as well as mono- or bis-reactive agents of the haloheterocyclic type [56,57]. The first product of this type on the market was Glytac A (Protex) (Figure 3.18), which reacted with cellulose via the glycidyl group at alkaline pH [58,59]. Cellulose modified in this way can be dyed with acid dyes and shows enhanced uptake of direct or reactive dyes, although some of the early claims of improved wet fastness were later shown to be exaggerated [60,61].

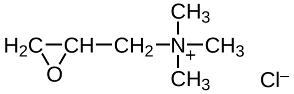

Figure 3.18

More recent developments have been concerned with application of the epichlorohydrin precursor of Glytac A and the evaluation of analogues with larger substituent groups on the quaternary nitrogen, in order to minimise the unpleasant odour of tertiary amine released during application.

Later research covered quaternary agents of the haloheterocyclic type, including mono-reactive mono- or bis-quaternary compounds and exploiting either monochlorotriazine or difluoropyrimidine as the reactive group. Such agents react more readily with cellulose and show better thermal stability than the epoxypropyl types. Both classes of monofunctional reactive system, however, share the disadvantages of relatively low substantivity for cellulose; they must be applied by a padding process. More complex multifunctional structures were evaluated by exhaust application and these gave effective enhancement of dye uptake, although there are practical drawbacks to all of these treatments, including hue changes, poor penetration into the fibre [62] and light fastness limitations [63].

Alternatives to the use of quaternary nitrogen compounds in this context have included the application of ethylenediaminetetramethylphosphonic acid to cotton prior to dyeing with a disazo direct dye [64], as well as the reaction of selected arylsulphonium salts with mercerised cotton, in order to confer improved substantivity for direct or reactive dyes [65].

Many cationic polymers have been applied to cellulose with a view to enhancing uptake of direct or reactive dyes and it is considerably more difficult in these instances to interpret the precise mechanism of the interactions involved, apart from the obvious participation of electrostatic forces between the dye anions and the basic groups (often quaternary nitrogen atoms) in the polymer. Quaternary ammonium-substituted polymers can be derived from the reaction of epichlorohydrins with carbamides or aminoalkylimidazoles, from polymethylol-biguanides or quaternised polyurethanes, from the condensation of polyalkylenepolyamines with cyanamides or guanidines, or from polyamines such as polyethyleneimine with epichlorohydrin.

The application of the polyamide–epichlorohydrin resin Hercosett 125 (Hercules), originally marketed as a shrink-resist treatment for wool, has recently been applied to cotton, mainly with a view to producing a modified fibre suitable for the absorption and fixation of reactive dyes at neutral pH in the absence of salt [66]. Incorporation of thiourea or ethylenediamine into the Hercosett polymer during the application process has beneficial effects on the results obtained. Thiourea addition gives rise to the formation of isothiouronium groups and inhibits crosslinking of the resin, leaving more nucleophilic NH groups as sites for dye reaction [67]. Ethylenediamine promotes crosslinking of the resin but itself provides extra NH groups as dye-reactive sites [68]. These approaches could be equally useful to enhance the uptake of direct dyes.

3.4 APPLICATION PROPERTIES OF DIRECT DYES

Direct dyes are usually applied with the addition of electrolyte at or near the boil. Less frequently, dyeing may be carried out at temperatures above the boil, as in package dyeing of blended yarns. An addition of alkali, usually sodium carbonate, may be made with acid-sensitive direct dyes and with hard water.

When cellulose is immersed in a solution of a direct dye it absorbs dye from the solution until equilibrium is attained, and at this stage most of the dye is taken up by the fibre. The rate of absorption and equilibrium exhaustion vary from dye to dye. The substantivity of the dye for cellulose is the proportion of the dye absorbed by the fibre compared with that remaining in the dyebath.

3.4.1 Absorption of direct dyes by cellulose

The structural features of direct dyes that confer high substantivity for cellulose have been discussed already (section 3.3.1). Measurements of the absorption spectra of azo direct dyes on cellulose film have shown that dyes enter the cellulose as single molecules and then aggregate inside the cellulose. One method of analysing the absorption of direct dyes by cellulose is to use the diffuse absorption model [69]. This method can account adequately for the absorption of mixtures of direct dyes by cellulose, provided that no interaction occurs between the dyes in either phase and that allowance is made for ionised carboxy groups in the cellulose [70].

3.4.2 Dyeing kinetics and dye structure

The rates of uptake of direct dyes by cellulose vary extremely widely [5]. The time of half-dyeing (the time to reach an exhaustion level half of that attained at equilibrium) on viscose for the disazo J acid derivative CI Direct Red 23 (Figure 3.19) is approximately 400 times that for the rapidly diffusing stilbene dye CI Direct Yellow 12 (Figure 3.5). A decisive factor in determining the rates of dyeing of many direct dyes from aqueous salt solutions is their tendency to aggregate (section 3.2.5), since this greatly retards their mobility into the water-swollen voids of the substrate.

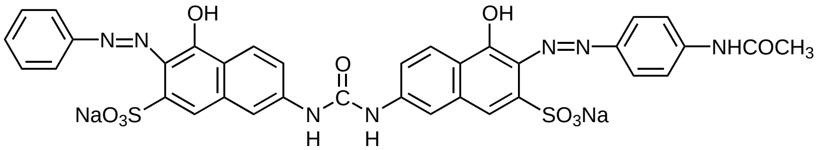

Figure 3.19

3.4.3 Classification according to dyeing properties

The variations in behaviour between individual direct dyes necessitate care in selection for mixture recipes, in order to achieve optimum results and to prevent the occurrence of faults, such as uneven or insufficiently penetrated dyeings on all types of materials and listing or ending with jig-dyed fabrics. Considerable work was carried out by Courtaulds in the 1940s [71,72] and later by ICI [73] and an SDC committee [74] to characterise the dyeing behaviour of individual direct dyes and thereby enable the best selection to be made for a particular dyeing method, highlighting the parameters to be observed in controlling the dyeing cycle. The time of half-dyeing is an indication of the rate at which a direct dye is absorbed by the fibre. Dyes exhibiting a similar time of half-dyeing were thus regarded as the preferred choice in mixtures. It was found later, however, that rate of dyeing alone is insufficient to predict compatibility and that rate of migration and salt controllability are of greater importance [73].

From this work it was concluded that determination of four parameters was necessary, i.e. migration (or levelling power), salt controllability and the influence of temperature and of liquor ratio on exhaustion. Direct dyes were classified accordingly as follows:

(1) Class A – dyes that are self-levelling, i.e. dyes of good migration or levelling properties.
(2) Class B – dyes that are not self-levelling, but which can be controlled by addition of salt to give level results; they are described as salt-controllable.
(3) Class C – dyes that are not self-levelling and which are highly sensitive to salt, the exhaustion of these dyes cannot adequately be controlled by addition of salt alone and they require additional control by temperature; they are described as temperature-controllable.

Widespread use was made of the SDC classification in batchwise dyeing but it proved of much less value in the selection of compatible dyes for padding and jig dyeing processes. This can be done, however, by carrying out simple dip or strike tests in which fabric or yarn samples are dyed for a few minutes, removed from the dyebaths, replaced by fresh samples and the procedure repeated several times; the specimens are mounted in series and assessed visually for change of hue and depth.

3.4.4 Dyebath variables that influence dyeing behaviour

The principal parameters affecting the absorption of direct dyes by cellulose from aqueous solutions are temperature, time of dyeing, liquor ratio, solubility of the individual dye, salt controllability and to a lesser degree the influence of auxiliary agents.

Temperature

Strike and fibre penetration are governed by application temperature and are improved by an increase in temperature. Dyeing above the boil has the advantage of shortening the period at top temperature and producing more level and better penetrated dyeings, an important factor when dyeing yarn packages. The effect of an increase in temperature is to increase the dyeing rate but to decrease the equilibrium exhaustion. Consequently, for a fixed dyeing time there is an optimum temperature at which absorption is at a maximum attainable level.

Time of dyeing

The production of level and well-penetrated dyeings is usually favoured by an increased time of dyeing, although prolonged dyeing at the boil when several successive additions of dye are made for matching purposes sometimes results in the decomposition of direct dyes (section 3.2.6).

Liquor ratio

Dyebath exhaustion is governed by liquor ratio but other factors such as solubility of dyes in water, levelling properties and strike have to be taken into consideration. Appreciable variations in liquor ratio apply in dyeing cotton, viscose and other cellulosic fibres. Padding processes operate at very low liquor ratios (2:1 or less), jig methods operate at 3:1 to 5:1, and loose stock or yarn on wound packages are dyed at about 10:1. Longer liquor ratios are operative when dyeing fabrics in winches (20:1 to 30:1), overflow machines or jets (5:1 to 15:1).

Dye solubility

Dyes of good solubility are preferred for package dyeing and particularly at the low temperatures and liquor ratios necessary in padding processes. The water supply for pad liquors should have a low electrolyte content.

Salt controllability

The extent to which direct dyes are affected by the addition of electrolytes to the dyebath is known as salt sensitivity. Direct dyes vary appreciably as regards the effect of electrolytes. The addition of electrolyte increases the rate of strike of the dye. In general, the lower the ratio of relative molecular mass to number of sulphonate groups per molecule, the less absorption can take place without electrolyte addition. The commonly used electrolytes are Glauber's salt (sodium sulphate) and common salt (sodium chloride), the latter being preferred with hard water. Glauber's salt may cause precipitation of calcium sulphate on the dyed material, resulting in a somewhat harsh handle.

The role played by various electrolytes in promoting dyebath exhaustion has been examined in relation to dye structural features. Cotton cellulose was dyed under neutral conditions with two purified direct dyes differing in relative molecular mass and degree of sulphonation, in the presence of various electrolytes and a phosphate buffer system. Under these conditions it was observed that the uni-divalent electrolytes, e.g. calcium chloride, were more effective than other types in promoting dyebath exhaustion [75].

The effect of alkali-metal ions, quaternary ammonium ions, bivalent and trivalent cations on the absorption of CI Direct Violet 66 (Figure 3.11) by viscose fibres at various temperatures has been examined [76,77]. Dye absorption does not seem to depend on the charge of the cations present but only on their size. A reasonably good linear relationship was found between the saturation values in the presence of various ions and their ionic radii. The rate of absorption also increased with an increase in the size of the cation, especially at low temperatures. The difference in rate and extent of absorption in relation to ion size tended to decrease as the temperature increased.

Equilibrium adsorption isotherms and rates of dyeing of CI Direct Blue 1 (Figure 3.1) on viscose fibres at various temperatures were determined in the presence of electrolytes having predictably different capacities to modify water's structural characteristics. The results clearly demonstrated that variations in water molecular clustering around the hydrophobic portions of the dye molecules and the cellulosic fibre surface influence the dye-binding mechanism [78]. In the presence of single electrolytes the absorption of CI Direct Blue 1 by viscose fibres and the rate of dyeing at constant electrolyte concentration increased in the order: LiCl < NaCl < KCl. In binary mixtures of these electrolytes the cation with the greater ability to disrupt the clustering of water molecules (the ion with the larger radius) could considerably enhance the ability of the smaller cation to influence dye absorption and dyeing rate [79].

CI Direct Red 28 (Figure 3.8) is a highly aggregated dye. When it is applied to viscose fibres in the presence of electrolytes capable of modifying water's structural characteristics in a predictable manner, the absorption and rate of dyeing are very close to those for much less aggregated anionic dyes. Thus although this dye shows a strong tendency to form large aggregates by electrostatic attraction between cationic ammonium and anionic sulphonate substituent groups, the influence of electrolyte cations on the clustering of water molecules around dye ions and the substrate surface is unaffected [80].

Influence of auxiliaries on dye sorption

The effect of anionic and nonionic surfactants on the state of aggregation of direct dyes in solution has been studied. Nonionic agents tend to inhibit the formation of larger aggregates and increase the proportion of dye in the monomolecular form. Solubilisation of direct dyes by nonionic agents proceeds effectively up to the critical micelle concentration of the surfactant. Thus concentrated solutions of direct dyes can be stabilised using nonionic additives but the absorption of the dyes by cellulose is decreased when nonionic agents are present [81].

3.5 BATCHWISE APPLICATION OF DIRECT DYES TO CELLULOSIC TEXTILES

Direct dyes are dissolved by pasting with cold water, then adding boiling water

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with stirring. To ensure that dissolution is complete, the solution formed should be sieved before addition to the dyebath. A wetting agent (0.5–1 g l^{-1}) should be added to the dyebath to assist penetration and level dyeing.

Direct dyes are normally applied to cellulosic fibres at the boil. The dyebath is set at 40°C, raised to the boil at 2 degC min^{-1} and maintained at the boil for 30–45 min, during which 10–15 g l^{-1} of sodium chloride or calcined Glauber's salt should be added. Pastel hues are preferably dyed without addition of salt. An addition of 0.5–2 g l^{-1} sodium carbonate may be advantageous when applying dyes of only moderate solubility in full depths. Improved yields can be achieved when applying full depths by cooling to 80°C at the end of the period at the boil, adding a further 5 g l^{-1} salt and rising to the boil again.

There is increasing interest in the controlled dosage of salt in solid form in the dyeing of cotton yarns and fabrics. The effects on levelness in package dyeing of the type of salt dosage, process and machine design factors have been investigated. Electrical resistance measurements were used to monitor salt concentrations in the dyebath [82].

Many direct dyes are suitable for application by combined scouring and dyeing of either woven fabrics on jigs or knitted fabrics on jets or winches. In this process the usual practice is to employ soda ash and a nonionic detergent. Dyes containing amide groups should be avoided because of the risk of hue change owing to alkaline hydrolysis.

Combined peroxide bleaching and dyeing with selected direct dyes is another long-established process. It offers savings of process time and energy but more care is necessary to ensure satisfactory levelness and reproducibility. The essential factors are thorough and effective preparation, as well as selection of suitable dyes. Sodium carbonate is preferred to caustic soda because the risk of oxidative degradation of the dyes is greater at higher pH. An organic stabiliser for the peroxide is preferred to sodium silicate, which tends to confer harshness of handle on terry towelling, for example.

This process is of special interest for dyeing pastel colours and Class A or B dyes are preferred to attain satisfactory levelling. Components of green mixtures should be carefully chosen because of the risk of catalytic fading; certain yellow direct dyes fade more quickly in the presence of phthalocyanine or triphenodioxazine blues. Copper-complex azo direct dyes are sensitive to oxidation and cause catalytic decomposition of hydrogen peroxide. They are unsuitable for inclusion in recipes for the combined bleaching and dyeing process. Copper phthalocyanine blues, on the other hand, do not catalyse peroxide decomposition.

3.6 SEMI- AND FULLY CONTINUOUS DYEING PROCESSES FOR DIRECT DYES

Direct dyes are much less suitable for continuous application than for batchwise dyeing. Tailing is a serious problem in continuous dyeing and prolonged diffusion is necessary in pad–batch or pad–steam methods. As far as possible, close attention should be given to selecting dyes with similar absorption characteristics and to controlling the rate of supply of feed liquors. The wet fastness of direct dyes may be lower when they are applied by continuous processes than by conventional batchwise methods, but this property can be maximised by adding electrolyte or by increasing the impregnation temperature.

The pad–roll process is probably the most suitable semi-continuous method of dyeing cellulosic fabrics with direct dyes at 80–100°C. Problems with listing and ending have been minimised in the Variflex S pad–roll unit with i.r. heating [83]. Advice has been given with regard to control of fabric moisture content and pad liquor temperature, dye selection for optimum compatibility and the use of appropriate auxiliaries [84].

The pad–roll system is more versatile in production conditions than are steaming methods but the development of compact pad–steam ranges in recent years has enabled more valid cost comparisons to be reached against the semi-continuous alternatives [85]. Padding assistants that facilitate the application of direct dyes to cellulosic fabrics without tailing problems have been developed. A method for determining in advance the exchange factor in the pad dyeing of cotton and viscose fabrics with direct dyes has been described [86].

3.7 AFTERTREATMENT PROCESSES FOR DIRECT DYEINGS

The wet fastness properties (particularly washing, water and perspiration) of virtually all dyeings of direct dyes are inadequate for many end uses but notable improvements can be brought about by aftertreatments. All such treatments, however, incur increased processing costs because of the extra time, energy, labour and chemicals involved.

3.7.1 Diazotisation and development

Many long-established direct dyes containing primary amino groups could be diazotised and coupled on the fibre with a variety of developers, including naphthols (e.g. 2-naphthol), diamines (e.g. *m*-phenylenediamine) and phenols, to give larger molecules with improved wet fastness properties. A change in hue often occurred, depending on the developer employed, and frequently the light fastness was impaired. Diazotised and developed direct dyes were widely used at one time for the production of dischargeable ground colours on cotton and viscose fabrics. They have now been largely replaced by reactive dyes. The complexity of this approach and the associated problems of hue change and light fading have rendered this technique virtually obsolete.

3.7.2 Metal salt treatments

The aftertreatment of dyeings with metal salts to confer improved fastness was practised by dyers long before direct dyes were discovered [1]. Treatment with acidified copper salt solution (typically with 0.25–2% copper sulphate and 1% acetic acid for 20–30 min at 60°C) results in a marked improvement in the light fastness of certain direct dyes, e.g. CI Direct Blue 1 (Figure 3.1), which is converted into the derived copper complex (Figure 3.2). Subsequent washing or alkaline treatment removes the copper, however, so that the light fastness reverts to the original rating. Ranges of direct dyes have been produced that are of no commercial interest in the uncoppered state, but when aftertreated with copper salts give dyeings of reasonable light and wet fastness. Many of the dyes of this type are pH-sensitive before coppering and this necessitates care in handling. Control of application is essential, since once coppering has taken place, unlevel results can only be rectified by stripping.

Apart from chelation taking place with certain direct dyes containing two hydroxy groups in positions *ortho* to the azo group, it is also possible with dyes containing other groups such as *o*-hydroxy-*o*-methoxy (Figure 3.1), *o*-hydroxy-*o*-carboxy or salicylic acid groups. Instead of copper sulphate, treatment with chromium fluoride or acetate, or sodium or potassium dichromate, will enhance wet fastness, typically using 1–2% of the chromium salt and 1–2% acetic acid for 20–30 min at 60–80°C. Treatment with a mixture of copper sulphate and a dichromate will improve both light and wet fastness of certain direct dyes.

3.7.3 Cationic fixing agents

These compounds interact with the sulphonate groups present in direct dyes, conferring increased wet fastness in all tests at temperatures below 60°C. They will also precipitate direct dyes from solution, and therefore the dyed material must be cleared of loosely held dye before treatment. Hue changes may occur and, in some cases, light fastness may be reduced. The dye–auxiliary complex usually dissociates in hot detergent solutions above 60°C. Many such agents are available, including quaternary ammonium or pyridinium compounds, amide-

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formaldehyde adducts, complex fatty amides and melamine derivatives. Many of the cationic polymers evaluated as pretreatments to enhance the dyeability of cellulosic materials (section 3.3.6) are also applicable as conventional aftertreatments to improve wet fastness properties.

3.7.4 Formaldehyde treatment

Treatment of certain direct dyeings, mainly blacks, with 2–3% formaldehyde (30%) and 1% acetic acid (30%) for 30 min at 70–80°C improves the wet fastness (to both water and washing) of the dyeing. A drop of light fastness may occur, however. The improvement in wet fastness is most pronounced with dyes containing an end component with two hydroxy or amino groups *meta* to each other. CI Direct Black 38 and 166 (Figures 3.9 and 3.10) are examples of dyes suitable for this type of aftertreatment. It is believed that when dyes of this type react with formaldehyde, methylene bridges are formed in the 5-positions of the terminal 2,4-diamino- or 2,4-dihydroxy-phenylazo groupings of two dye molecules. These dimeric products have lower solubility in water than the parent dye molecules.

3.7.5 Crosslinking agents and resin treatments

Improvements in wet fastness properties can be ensured by treatment with cellulose reactants or amide-formaldehyde resins. Subsequent removal of the resin by acid hyrolysis (e.g. formic acid at 90°C or hydrochloric acid at 60°C) leaves the unfixed direct dye on the fibre with its originally low level of wet fastness. Treatment with crosslinking agents in resin finishing improves the wet fastness but hue and light fastness may be adversely affected.

3.7.6 Comparisons of aftertreatments for direct dyeings

In a recent investigation, bleached and mercerised cotton poplin was dyed with the trichromatic series of CI Direct Yellow 12 (Figure 3.5), Red 81 (Figure 3.14) and Blue 1 (Figure 3.1). Four cationic dye-fixing agents, a long-chain polyamine and copper sulphate were applied as aftertreatments. The polyamine gave consistently better wet fastness than dicyandiamide-formaldehyde adducts. Fastness performance varied with the number of sulpho groups and hydrogen-bonding sites and their positions in the dye molecule, as well as the active agent content of the fixing agent [87].

Efficiency indices have been devised to assist users of direct dye-fixing agents to evaluate their cost-effectiveness in improving wet fastness, but also taking into account their adverse effects on hue and light fastness [88]. Fastness to wet rubbing can be a serious problem in full depths of direct dyes aftertreated with a cationic agent in the usual way. Mechanical destruction of the dyed fibres produces microscopically small fragments that stain the adjacent white fabric. Aftertreating agents themselves do not significantly modify fastness to wet rubbing, however [89].

3.7.7 Application of reactant-fixable direct dyes to cellulose

The patent literature relating to Indosol CR (S), the first of the special aftertreating agents developed for the fixation of Indosol SF (S) dyes (see section 3.2.3), revealed that it was a mixture of three components and that it was designed for the continuous process of simultaneous crosslinking and dye fixation. The components were:

(1) a polybasic condensate of diethylenetriamine and an amide, such as cyanamide, dicyandiamide, guanidine or biguanide;
(2) an *N*-methylol precondensate of the dicyandiamide-formaldehyde type;
(3) a latent acid catalyst, such as lactic acid.

The polybasic condensate (1) was later marketed alone as Indosol E-50 (S) for the exhaust aftertreatment of Indosol dyeings; this component did not confer any improvement in crease recovery.

Compared with reactive dyes, Indosols showed economic advantages in respect of consumption of dyes, chemicals and water, and of reduced process time. Treatment with Indosol CR eliminated the need for any subsequent resin finishing process. Trends in washing and laundering practice were shown to be favourable towards the introduction of the Indosol system [2–4].

The cold pad–batch process was proved to be eminently suitable for the Indosol SF dyes, using urea and Vicontin I (S) to assist solubility and diffusion during the 12 h batching time [90,91]. A third type of Indosol aftertreating agent was later introduced to achieve even better fastness to washing. Indosol E-F forms the same type of dye–agent complex as is formed from Indosol E-50, but this complex is held in the fibre more securely by virtue of a covalent bond between agent and fibre that resembles the dye–fibre bonds of conventional reactive dyeings. Although Indosol E-F is designed for exhaust application, a final fixation in alkaline solution at 40°C is necessary [92,93].

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3.7.8 Effluent treatment after direct dyeing

Environmental considerations now impinge on every aspect of the dyer's activities. Although direct dyes are particularly easy to apply, the presence of chelated copper in many structures of above average fastness to light and the frequent need to apply cationic aftertreating agents means that care must be taken to minimise difficulties in effluent treatment. Reviews of water supply and recovery that are of interest to the dyer of cellulosic textiles [94,95] provide information on the sources and conservation of water and the effects of common contaminants on textile processing. Trace metals can affect the performance of many dyes, not least the copper-complex direct types. Although sequestering agents are used to minimise the influence of alkaline earth or transition metal ions on unmetallised dyes, they can obviously exert undesirable effects on the colour and fastness of metal-complex dyes.

The rising costs of water procurement and effluent disposal are forcing dyers and finishers to re-examine the potential for repeated use of dyebaths and other process liquors. Equations have been derived to show how electrolytes build up during repeated use of direct dyebaths. They can be used to calculate the amounts to be added after each dyeing or the amount of the bath to be discharged [96]. Studies of the sorption of anionic dyes by activated carbon from dyehouses wastes demonstrated that the saturation adsorption of direct dyes increased with:

(1) increasing relative molecular mass of the dye;
(2) sodium sulphate concentration in the waste water;
(3) integral pore volume of the carbon.

Methods of measuring the colour of waste dye liquors and minimising the contribution of dyeing and printing processes to this problem have been reviewed. A survey found that reactive red dyes and sulphur blacks caused most difficulty in this regard, but direct dyes can be readily removed by adsorption or precipitation [97].

Ozone treatment has potential as a means of decolorising exhaust dyebaths for reuse. A dose of 200 mg l^{-1} ozone was found to remove more than 95% of the colour present [98]. Large-scale trials on dyehouse effluents containing direct and other dyes were successful and a relationship was established between colour removal, pH and ozone consumption [99]. Fundamental studies of the ozonolysis of model azo dyes have deomonstrated that CI Direct Yellow 12 (Figure 3.5) yields mainly 4-carboxy-4′-ethoxyazobenzene-3-sulphonate and hydrogen peroxide [100].

3.8 SIGNIFICANCE OF FINISHING FOR DIRECT DYES ON CELLULOSIC FABRICS

Any effect of durable finishes on the hue and fastness properties of direct dyeings depends on the chemicals and treatment conditions employed as well as on the individual dyes. No significant effect on either hue or light fastness of direct dyes has been reported with either fluorocarbon stain-repellent finishes or the acrylate resins often used in soil-resistant finishing. The majority of softening agents applied to cellulosic fabrics, with the exception of those derived from *N*-methylol compounds, are likely to have any adverse effects on direct dyeings [101]. Although some softeners are mildly cationic, no effect on the light fastness of direct dyes has been reported. Amongst compounds used for water-repellent finishing of cellulosic materials, only those containing melamine derivatives adversely affect either the hue or the fastness of direct dyeings.

3.8.1 Effect of resin precondensates and cellulose reactants on direct dyeings

The application of resin finishes is of great importance for conferring dimensional stability to fabrics made from cotton or viscose, either alone or in blends with synthetic polymer fibres, especially polyester. An important benefit of resin finishing is to bring about a marked improvement in wet fastness of direct dyes. In the case of wash fastness, resin-treated direct dyeings will withstand washing at temperatures below 60°C, even in full-depth dyeings. This notable improvement in wet fastness on resin finishing means that direct dyes can be used for many end uses in which they would be quite unsuitable without this treatment. On the other hand, hue may be affected and light fastness may decrease, the effect in both cases varying with the individual direct dye and the crosslinking system.

Numerous products and processes are used for crosslinking cellulose; these include cellulose reactants such as dimethylolethyleneurea, dimethyloldihydroxyethyleneurea and dimethylolpropyleneurea, as well as urea- and melamine-formaldehyde precondensates. Certain inorganic salts, such as magnesium chloride or zinc nitrate, are used as catalysts in resin finishing, with curing conditions showing wide variations in respect of humidity and temperature. Zinc nitrate has a greater effect on both hue and light fastness than magnesium chloride, but metal-salt catalysts show less effect on light fastness than ammonium salts.

Studies of the relationship between dye structure and light fastness after resin treatment have shown that hydroxy and amino groups are normally the most sensitive, although their positions in the dye molecule play a significant role. Unbound formaldehyde together with the catalyst reduce the light fastness of naphthylazo dyes with an amino group located *ortho* to the azo group. The higher the residual amount of unbound formaldehyde on the finished fabric, the greater the adverse effect on light fastness.

3.8.2 Simultaneous dyeing and finishing of cellulosic fabrics

An obvious way to minimise processing costs in continuous dyeing and finishing is to try to carry out the two stages simultaneously rather than in sequence. Unfortunately, the moist or wet alkaline fixation conditions necessary for most of the dyeing classes used on cellulosic fabrics (reactive, sulphur, vat, azoic coupling) are highly incompatible with the dry cure in the presence of a latent acid catalyst that is required for all the important cellulose reactant finishes. Direct dyes, on the other hand, do not need alkali addition and they benefit greatly from the improved wet fastness conferred by a crosslinked finish.

Cotton fabrics padded with selected acid, direct or disperse dyes, *N*-methylol reactant and ammonium chloride as catalyst were dried and then cured at 160°C. In general, increasing the number of nucleophilic groups in the dye molecule gave a higher colour yield within a dye class, but molecular size was also significant. Fastness to rubbing and perspiration was good, but light fastness varied from 1 to 6 depending on dye structure and resin type [102]. In a similar investigation, typical direct dyes were applied to cotton together with dimethyloldihydroxyethyleneurea (DMDHEU) reactant and a catalyst. Colour yield increased with curing temperature and the deepest dyeings were achieved using ammonium persulphate as catalyst [103].

The phthalocyanine turquoise CI Direct Blue 86 was padded with DMDHEU and magnesium chloride on untreated, alkali-treated and diethylaminoethylated cotton fabrics. The substrate containing cationic dyeing sites invariably showed the highest colour yield and crease recovery, irrespective of the finish concentration and curing conditions [104]. Various direct and other dyes were applied to cotton in conjunction with various *N*-methylolacrylamide derivatives and catalysts. The modes of reaction between the dye, reactant and cellulose were interpreted from the colour yields and physical properties of the treated fabrics [105].

3.8.3 Subsequent dyeing of crosslinked cotton

The reorganisation by retailers of fashion garments in recent years to bring their

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garment orders closer in line with customer demands in terms of colour and style has resulted in a revival of activity in dyeing made-up garments or garment blanks, rather than fabric dyeing. If a resin finish is required to provide easy-care performance, however, this is only feasible as a continuous treatment of the fabric before garment manufacture. Accordingly, there has been a great deal of interest and development, mainly in the USA, of methods of garment dyeing suitable for cotton that has already been crosslinked and is therefore difficult to dye using conventional processes. If dyes are to be applied after finishing, this also puts greater demands than usual on the uniformity of the finish.

Cotton fabrics finished with DMDHEU or a methylolated melamine precondensate and various catalysts were then dyed with CI Direct Red 81 (Figure 3.14). In general, the colour yield, bound nitrogen and physical performance of the fabrics cured with semicarbazide hydrochloride were equal or superior to those where conventional inorganic salts were used [106]. Untreated, alkali-treated and diethylaminoethylated cotton poplin fabrics were treated with cold solutions of mineral acids and neutralised before crosslinking with DMDHEU and magnesium chloride and dyeing with a copper-complex disazo direct dye of the dinaphthylurea type. Colour yield, fastness and finish effects were dependent on substrate, type and concentration of mineral acid, and curing conditions for the finish [107].

An alternative approach to applying the crosslinking finish to cellulose that already contains cationic sites is to incorporate the cationic modifier into the resin finish formulation [108]. Thus a formulation containing trimethylolacetylenediurein (TACD) (Figure 3.20), choline chloride (2-hydroxyethyltrimethylammonium chloride) and a catalyst was applied to mercerised cotton and cured in the usual way. Tests with CI Direct Blue 1 (Figure 3.1) and CI Reactive Red 2 demonstrated that this route provided an easy-care finish that could be readily dyed in full depths after crosslinking [108]. A subsequent investigation compared choline chloride with methylpolyoxyethylene cocoammonium chloride and with a water-soluble polymer containing grafted quaternary groups and active hydroxy groups. Dyeing with a selected series of dyes, including the components of the red–green test (Figures 3.14 and 3.15), showed that choline-based treatments were superior to the others in terms of colour yield and light fastness retention. Direct dyes invariably gave higher light fastness on the cationic-modified finishes.

Factors influencing the dyeability of crosslinked cotton with direct dyes have been studied in more detail [109,110]. Cotton fabrics crosslinked with formaldehyde, dimethylolethyleneurea (DMEU) and DMDHEU were dyed with CI Direct Red 81 (Figure 3.14) and a tetrasulphonated trisazo direct blue. Dye uptake was dependent on whether the cotton had been mercerised, the type of crosslinking agent and the dye structure, as well as the curing and dyeing conditions. In general, sorption of the larger trisazo blue dye was favoured by formaldehyde-linked cellulose, whereas sorption by the fibres crosslinked with DMEU or DMDHEU was greater for the smaller disazo red [109]. The pore structures of cotton crosslinked with DMDHEU or 4,5-dihydroxy-1,3-dimethylimidazolidone (DHDMI) (Figure 3.21) were compared using reverse gel permeation chromatography. The results were interpreted in relation to the uptake by these fabrics of CI Direct Red 81 (Figure 3.14). Although crosslinking reduced the accessible internal volume, samples reacted with DHDMI retained substantially more accessible internal volume across the entire range of pore sizes [110].

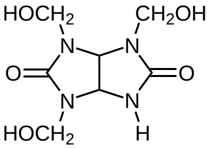

Figure 3.20

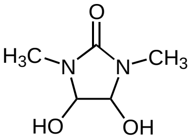

Figure 3.21

Several methods for the production of readily dyeable garments made from easy-care cotton fabrics have been summarised [111–113]:

(1) The use of DHDMI to give a finished fabric free from formaldehyde that is dyeable with direct, vat or reactive dyes.

(2) Wet treatment with formaldehyde to give Form W cotton, which is more dyeable with direct dyes than untreated cotton but shows poor dry crease recovery.

(3) Additives such as choline chloride or triethanolamine to TACD finishes to confer affinity for acid, direct or reactive dyes.

(4) Aftertreatment of a urea–formaldehyde finish with 5% acetic acid solution at 60°C to achieve partial hydrolysis and improved dyeability but some sacrifice of finish performance.

Cotton crosslinked with DHDMI was dyed with several direct and reactive dyes. Dyeability was adequate with direct dyes of relatively small molecular size but the substantivity of more complex structures for the modified cellulose was much lower.

Mono-, di- and tri-ethanolamines were compared as additives to a DMDHEU finish on cotton. Triethanolamine was the most effective in enhancing dyeability, giving results approximately equivalent to direct dyes on the untreated fibre. Two carbamoylethylamine adducts, prepared by the reaction of acrylamide with diethylamine or diethanolamine, were also investigated with DMDHEU in a similar way. Nitrogen analyses confirmed that the additives became part of the finish, and if methylolated to render then reactive with cellulose they could be used alone to enhance dyeability with anionic dyes, although they were not capable of crosslinking independently [111–113].

The dyeing characteristics of cotton crosslinked with DMDHEU in the presence and absence of triethanolamine were compared with those of mercerised and untreated controls. Crosslinking reduced most of the kinetic constants (dyeing rate, structural diffusion resistance, maximum exhaustion, activation energy, diffusion coefficient) but the incorporation of triethanolamine reversed these trends and thus enhanced dyeability. It was shown that in the crosslinked cellulose, triethanolamine reacted preferentially with DMDHEU crosslinks rather than with the remaining free hydroxy groups of the substrate [114].

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CHAPTER 4

Dyeing with reactive dyes

John Shore

4.1 INTRODUCTION

The discovery in 1884 of substantive dyes that could be applied directly to cotton without prior treatment with a mordant greatly simplified subsequent developments in the dyeing of cellulosic fibres. It simultaneously initiated a prolonged search for novel approaches and techniques that would satisfy consumer demand for dyed materials that withstand the severe washing conditions to which cotton textiles are normally subjected. The vat, sulphur and azoic ranges of dyes, all developed mainly in the three decades following the discovery of the first direct dye, depended on various techniques for depositing insoluble colorants inside the amorphous regions of the cellulosic polymer. For a further four decades, this remained the only feasible method of achieving dyeings of high fastness to washing on cellulosic textiles.

During this period much fundamental work on the structure of cellulose and the morphology of cellulosic fibres was undertaken and numerous ethers and esters of cellulose were prepared. It would be surprising if none of these had involved the formation or attachment of coloured sidechain substituents on the cellulose chain. Although such necessarily complex and esoteric reactions did indeed confirm the formation of covalent bonds between typical chromophoric groups and the hydroxy groups in the cellulose molecule, they remained essentially of academic interest only [1,2].

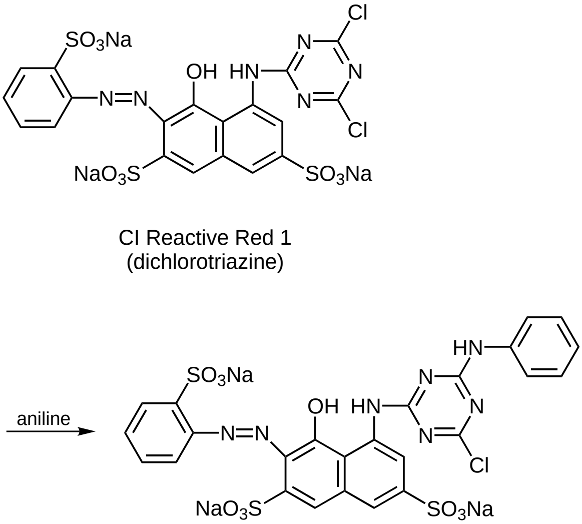
Surprisingly, few attempts were made to adapt such reactions or to develop appropriate reagents that would allow such derivatives to be formed under typical dyehouse conditions. Some of the drawbacks of the treatments applied in this period, apart from their multi-stage complexity or the use of costly and hazardous solvent media, were degradative attack of the cellulose chains by some of the vigorous reagents or reaction conditions necessary, or sensitivity of the colorant–fibre bond to hydrolytic attack during subsequent handling or storage of the coloured product [1,3].

4.2 HISTORICAL BACKGROUND

It was not until the early 1950s, following the marketing in 1952 by Hoechst of two Remalan (HOE) vinylsulphone dyes capable of reacting with wool, that ICI was successful in devising a reactive dyeing process that enabled cellulose to be dyed with a trichromatic mixture of dyes under practical conditions. Cotton fabric was pretreated with alkali and dried before immersion in a solution of the highly reactive dichlorotriazine dyes. Various refinements of the process were necessary (adding salt to enhance substantivity, lowering the pH and buffering the dyebath to minimise dye hydrolysis) before these novel Procion (ICI, now Zeneca) dyes could be marketed in 1956.

Exploitation of the dichlorotriazine reactive system soon led to parallel development of the much less reactive monochlorotriazine dyes, readily made by a substitution reaction between an arylamine and the dichlorotriazine precursor (Scheme 4.1). More stable padding liquors could be prepared using the aminochlorotriazine types and the range of reactivities offered by these two classes of dyes in combination with various alkalis greatly extended the scope of novel continuous dyeing methods for them.

At this stage, however, the limitations of continuous dyeing requirements became a temporary constraint on the adoption of reactive dyeing and attention turned to the development of batchwise methods. It was quickly demonstrated



CI Reactive Red 1
(dichlorotriazine)

CI Reactive Red 3
(aminochlorotriazine)

Scheme 4.1

that optimal temperatures of dyeing should be sought (40°C or lower for dichlorotriazines, 70°C or higher for aminochlorotriazine dyes). The major breakthrough came when it was realised that a neutral exhaustion in salt solution to achieve moderate uptake should precede the alkali addition to promote further exhaustion at a controlled rate determined by the dye–fibre reaction that proceeds at an optimal alkaline pH and temperature.

Over the decades since the commercial introduction of reactive dyes, their use has grown steadily rather than spectacularly [4]. When they first appeared it was predicted that reactive dyes would largely replace azoic combinations, direct dyes and sulphur dyes, displace vat dyes from outlets where fastness to bleaching was not essential and eventually dominate the dyeing of cellulosic materials. This did not occur and even in the relatively sophisticated markets they do not account for more than 30% of all dyes consumed on cellulose. World-wide, the traditional uses of direct and sulphur dyes on woven cotton fabrics remain dominant and reactive dyes only account for about 10% of total consumption on this basis of comparison [1,4]. In the USA, however, where vat dyes have been used preferentially for fast-dyed cottons, there has been a more gradual trend in favour of reactive dyes. Greater demand for brilliant hues, a shift towards cotton and cotton-rich blends for apparel and a greater prevalence of short-run lots in the US textile industry have all contributed to this trend.

Although the dyeing cycles of direct and reactive dyes are broadly similar, a major difference becomes apparent when unfixed or hydrolysed reactive dye has to be washed off thoroughly in order to achieve the desired superior wet fastness of the reactive dyeing. As much as 50% of the total cost of a reactive dyeing process must be attributed to the washing-off stages and treatment of the resulting effluent. This aspect of the process should be recognised as a major limitation that prevents reactive dyes from achieving the degree of success that was predicted for them at the time of their discovery [1]. Certain other deficiencies are associated with the limited stability of specific types of dye–fibre bond to various conditions of treatment of the dyed fibres (section 4.8).

Research into novel reactive dyeing systems and application methods has remained highly active and some notable developments have taken place during recent years. Aminofluorotriazine dyes have joined the vigorous competition between the major reactive systems (section 4.3), and bifunctional systems reacting by two distinctly different mechanisms (section 4.3.2) have also appeared. Bis(aminonicotinotriazine) dyes that react with cellulose under neutral conditions and reactive dyes containing phosphonic acid groups capable of fixation under hot, dry, acidic conditions represent two quite different novel approaches to reactive dye fixation that have been commercialised.

Pretreatment of cellulosic materials with cationic agents of various kinds that enhance uptake of anionic dyes and facilitate the fixation of reactive dyes in the absence of either salt or alkali [5,6] has also attracted considerable interest (section 3.3). Novel chromophores, cold-dissolving granules and liquid brands (section 4.4), improved automation of application methods (sections 4.5 and 4.6) and greater awareness of the environmental impact of reactive dye wastes (section 4.9) have all received attention over this recent period.

4.3 REACTIVE SYSTEMS

The four characteristic features of a typical reactive dye molecule are:

(1) the chromophoric grouping, contributing the colour and much of the substantivity for cellulose;
(2) the reactive system, enabling the dye to react with the hydroxy groups in cellulose;
(3) a bridging group that links the reactive system to the chromophore;
(4) one or more solubilising groups, usually sulphonic acid substituents attached to the chromophoric grouping.

In a few cases the reactive grouping is attached directly to the chromophore and most reactive systems contain a heterocyclic ring that contributes some substantivity for cellulose. The nature of the bridging group and other substituents on the heterocyclic ring greatly influences the reactivity and other dyeing characteristics of such dyes [7]. The sulphatoethylsulphone precursor of the vinylsulphone reactive group contributes significantly to the aqueous solubility of reactive dyes of this type.

Many reagents can be used to acylate cellulose when it is partially ionised under alkaline conditions but in the production of reactive dyes of commercial interest numerous factors other than the chemistry of such reactions have to be taken into account [8]. Some of the most important are the following:

(1) Economy – any reactive system selected as the basis of a range of dyes must enable them to be produced at acceptable cost.
(2) Availability – the system selected must be free from patent restrictions, health hazards or other limitations to exploitation.
(3) Facility – it must be possible to attach the reactive system to the dye chromophoric groupings readily in manufacture.
(4) Storage stability – the dye containing the reactive groups must be stable to storage under ambient conditions.

(5) Efficiency – the yield in manufacture of the reactive dye must be efficient and the dye fixation must be high under conventional conditions of application.

(6) Bond stability – the dye–fibre bond must be reasonable stable under severe conditions of washing and durable finishing.

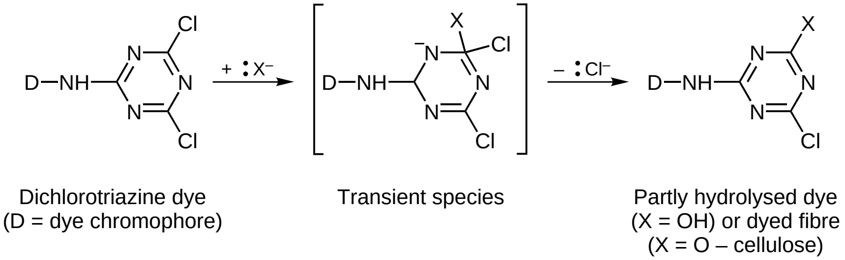
Only a few reactive systems (Table 4.1) have met these requirements sufficiently well to become commercially established in a significant segment of the market for reactive dyes on cellulosic fibres. In addition to these important types, several others have been marketed [2,3,9] as alternative ranges that have failed to maintain a foothold in the market-place, or as individual members of established ranges where they show reactivity characteristics similar to one of the more important reactive systems. These systems of relatively minor significance include: 2-alkoxy-4-chloro-*s*-triazine, 2,4-dichloropyrimidine-5-carbonylamino, 5-cyano-2,4-dichloropyrimidine, 5-chloro-2-fluoro-4-methylpyrimidine, 5-chloro-4-methyl-2-methylsulphonylpyrimidine, 1,4-dichloropyridazine-5-carbonylamino, 2-chlorobenzothiazole-6-sulphonylamino, sulphatoethylsulphamoyl and sulphatopropionylamino.

During the early years of development of reactive dyes it was soon recognised that the important reactive systems could be classified into two distinct categories, depending on the mechanism of formation of the dye–fibre bond and the stability of this bond to subsequent treatments [8,10]. Those based on nitrogen-containing

Table 4.1 Important reactive systems

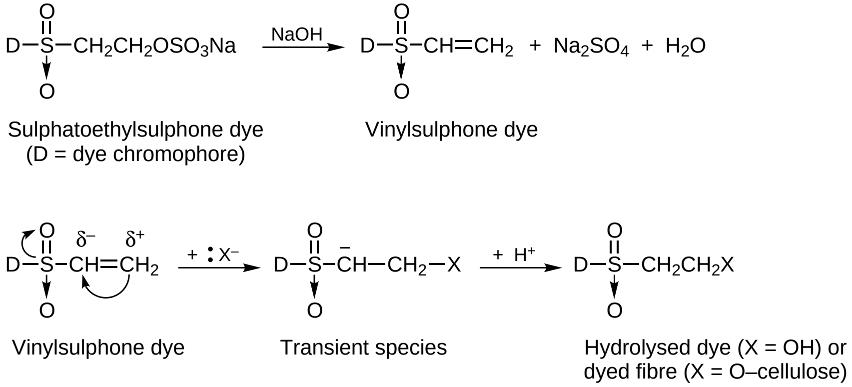
System	Typical brand name
Monofunctional	
Dichlorotriazine	Procion MX (Zeneca)
Aminochlorotriazine	Procion H (Zeneca)
Aminofluorotriazine	Cibacron F (CGY)
Trichloropyrimidine	Drimarene X (S)
Chlorodifluoropyrimidine	Drimarene K (S)
Dichloroquinoxaline	Levafix E (BAY)
Sulphatoethylsulphone	Remazol (HOE)
Sulphatoethylsulphonamide	Remazol D (HOE)
Bifunctional	
Bis(aminochlorotriazine)	Procion H-E (Zeneca)
Bis(aminonicotinotriazine)	Kayacelon React (KYK)
Aminochlorotriazine-sulphatoethylsulphone	Sumifix Supra (NSK)
Aminofluorotriazine-sulphatoethylsulphone	Cibacron C (CGY)

heterocyclic rings bearing halogeno substituents undergo nucleophilic substitution (Scheme 4.2). The heteroatoms in the aryl ring activate the system for nucleophilic attack because of their electronegativity. The attacking nucleophile can be either a cellulosate anion or a hydroxide ion, the former leading to fixation on the fibre and the latter resulting in hydrolysis of the reactive dye.



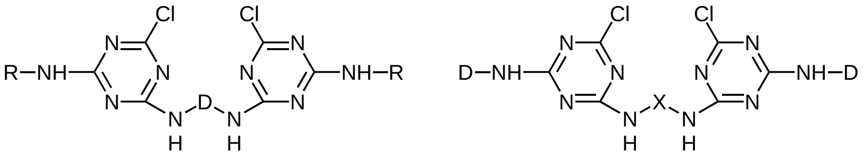
Scheme 4.2

Remazol (HOE) dyes, based on the 2-sulphatoethylsulphone precursor of the vinysulphone reactive system (Scheme 4.3) or related species, function by a nucleophilic addition mechanism rather than substitution. Before this can occur, however, alkaline 1,2-elimination of the precursor grouping is necessary to release the reactive vinylsulphone system. In this system the carbon–carbon double bond is polarised by the powerfully electron-attracting sulphone group. This polarisation confers a positive character on the terminal carbon atom, favouring nucleophilic addition of either a cellulosate anion or a hydroxide ion, again leading to either fixation or hydrolysis respectively.



Scheme 4.3

The first range of bifunctional reactive dyes containing two distinct reactive systems in the same molecule was the Procion H-E (Zeneca) range, in which the two aminochlorotriazine groupings normally show the same level of reactivity, since these dyes are symmetrical in structure (Figure 4.1). They may be based on one disazo chromophore having a reactive group at each end of the molecule, or on a pair of identical chromophores linked via chlorotriazine units to a central linking diamine. Such approaches have also been exploited in the recent development of the Kayacelon React (KYK) range of neutral-fixing bis(aminonicotinotriazine) dyes.

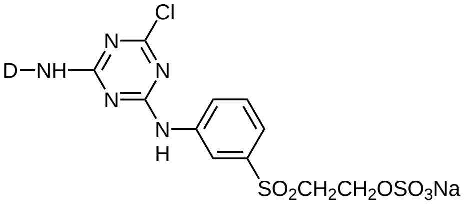


Disazo chromophore (D)
RNH_2 = arylamine

Identical chromophores (D)
$H_2N—X—NH_2$ = linking diamine

Figure 4.1

The past decade has seen the appearance of two further interesting ranges of bifunctional dyes that are capable of reacting with cellulose via both mechanisms, nucleophilic substitution and nucleophilic addition. In both systems one ring substituent in a halogenotriazine dye carries a 2-sulphatoethylsulphone grouping (Figure 4.2). The halogeno substituent can be either chlorine, as in the typical Sumifix Supra (NSK) arrangement shown, or the more reactive fluorine, as in the Cibacron C (CGY) range.



D = dye chromophore

Figure 4.2

4.3.1 Monofunctional systems

Some of the most important monofunctional reactive systems contain only one possible reactive centre, such as the halogeno substituent in the aminohalotriazine dyes, or the activated terminal carbon atom in the vinylsulphone system. In others there are two equivalent replaceable halogeno substituents, as in the dichlorotriazine, difluoropyrimidine or dichloroquinoxaline heterocyclic ring systems. When one of these halogen atoms is displaced by reaction or hydrolysis, as in Scheme 4.2 for example, the reactivity of the remaining halogeno substituent is greatly decreased by the presence of the new hydroxy or cellulosyl substituent.

Dichloro-s-triazine dyes

In a typical dye of this type, such as CI Reactive Red 1 (Scheme 4.1), the partial polarisation of the ring C=N and C–Cl bonds, because of the greater electronegativity of the N and Cl atoms, makes the 2- and 4-chloro substituents susceptible to nucleophilic displacement, although these influences are muted by feedback of electrons from the NH bridging group linking the triazine ring to the phenylazonaphthyl chromophore. Such dyes are stable in neutral solution at ambient temperature but subject to hydrolytic attack by hydroxide ions at alkaline pH and to autocatalytic hydrolysis under acidic conditions. To guard against this, a buffer is added to the solution to ensure stability during isolation and further buffer is added to the dyestuff paste before drying [3].

The dichlorotriazine dyes are highly reactive and can be readily fixed to cellulosic materials by pad–batch dyeing at ambient temperature or by batchwise methods at 30–40°C. This means that relatively small chromogens are preferred to ensure adequate mobility of dye on the fibre during the exhaustion stage. This requirement makes these dyes eminently suitable for bright dyeings but less satisfactory for deep tertiary hues, since the larger-size chromogens used for this purpose often fail to give acceptable performance by low-temperature application. A weakness with certain dichlorotriazine dyes, particularly red dyes based on H acid as coupling component, such as CI Reactive Red 1, is that under conditions of low pH the dye–fibre bond is broken by acid-catalysed hydrolysis, leading to deficiencies in fastness to washing or acid perspiration.

When partial hydrolysis occurs as in Scheme 4.2 to form the 2-chloro-4-hydroxy-*s*-triazinylamino species, the dye does not have a further chance to achieve fixation via the remaining chlorine atom. Under the alkaline conditions of the fixation stage, ionisation of the acidic 4-hydroxy substituent leads to a massive feedback of negativity into the triazine ring, causing total deactivation of the remaining 2-chloro substituent.

Controlled reaction of dichlorotriazine dyes with either amines or alcohols leads to two further classes of monofunctional dyes, the 2-amino-4-chloro- and 2-alkoxy-4-chloro-triazines respectively. The latter are more reactive than the former but less reactive than the parent dichlorotriazine types. They are now only of historical interest, the 2-isopropoxy-4-chloro system forming the basis of the Cibacron Pront (CGY) range for printing. The bulky isopropoxy group was chosen in order to disrupt the planarity of the substituted triazine system and thus favour removal of unfixed dye from the printed fabric during the washing-off stage.

In a recent investigation, the relative reactivities of model 2-alkoxy-4-chlorotriazine dyes were compared. Surprisingly, the hydroxide ion preferentially displaced the alkoxy group rather than the chloro substituent. Increasing the size and electron-donating capacity of the alkoxy group resulted in a decreasing propensity for substitution, so that displacement of methoxide ion was 12 times faster than displacement of isopropoxide ion [11].

Aminochloro-s-triazine dyes

Reaction of a dichloro-*s*-triazine dye with an amine at about 25–40°C (Scheme 4.1) produces a much less reactive 2-amino-4-chloro derivative as exemplified by CI Reactive Red 3. More energetic reaction conditions, typically 80°C and pH 11 for batchwise application, are necessary for efficient fixation on cellulosic fibres. Early studies of the relationships between structure and substantivity of aminochlorotriazine dyes revealed that the NH bridging groups linking the chromogen and the uncoloured arylamino substituent to the heterocyclic ring had marked effects on the solubility and dyeing properties of the dyes [1]. Replacement of the simple NH imino group by an *N*-methylimino bridge tended to lower the substantivity for cellulose. The use of a sulphonated arylamine to form the uncoloured 2-arylamino substituent of a monochlorotriazine dye was helpful to enhance solubility and modify the dyeing behaviour.

Aminofluoro-s-triazine dyes

A fluorine atom is used as the leaving group in the Cibacron F (CGY) range of 2-amino-4-fluoro-*s*-triazine dyes. The greater electronegativity of fluorine compared with chlorine results in a markedly higher level of reactivity for these dyes than for the 2-amino-4-chloro analogues. The substantivity and solubility of the dye structures can be modified considerably by careful introduction of appropriate substituents on the chromogen, the uncoloured arylamine and the bridging NH groups (Figure 4.3).

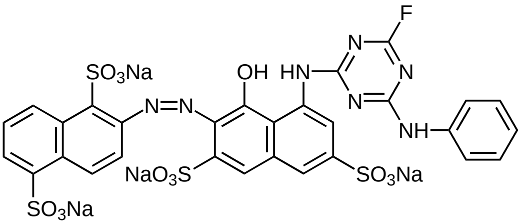


Figure 4.3

Trichloropyrimidine dyes

The 1,3-diazine grouping in the pyrimidine ring provides much less activation of chloro substituents than the 1,3,5-triazine system. Fixation to the fibre by batchwise application methods requires treatment at the boil rather than the 80°C found to be optimum for the aminochlorotriazine dyes, but the dye–fibre bond containing a diazine ring is more stable than that containing a triazine nucleus [10]. A study of the relative reactivities of the chlorine atoms in tetrachloropyrimidine with arylamines demonstrated [12] that formation of a trichloropyrimidine dye occurs by nucleophilic substitution of the 4-chloro substituent to form a bridging NH link with the chromophore, as indicated in the structure of CI Reactive Red 17 (Figure 4.4).

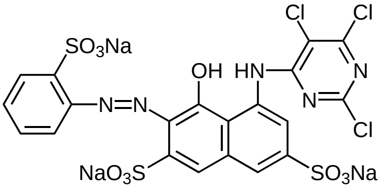


Figure 4.4

This preferential substitution at the 4-chloro position is much less pronounced in the reaction of 2,4,6-trichloropyrimidine with arylamines, so that the dichloropyrimidine dyes formed in this way contain a mixture of 2,6- and 4,6-dichloro isomers. These dyes are even less reactive than the trichloropyrimidine dyes but are correspondingly more resistant to acidic and alkaline hydrolysis.

The 5-chloro substituent in the trichloropyrimidine reactive system is much less activated by the nitrogen atoms in the heterocyclic ring and is thus not normally capable of hydrolysis or reaction with the fibre. Dyes prepared with a more electronegative substituent in the 5-position, such as 5-cyano or 5-nitro, show enhanced reactivity of the 2,6-dichloro substituents but somewhat lower stability of the dye–fibre bond. Conversely, dichloropyrimidine dyes containing a 5-methyl substituent are less reactive but more stable than trichloropyrimidines [10].

Chlorodifluoropyrimidine dyes

Another important route to more reactive halopyrimidine dyes is to use fluorine rather than chlorine in the reactive centres. As with the fluoro-*s*-triazine dyes, this results in a markedly higher level of reactivity compared with the corresponding chloro-substituted analogues. The Drimarene K (S) and Levafix E-A (BAY) ranges are both based on the 5-chloro-2,6-difluoropyrimidine reactive system (Figure 4.5). Batchwise dyeing temperatures for optimal fixation of these dyes are about 40–50°C. The dye–fibre bond formed by reaction of cellulose with the highly reactive difluoropyrimidine system is more stable to acid conditions than that of the competing dichlorotriazine system but it does tend to undergo oxidative cleavage more readily under the influence of light exposure in the presence of peroxy compounds (see section 4.8).

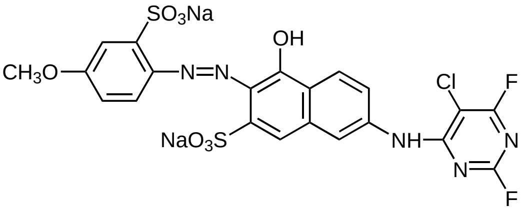


Figure 4.5

Dichloroquinoxaline dyes

One of the interesting intermediates exploited in the early years of reactive dye development was 2,3-dichloroquinoxaline-6-carbonyl chloride which could be condensed with the amino group of the dye base to form an amide bridging link between the chromogen and the reactive system [13]. The reactivity of this system is much higher than that of corresponding dichloropyrimidine dyes and comparable with that of the dichlorotriazine and difluoropyrimidine systems, optimal fixation being achieved by batchwise dyeing at about 50°C. Thus the Levafix E (BAY) dichloroquinoxaline dyes are fully compatible with the Levafix E-A (BAY) difluoropyrimidine members of this composite range.

The structure of a typical red Levafix E dye is shown in Figure 4.6. Unlike all other important haloheterocyclic reactive systems, the bridging link between chromogen and reactive grouping is amidic and thus expected to be readily hydrolysed under acidic conditions. The 1,4-diazine ring in the dye–fibre bond formed by these dyes, like the 1,3-diazine ring present after fixation of the difluoropyrimidine system, tends to undergo oxidative cleavage when exposed to light or heat under peroxidic conditions. In spite of these potentially severe defects, the continued commercial success of the Levafix E dyes over a long period suggests that they do not give rise to serious practical problems under normal circumstances [1].

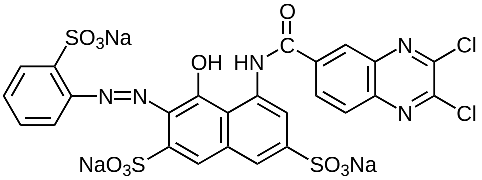
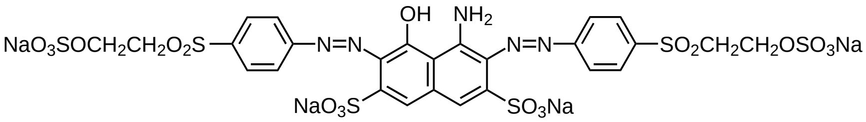


Figure 4.6

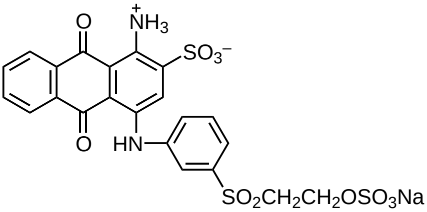
Sulphatoethyl-sulphone and -sulphonamide dyes

The Remazol (HOE) vinylsulphone dyes, containing the characteristic 2-sulphatoethylsulphonyl precursor grouping, are intermediate in reactivity between the high-reactivity heterocyclic systems, such as dichlorotriazine or difluoropyrimidine, and the low-reactivity ranges, such as aminochlorotriazine or trichloropyrimidine. Exhaust dyeing temperatures between 40 and 60°C may be chosen, depending on pH, since caustic soda is often selected to bring about alkaline hydrolysis of the precursor sulphate ester. These dyes are applicable by a wide variety of batchwise and continuous processes. The substantivity of many of these dyes is markedly lower than that of typical haloheterocyclic dyes. Not only has the vinylsulphone group, unlike the heterocyclic ring systems, little if any inherent affinity for cellulose, but the terminal sulphato group enhances the aqueous solubility of the precursor form before 1,2-elimination to the vinylsulphone. In contrast to the haloheterocyclic systems, the dye–fibre bonds formed by the vinylsulphone dyes are at their weakest under alkaline conditions [14].

For three decades the two most widely used reactive dyes have been those illustrated in Figure 4.7: Remazol Black B and Remazol Brilliant Blue R. The four solubilising groups in the precursor form of CI Reactive Black 5 confer high solubility but unusually low substantivity. It is a nearly symmetrical bis(sulphatoethylsulphone) structure and as these precursor groups lose their ionic charge by 1,2-elimination, the substantivity for cellulose is enhanced and the bis(vinylsulphone) structure formed shows excellent fixation efficiency under alkaline conditions. After fixation the inherently low substantivity of the unfixed bis(hydroxyethylsulphone) dye makes washing-off easy in a region of the colour gamut where this is often notoriously difficult [3].



CI Reactive Black 5



CI Reactive Blue 19

Figure 4.7

The extremely attractive bright blue hue combined with excellent light fastness of CI Reactive Blue 19 could not be challenged by other reactive blue dyes for many years. The aqueous solubility of this dye is inherently low and depends on the zwitterionic 1-amino-2-sulpho grouping after 1,2-elimination of the sulphate ester has taken place. This has led to poor reproducibility and levelling problems, but nevertheless this dye has remained second only to Black 5 in terms of market share amongst reactive dyes.

In a recent investigation of the effect of low-frequency ultrasonic waves on the stability of the copper-complex phenylazo H acid dye Remazol Brilliant Violet 5R (Figure 4.8), reaction rates were recorded for the 1,2-elimination of the sulphato group to form the vinylsulphone and for hydrolysis of the latter to form the 2-hydroxyethylsulphone [15].

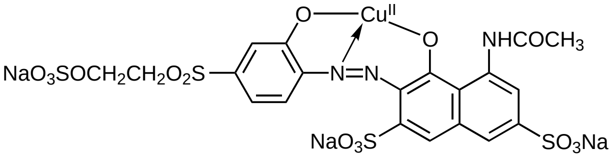


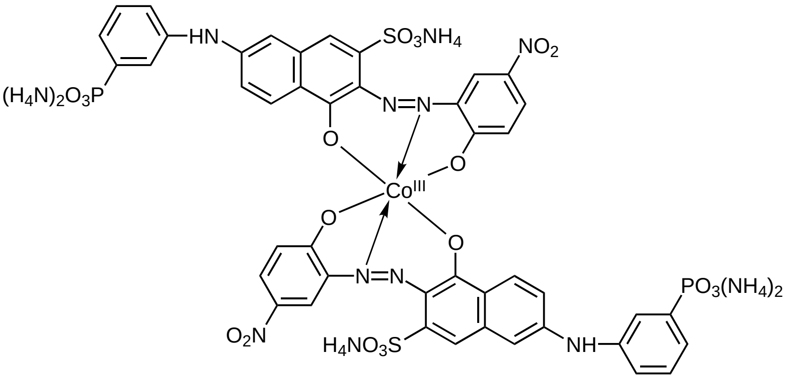
Figure 4.8 CI Reactive Violet 5

Certain members of the Hoechst range are designated Remazol D brands and these contain a 2-sulphatoethylsulphonamide precursor grouping formed by reacting the dye base with carbyl sulphate [3]. As in the case of the conventional vinylsulphone types, 1,2-elimination occurs under alkaline conditions to give the reactive vinylsulphonamide group and this is capable of either reaction with cellulose or hydrolysis to the hydroxyethylsulphonamide according to the usual nucleophilic addition mechanism (see Scheme 4.3).

Phosphonic acid dyes

As in the case of chlorotriazines and vinylsulphones, dyes containing phosphonic acid groups had been prepared long before their utility as reactive dyes for cellulose was recognised [4]. The realisation that phosphonic acid derivatives could, under certain circumstances, react with alcohols to give phosphonate mono-esters was made in 1973 at the Stanford Research Institute. Subsequent development work by Burlington Industries and later ICI led to the commercial launch of the Procion T (ICI, now Zeneca) range of dyes in 1977. These dyes were unusual in being applied to cellulosic and blend fabrics under mildly acidic conditions (pH 5–6). This made them particularly suitable for polyester/cotton dyeing by the pad–dry–thermosol process, since the alkaline conditions normally required to fix conventional reactive dyes could be avoided.

The structures of many of these dyes were based on the versatile intermediate 3-aminophenylphosphonic acid attached to typical monoazo chromogens in various ways [4]. One example was the 1:2 cobalt complex Procion Rubine T-6BD (Figure 4.9). These dyes were sold as aqueous solutions of the ammonium salts, which facilitated thermal dissociation to generate the free acid form. This in turn reacted with a carbodiimide, e.g. dicyandiamide, by one of two possible mechanisms, either or both of which may be operative. One mechanism involves formation of an *O*-acylisourea derivative of the dye phosphonate and the carbodiimide [4], the other proceeds via a dye phosphonic anhydride derivative [16]. Dye fixation can occur by reaction of either of these derivatives with the hydroxy groups of cellulose.



CI Reactive Red 179

Figure 4.9

More recently, the role of the carbodiimide in the dyeing process has been examined and it was concluded that the loss of this auxiliary by thermal decomposition was the most important factor limiting dye fixation [17]. Later it was shown that fixation yields as high as 95% could be achieved by minimising the decomposition of the carbodiimide [18].

A major attraction of the phosphonic acid dyes was the exceptional stability of the dye–fibre bonds, more stable than those from chlorotriazine dyes in acidic media and those from vinylsulphone dyes under alkaline conditions. Technical drawbacks of these first acid-fixing reactive dyes, however, included dye migration during drying, especially on heavy fabrics such as corduroy, and strength loss of the cellulosic fibres during thermofixation under the acidic conditions necessary for fixation. Consequently, the Procion T (ICI, now Zeneca) dyes were withdrawn in 1987, essentially for economic reasons [4].

4.3.2 Bifunctional systems

In the early years of the commercial exploitation of reactive dyes, it was soon noted that anomalously high values of cuprammonium fluidity were observed for dyeings of many reactive dyes in full depths, although tests of tensile strength demonstrated that the cellulose remained undamaged [19]. Investigation showed that these anomalous results were associated with those dyes capable of forming crosslinks between neighbouring cellulose chains, such as the bis(sulphatoethylsulphone) dye CI Reactive Black 5 (Figure 4.7) or the dichlorotriazine dyes with two chloro substituents capable of attack by cellulosate segments of the polymer chains, such as CI Reactive Red 1 (Scheme 4.1).

These phenomena attracted further interest when ICI introduced the Procion

H-E dyes, a full range of high-fixation dyes containing two aminochlorotriazine groups per molecule. A detailed study of representative members of this range, as well as other potentially crosslinking reactive systems (dichlorotriazine, chloromethoxytriazine, dichloroquinoxaline, trichloropyrimidine and chlorodifluoropyrimidine) provided convincing evidence of the extent of crosslinking that could take place. The degree of crosslinking was non-existent or relatively insignificant for typical pad–batch dyeings at ambient temperature, but thermal fixation by the pad–dry–steam method resulted in a much higher proportion of crosslinked dye molecules [20].

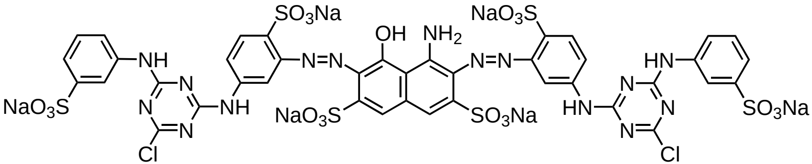
Recently attention has turned to the more difficult problem of analysing the mode of fixation to cellulose of a bifunctional reactive dye of the Sumifix Supra (NSK) range that contains two dissimilar reactive systems (vinylsulphone and chlorotriazine). Controlled enzymatic degradation of a mechanically milled cotton fabric that had been batchwise dyed at 60°C yielded interesting results [21]:

(1) About 80% of the vinylsulphone groups had reacted with the cellulose.
(2) About 50% of the chlorotriazine groups had not reacted with cellulose and only half of these had hydrolysed to OH groups.
(3) A considerable proportion of the dye molecules had formed crosslinks by reacting via both mechanisms.

Bis(aminochlorotriazine) dyes

The concept of dyes with two reactive systems of the same type dates back to the early days of reactive dyes but it was not until the early 1970s that the advantages accruing from this arrangement were fully realised in a commercial range of dyes designed in this way. The objective was to produce bifunctional dyes for exhaust dyeing (the major sector, accounting for more than 50% of the total market for reactive dyes) that exhibited substantially higher substantivity, exhaustion and fixation values compared with corresponding monofunctional aminochlorotriazine dyes. Unlike the sulphatoethylsulphone group, substituted triazine reactive systems readily lend themselves to substantivity enhancement [4].

These bifunctional dye molecules (Figure 4.1) are approximately twice the size of analogous monofunctional types (e.g. CI Reactive Red 3, Scheme 4.1). Their high substantivity allows them to achieve excellent exhaustion at the preferred batchwise dyeing temperature of about 80°C, leading to fixation values of about 70–80%, although typical members of the range, such as Procion Navy H-ER (Figure 4.10), may require salt concentrations as high as 100 g l^{-1} for optimal yield. High-temperature application conditions ensure good levelling and the high fixation leads to better utilisation of the applied dye, with less hydrolysed



CI Reactive Blue 171

Figure 4.10

dye and less discoloration of the effluent. Unfortunately, the rate of removal of unfixed dye at the washing stage is slow owing to the high intrinsic substantivity of these dyes.

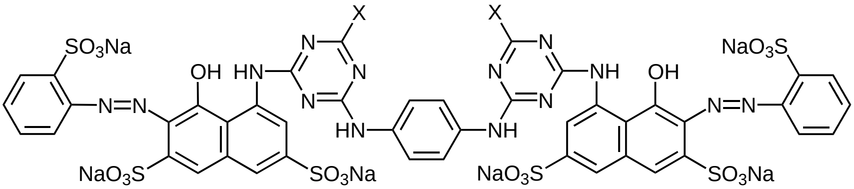
Bis(aminonicotinotriazine) dyes

An aminochlorotriazine dye will react with a tertiary amine possessing a sterically accessible nitrogen atom to produce a quaternary ammonium derivative. The positive charge carried by the quaternary nitrogen atom increases the polarisation of the C–N bond that links it to the triazine ring, so making these compounds much more reactive than the parent dyes. Within a few years of the introduction of reactive dyes, the utility of tertiary amines as catalysts to assist the fixation of aminochlorotriazine dyes to cellulose was evaluated. Suitable tertiary amines include trimethylamine, *N*,*N*-dimethylhydrazine, pyridine and the cycloaliphatic compound 1,4-diazabicyclo[2,2,2]octane (DABCO).

This approach appeared to offer the opportunity to achieve a range of reactivities between those of aminochloro- and dichlorotriazine dyes without loss of the desirable stability of the dye–fibre bond to acidic conditions that is characteristic of the aminochlorotriazine types. Unfortunately, this ideal was not attainable because of the objectionable odours of the parent tertiary amines liberated by the fixation reaction and the sensitivity of the reactivity behaviour of the quaternised derivatives to the nature of the chromogenic substituent on the triazine ring, making it difficult to select compatible combinations of dyes.

Nicotinic acid (3-carboxypyridine) readily dissolves in the dyebath and thus overcomes the odour problem. Advantage of this was taken at ICI in 1979 with the introduction of the bis(aminonicotinotriazinyl)-substituted triphenodioxazine dye Procion Blue H-EG (CI Reactive Blue 187) for exhaust dyeing at 80°C with the other bis(aminochlorotriazine) members of the range. Although this product enjoyed some commercial success it was more reactive than typical Procion H-E dyes, rendering it somewhat incompatible in terms of reactivity profile. Indeed, it was noted that the fixation to cellulose began prior to the addition of alkali to the dyebath. Procion Blue H-EG was eventually superseded by the more conventional bis(aminochlorotriazinyl)-substituted triphenodioxazine analogue Procion Blue H-EGN (CI Reactive Blue 198).

The observation that alkali was not essential for fixation of nicotinotriazines to take place was exploited in 1984 by Nippon Kayaku. A full range of bis(aminonicotinotriazine) dyes was introduced, an example being Kayacelon React Red CN-3B, the nicotino analogue of Procion Red H-E3B (Figure 4.11) [22]. Exhaust dyeing is recommended from a neutral bath at temperatures above the boil, conditions that render these dyes suitable, in combination with disperse dyes, for the one-bath dyeing of polyester/cotton blends. By operating at a temperature in the region of 130°C, the diffusion problems expected with such large molecules are minimised [4].



CI Reactive	*Substituent X*	
Red 120	chloro	Procion Red H-E3B (Zeneca)
Red 221	nicotino	Kayacelon React Red CN-3B (KYK)

Figure 4.11

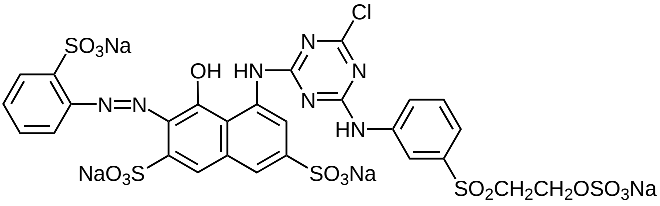
The product of reaction of a bis(aminonicotinotriazine) dye with cellulose is the same as that from the analogous bis(aminochlorotriazine) dye in terms of hue, colour fastness and stability of the dye–fibre bond. If desired, these bis-quaternary dyes can be applied with optimum fixation at 80°C and pH 11, as in the case of Procion Blue H-EG. They have a slightly higher reactivity than vinylsulphone or chlorodifluoropyrimidine dyes, but are less reactive than dichlorotriazine or dichloroquinoxaline systems [23].

The kinetics of quaternisation with DABCO or nicotinic acid and the use of these tertiary amines as catalysts for the high-temperature neutral fixation of the aminochlorotriazine dye CI Reactive Red 3 (Scheme 4.1) and its bis(aminochlorotriazine) analogue Red 120 (Figure 4.11) have been investigated recently [22]. A series of bis-quaternary derivatives of CI Reactive Red 120, including Red 221 as a control, have also been synthesised using trimethylamine, DABCO, pyridine, nicotinamide (pyridine-3-carbonamide) and isonicotinic acid (4-carboxypyridine), as well as nicotinic acid for the control dye. All these dyes performed well in neutral or alkaline dyeing conditions with the exception of the nicotinamido derivative at alkaline pH or at 130°C and pH 7; this was attributed to nucleophilic attack by hydroxide ions leading to ring opening to form an aminotriazine [24].

Aminochlorotriazine-sulphatoethylsulphone dyes

Reaction of a dichlorotriazine dye with an arylamine containing a 2-sulphatoethylsulphone grouping is the preferred route to mixed bifunctional reactive dyes capable of reacting with cellulose either via a monochlorotriazine moiety or a vinylsulphone group. A typical example is Sumifix Supra Brilliant Red 2BF (NSK) shown in Figure 4.12 [25]. Both reactive systems can contribute to the fixation process but the relatively greater reactivity of the vinylsulphone group ensures that most of the fixation arises via this function [21]. Further benefits of this type of structure, however, include the higher substantivity contributed by the triazine bridging residue and the capability this gives to link a sulphatoethylsulphone grouping to a wide range of chromogens.

The presence of two reactive groups that differ in reactivity gives dyes that are less sensitive to exhaust dyeing temperature than typical monofunctional reactive dyes. They can be applied over a wider range of temperatures (50–80°C) and reproducibility of hue in mixture recipes is improved. Moreover, they show minimal sensitivity to electrolyte concentration and are less affected by changes in liquor ratio [26]. Low dyeing temperatures favour reaction via the vinylsulphone group and at higher temperatures the contribution of the chlorotriazine system to fixation becomes more important [27].



CI Reactive Red 194

Figure 4.12

The presence of two types of dye–fibre bond has certain consequences for fastness properties. Mixed bifunctional dyes show superior fastness to acid storage than dichlorotriazine or dichloroquinoxaline systems and better fastness to peroxide washing than difluoropyrimidine or dichloroquinoxaline dyes [28]. Conversely, mixed bifunctional dyes do show some of the weakness to alkaline treatments characteristic of vinylsulphone dyes, although less so than monofunctional dyes relying solely on these groups for fixation [29].

An admirable investigation of 18 isomeric dyes of the 7-phenylazo-*N*-(anilinochlorotriazinyl) H acid series, including CI Reactive Red 194 (Figure 4.12) and two other commercial products, was reported recently [25]. All possible combinations of *o*-, *m*-, *p*-orientation of the sulpho and sulphatoethylsulphonyl groups in the phenylazo and anilino rings at opposite ends of the molecule were evaluated. Interestingly, the three commercially utilised structures showed the highest fixation yields amongst the series of 18 dyes studied.

Aminofluorotriazine-sulphatoethylsulphone dyes

Early in 1988 Ciba-Geigy launched the Cibacron C range of mixed bifunctional dyes. They contain a new aliphatic vinylsulphone system and either a monofluorotriazine bridging group (Figure 4.13) or an arylvinylsulphone function [30]. They are designed mainly for pad applications and appear to be characterised by medium to low affinity, good build-up, easy wash-off and high fixation. Their outstanding bath stability and high fixation make them especially suitable for pad–batch dyeing [31]. The manufacturing cost of these structures is believed to be relatively high but the purchase cost to the dyer may be offset by enhanced cost-effectiveness in use attributable to efficient fixation and easy wash-off, possibly the best approach so far towards environmentally acceptable reactive dyes [4].

An important feature of the Sumifix Supra (NSK) type of bifunctional system (Figure 4.12) is the major difference in reactivities between the amino-

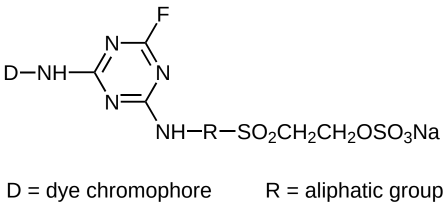


Figure 4.13

chlorotriazine moiety and the much more reactive vinylsulphone group. There are some practical conditions, notably in pad–batch application, that do not allow full advantage to be taken of both types of reactive group present. The combination of aminofluorotriazine and vinylsulphone in the Cibacron C (CGY) system, both groups offering effective fixation under virtually the same conditions, exploits the concept of bifunctionality more effectively.

These factors have been demonstrated elegantly in a detailed evaluation by pad–batch dyeing of cotton with three commercially important copper formazan reactive dyes:

(1) Cibacron Blue F-R (CI Reactive Blue 182) with a monofunctional 2-fluoro-4-sulphoanilinotriazine system.
(2) Sumifix Supra Blue BRF (CI Reactive Blue 221) with a mixed bifunctional 2-chloro-4-vinylsulphonylanilinotriazine system.
(3) Cibacron Blue C-R with a synchronised bifunctional 2-fluoro-4-vinylsulphonylalkylaminotriazine system.

Under the relatively mild conditions of pad–batch fixation within 6 h batching time, the mixed bifunctional system behaved more like a monofunctional vinylsulphone dye and only the synchronised Cibacron C (CGY) system showed truly bifunctional performance [32].

4.4 STRUCTURE AND PROPERTIES

As already noted in the preceding section, the four characteristic features of a monofunctional reactive dye are the chromogen, the reactive system, the bridging link and at least one (but usually more) solubilising group. In a mixed bifunctional structure there are at least two of these except the chromogen, and in symmetrical bis(aminochlorotriazine) or bis(aminonicotinotriazine) dyes there may be twin chromogens (Figure 4.11). The design of reactive dye structures almost always involves one or more compromises between conflicting requirements. There is seldom an ‘ideal’ structure of a desired hue that embodies all possible attractive features with regard to application and fastness properties. The gain in aqueous solubility provided by an extra sulpho group often has to be paid for by a decrease in affinity for cellulose. Enhancement of substantivity is beneficial for high exhaustion but may impair migration or washing-off characteristics. High reactivity offers the possibility of rapid fixation but storage stability may be adversely affected.

4.4.1 Chromogens in reactive dye structures

Providing there are enough sulpho groups to ensure adequate solubility in water, the only essential feature of a chromogen needed to incorporate it into a reactive dye molecule of the haloheterocyclic type is a primary or secondary amino group to which the heterocyclic bridging group can be attached. This also applies to the various ranges of bifunctional systems described in section 4.3.2, since they all contain this same type of amino-*s*-triazine bridge attached to the chromogen. Only in the case of the monofunctional sulphatoethylsulphone dyes is the selection of chromogens more limited by the various ways in which intermediates such as *m*- or *p*-(2-sulphatoethylsulphonyl) aniline derivatives (see, for example, Figure 4.7) can be exploited as an integral part of the chromogenic grouping [3].

Greenish yellow reactive dyes are invariably monoazo types with a heterocyclic coupling component and the reactive system usually located in the diazo component, whereas reddish yellows are usually arylazoanilines with the reactive group on the anilino ring. A recent study of the photochromism of such dyes demonstrated that they tend not to be photochromic if they can form a hydrazine tautomer [33]. Typical orange and scarlet reactive dyes are monoazo derivatives of J acid (Figure 4.5) and in bright bluish reds the all-important coupling component is H acid (see, for example, Figure 4.3 or 4.11). Copper-complexes of 2-aminophenol derivatives, diazotised and coupled with J acid for rubines (Figure 4.9) or H acid for violets (Figure 4.8) dominate the duller and bluer reddish hues.

Twice-coupled H acid chromogens (Figure 4.10) predominate in the navy blue sector because of their economic advantages. The brighter royal blues were traditionally the province of anthraquinone dyes such as Remazol Brilliant Blue R (Figure 4.7) but in recent years the triphenodioxazine dyes such as Procion Blue H-EGN have gained an important share of these hues because they are tinctorially much stronger and hence economically advantageous. Turquoise blues remain totally dominated by copper and nickel phthalocyanine derivatives [3].

4.4.2 Structure and substantivity of reactive systems

The important influence on substantivity of the reactive system itself was recognised in the early years of the development of reactive dyes [10]. The dichlorotriazine group and even more so the aminochlorotriazine or dichloroquinoxaline systems considerably enhance the overall substantivity of the dye. The pyrimidine-based systems, with one less heterocyclic nitrogen atom than the corresponding triazine derivatives, contribute much less to the total substantivity of the structure. The non-aromatic reactive systems, notably the 2-sulphatoethylsulphone group, modify the substantive effect of the chromogen only slightly or not at all. This can offer a significant practical advantage, since a low overall substantivity that remains unaffected by the reactive system promotes completeness of removal of the unfixed dye on rinsing.

4.4.3 Factors governing reactive dye uptake

All conventional reactive dyes for cellulose, irrespective of whether they react by nucleophilic addition, substitution, or both mechanisms (section 4.3), rely on the reactivity of the cellulosate anion as the nucleophilic reagent and hence hydrolysis of the dye by reaction with hydroxide ions from water will always compete with the desired fixation reaction. Reaction between the dye and cellulose can occur only when the dye has been absorbed into the cellulose phase. Thus the kinetics of the dye–cellulose reaction are strongly influenced by the rate of absorption of dye. The ratio of the rate constants for reaction of the dye with the fibre and with water is a constant for a given dye over a wide range of alkaline pH values.

The efficiency of fixation is a function of:

(1) the reactivity ratio, the ratio of rate constants for the fixation reaction and hydrolysis;
(2) the substantivity ratio, the relative concentrations of dye absorbed into the substrate and remaining in the dyebath;
(3) the diffusion coefficient of the dye in the substrate;
(4) the liquor ratio; and
(5) the surface area of the substrate available for absorption of dye [34].

The lower the linear density of the fibre, i.e. the greater the surface area per unit weight, the more efficient is the dyeing. The substantivity ratio is the most influential of the factors governing fixation efficiency. Dyes of higher substantivity diffuse more slowly than less substantive dyes. Changes in dyebath conditions that increase substantivity tend to decrease the diffusion coefficient. Lowering the liquor ratio favours increases in the rate and efficiency of fixation. The full effects of this are never completely realised, however, because the higher dyebath concentration necessary at the lower liquor ratio implies a decrease in substantivity ratio, offsetting some of the expected gain.

Substantivity ratio remains approximately constant within the pH range 7–11 at a given electrolyte concentration, but above pH 11 there is a marked fall in substantivity, especially with highly sulphonated dyes. As the applied concentration of dye is increased at constant electrolyte concentration, the substantivity ratio and hence the efficiency of fixation are lowered. Thus full-depth dyeings require longer for completion of the reaction and the percentage fixation is usually inferior. In order to attain the maximum rate and efficiency of fixation, more electrolyte is needed, but this increases the risk of aggregation and possible precipitation with dyes of limited solubility.

An increase of dyeing temperature lowers the substantivity ratio and accelerates the rate of hydrolysis of the dye; both of these effects reduce the fixation efficiency. The rates of diffusion into and reaction with the fibre are also accelerated, however, and these factors both favour fixation of the dye. An increase in electrolyte concentration always enhances substantivity without impairing reactivity providing the dye remains completely dissolved. The beneficial effects of electrolyte addition are most evident with the more highly sulphonated dyes at relatively high pH and applied depth.

Informative studies of the relationships between dye structure and substantivity [35] and between dye structure and levelling properties [36] are available. The interaction between these dyeing properties and the controlling parameters in exhaust dyeing with reactive dyes, such as applied concentration, pH, temperature and electrolyte addition, is the key to achieving successful and reproducible dyeings.

A valuable classification of reactive dye types has been formulated recently [37]. Three groups relating to the most important control parameter in each case may be distinguished.

Group 1 Alkali-controllable reactive dyes

These dyes have optimal temperatures of fixation between 40 and 60°C. They are characterised by relatively low exhaustion in neutral salt solution before alkali is added. They have high reactivity and care in addition of alkali is necessary to achieve level dyeing, preferably at a controlled dosage rate.

Typical examples of dyes belonging to this group have dichlorotriazine, chlorodifluoropyrimidine, dichloroquinoxaline or vinylsulphone reactive systems.

Group 2 Salt-controllable reactive dyes

Dyes in this group show optimal fixation at a temperature between 80°C and the boil. Such dyes exhibit comparatively high exhaustion at neutral pH, so it is important to add salt carefully to ensure that dyeings are level. Electrolyte addition is often made portionwise or preferably at a controlled rate of dosage.

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Dyes with these properties typically have low-reactivity systems such as trichloropyrimidine, aminochlorotriazine or bis(aminochlorotriazine). Aminofluorotriazine dyes in the Cibacron F (CGY) range have high substantivity and should thus be regarded as salt-controllable but they are sufficiently reactive for fixation at 60°C or even lower temperatures by batchwise application.

Group 3 Temperature-controllable reactive dyes

This group is represented by those dyes that react with cellulose at temperatures above the boil in the absence of alkali, although if desired they can be applied under the same conditions as the salt-controllable group with alkaline fixation at a temperature between 80°C and the boil. Dyes in this group have self-levelling characteristics so there is no need to use auxiliary products to facilitate level dyeing. Good results can be achieved by controlling the rate of temperature rise.

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

4.4.4 Physical form and handling of reactive dyes

All reactive dyes are prone to hydrolysis in the presence of moisture, especially the highly reactive ranges, and they will deteriorate unless carefully handled and stored. Cool, dry conditions are essential and the lids of packages must be firmly replaced after use. Since reactive dyes in powder form may release dust when disturbed, it is always possible for respiratory allergies to arise with some workers who handle them [38]. For this reason suitable dust-excluding respirators should be used and weighing or dissolving procedures should be carried out in ventilated enclosures.

Conventional dye powders are usually dissolved by one of the following techniques:

(1) Pasting with cold water followed by the steady addition, with stirring, of the required amount of water at the correct temperature.

(2) Sprinkling a steady stream of dye powder into the vortex formed by the high-speed stirring of water at the correct temperature.

Few ranges of reactive dyes require boiling water, although Remazol (HOE) vinylsulphone dye powders are dissolved in boiling water followed by passing immediately through a fine sieve into the required volume of cold water. Highly reactive dyes, such as dichlorotriazine or chlorodifluoropyrimidine types, require water temperatures no higher than 50°C. Most dyes of lower reactivity, e.g.

aminochlorotriazine or trichloropyrimidine systems, require a dissolving temperature of 80°C.

The dusting problem with some reactive dye powder brands can be avoided by working with granulated or liquid formulations. A recent improvement that ensures troublefree weighing and handling of small amounts for batchwise dyeing has been the development of cold-dissolving granular brands such as the Drimarene CDG (S) dyes [39–43]. These are non-dusting, free-flowing grains that dissolve readily in cold water and offer ease of handling in automatic dissolving and metering devices.

The marked tendency of reactive dyes to undergo hydrolysis in solution has delayed the development of liquid formulations until recent years. For continuous dyeing and printing, however, especially where automated metering equipment is installed, liquids are particularly convenient. Liquid brands of the relatively stable types, such as sulphatoethylsulphones, aminochlorotriazines and bifunctional dyes containing both of these systems [44], are well established in commercial use. They are essentially isotropic aqueous solutions of the dyes, often with auxiliaries such as a buffer, a hydrotropic agent such as urea or caprolactam, and often a polymeric stabiliser to inhibit settling out on storage [4].

4.5 BATCHWISE APPLICATION

In spite of the essential simplicity of reactive dyeing methods, there are few instances where dyes based on one type of reactive system show fully satisfactory compatibility with those of another type. Even if competing dyes have identical chromophoric groupings, there may well be marked differences in application behaviour and fastness properties of the resulting dyeings. In selecting a range of reactive dyes for batchwise dyeing, however, the dyer has considerable freedom of choice since almost all required hues are fully represented in every range. Selection is largely based on application technique and consideration of the end use of the material.

Reactive dyes can be applied by any conventional batchwise dyeing method for cellulosic materials, including circulating-liquor machines for loose stock, yarn or woven fabrics, as well as jets, winches or jigs for piece dyeing. The conventional dyeing process entails three stages:

(1) Exhaustion from an aqueous bath containing electrolyte, normally under neutral conditions.
(2) Addition of alkali to promote further uptake and chemical reaction of absorbed dye with the fibre at the optimal pH and temperature.
(3) Washing of the dyed material to remove electrolyte, alkali and unfixed dye.

Numerous variants of this basic procedure in terms of chemical concentrations and fixation conditions have been devised to take account of the characteristic properties of the numerous ranges of reactive dyes now available.

Considerable research over several decades has led to the present selection of processes to apply each range of dyes in such a way that optimal fixation efficiency and level dyeing are achieved. In recent years these studies have been concerned particularly with dyes that contain bifunctional reactive systems. For example, a detailed investigation of levelling characteristics has compared a bis(vinylsulphone) and a bifunctional aminochlorotriazine–vinylsulphone with several conventional monofunctional vinylsulphone dyes [36]. Factors controlling the rates of exhaustion and level dyeing behaviour have been analysed to define optimised conditions recommended for batchwise dyeing with Procion H-EXL (Zeneca) bis(aminochlorotriazine) dyes [45] or with Sumifix Supra (NSK) aminochlorotriazine–vinylsulphone dyes [46].

4.5.1 Preparation and chemicals required

Except in special instances, batchwise preparation before reactive dyeing is carried out in the dyeing machine itself or in equipment of similar design reserved for the preparation stage. The essential requirements are that the material must be made available for dyeing in a neutral, uniform and readily absorbent state. In contrast to the application of vat or sulphur dyes, typical reactive dyeing processes will not eliminate natural or added fats and waxes.

Acceptable results are often possible on knitgoods without lengthy pretreatment, as in the pad–batch or hot batchwise dyeing processes in the presence of a powerful wetting agent. Residual size must always be removed from woven goods because of the risk of dye wastage by reaction with hydroxy groups in size components. Owing to the brilliant hues of many reactive dyes, sufficient brightness may be attainable on woven cotton without prebleaching. Thoroughly desized and scoured fabrics can be used in many cases. Where bleaching is necessary it is imperative to check that all traces of residual chlorine or peroxy compounds are removed prior to dyeing, otherwise loss of reactivity and even partial destruction of some dyes can occur. There is considerable variation in the ability of reactive dyes to cover dead or immature cotton. For this reason it may sometimes be necessary to causticise or mercerise woven fabrics in order to achieve a satisfactory appearance in certain hues. Such pretreatments give the further advantage of better colour yield.

With few exceptions, reactive dyes have good solubility in water. Although seldom sensitive to neutral hard water, precipitation of hardness constituents results at the alkaline fixation stage and thus soft water should be used for all dissolving and dyebath operations. Sources of water with variable bicarbonate content, as might arise in a water supply with temporary hardness, can adversely affect the reproducibility of the dye fixation conditions. The influence of the bicarbonate anions largely depends on the alkali used for fixation. Alkalis based on sodium hydroxide exhibit higher sensitivity than sodium carbonate systems [47].

The use of either common salt (sodium chloride) or Glauber's salt (hydrated sodium sulphate), in large amounts, is essential to all batchwise dyeing processes for reactive dyes. The relative prices, purity and availability of these electrolytes vary considerably in different parts of the world and selection must take account of this. Common salt is widely used, but Glauber's salt is preferred with certain bright royal blues based on anthraquinone chromogens and turquoise or green hues dyed with copper or nickel phthalocyanine derivatives. Common salt is more soluble and easier to dissolve than Glauber's salt. Electrolyte, from whatever source, must be free from alkali, since the latter causes premature fixation or hydrolysis of the dye.

The impurities that can significantly influence the reproducibility of the dyeing process are the alkaline earth metals calcium and magnesium, as well as the transition elements copper and iron. Their adverse effect on the process can be seen as inferior reproducibility, unlevel dyeing and lower wet fastness. The quality and source of electrolyte have a major influence on the levels of trace metal impurities introduced into the dyebath. Common salt is obtained from underground deposits or from seawater. The levels of metal ion impurities vary according to source and degree of purification [47]. These impurities can be controlled by the appropriate use of sequestering agents, taking into account the pH and temperature of the dyeing process. Uncontrolled use of organic sequestrants, such as ethylenediaminetetra-acetic acid, can lead to problems of hue change and lower light fastness. All metal-complex reactive dyes, with the exception of the phthalocyanine derivatives, will give rise to this effect.

Whilst soda ash (98% anhydrous sodium carbonate) remains the most widely used alkali for reactive dyeing, sodium bicarbonate, sodium silicate, caustic soda and various phosphates are also important. Alkalis of high purity are recommended and additions of solid brands should be well-diluted beforehand. Hot, damp conditions of storage should be avoided and dry scoops should be used when weighing. Sodium bicarbonate should be dissolved at low temperatures and direct heating by steam injection must be avoided. Caustic soda and sodium silicate are normally marketed and used as concentrated liquors of known concentration. In recent years, liquid buffer systems and liquid alkali products such as Alkaflo (Tanatex) have been introduced mainly for automatic dosing and metering systems [48].

Provided goods have been prepared efficiently for exhaust dyeing, it is unnecessary to add wetting or levelling agents to the dyebath. In winch or overflow dyeing of tubular-knitted cotton, however, minimal addition of a wetting agent can provide a lubricating action for the avoidance of rope marks. After any pretreatment with wetting agent, thorough rinsing is advisable before a fresh bath is set for dyeing, in the interest of reproducibility. Unwanted foam in jet or overflow machines can be minimised by careful addition of selected antifoam agents. When dyeing in enclosed machines at temperatures higher than 70°C, certain azo reactive dyes may undergo reduction owing to the combined effects of heat, alkali and aldehydic groups in the cellulose. If this problem is expected to occur, it is advisable to add 1–2 g l^{-1} of sodium *m*-nitrobenzenesulphonate as a protecting agent.

4.5.2 Package dyeing of yarn

Reactive dyes are well established for dyeing all types of cotton materials, including sewing threads, in circulating-liquor machines as loose stock, yarn packages or beams of woven fabric. These units are controlled by fully or semi-automatic systems, wholly or partially programmed to regulate temperature, process time, flow-direction cycles, dyebath additions, dosage rates and sequence changes. Machine functions and substrate form (type of fibre, uniformity and accessibility) determine not only the quality of dyeing but also the dyeing procedure.

The more thorough the access of dye liquor to the material, the better the levelness and penetration. Rapid dyeing cycles require uniform liquor circulation, which in turn depends on the efficiency of machine loading and the quality of package winding. The latter is determined by angle of wind, tension and material density, and it must allow uniform and consistent flow of liquor. If circulation is poor or non-uniform, good-quality dyeings might still be possible but relatively long dyeing cycles would be necessary, particularly at the critical stages of levelling in salt solution and alkali dosage. If feasible, chemical additions should be made when the liquor is circulating from outside to inside. Special care is necessary with yarns for plain weaving or knitting, as opposed to effect threads in a coloured woven or knitted design.

Where penetration problems are anticipated, as in certain mercerised high-twist or multi-ply yarns or in most narrow fabrics, it is advisable to use low-reactivity dyes at temperatures above 70°C, withholding the alkali addition until at least 30 min after the final addition of salt. When dyeing such materials as webbing, braid or zip-fastener tape, levelling in neutral salt solution can be improved by raising the temperature to the boil or preferably 120°C, before cooling to the optimal temperature for the alkaline fixation step. This technique is not always applicable and all copper-complex dyes are unsuitable, except the copper phthalocyanine derivatives. A reduction inhibitor should be present from the start of dyeing.

Conventional package-dyeing machines for cotton yarn operate at a liquor ratio between 10:1 and 15:1. By comparison, short-liquor processing equipment is designed for use at liquor ratios in the range of 4:1 to 6:1. The flow rate, i.e. the amount of liquor pumped through the material, depends on the resistance to flow of the substrate and the efficiency of the pump. The contact number, or rate of exchange of liquor, is one of the most important parameters in yarn dyeing [49]. In short-liquor dyeing the total liquor volume passes through the substrate mass much more frequently than in conventional equipment. The higher the contact number, the better the conditions for level dyeing. Short-liquor processing offers the possibility of tolerating faster rates of heating and cooling.

A short liquor ratio can be achieved either by lowering the liquor level in the vessel (sump dyeing) or by filling the chamber as full as possible with yarn packages. In the sump method, the packages are not immersed completely in the dyebath and dye liquor can only be pumped in one direction (out-to-in). This has no adverse effect on the quality of the dyeings but packages must be correctly prepared and leakages avoided. This is achieved using large cylindrical packages wound on special tubes, fitted together and compressed into a continuous column in a hydraulic press [50].

In order to introduce short-liquor methods successfully in yarn processing other developments must be considered, such as:

(1) automatic dosing techniques;
(2) adjustable flow of circulation pumps;
(3) synchronised dyeing;
(4) electronic control (section 4.5.8).

In synchronised dyeing systems for yarn packages the exchange of dye liquor is constantly adjusted throughout the process. The extent of the adjustment is dependent on substrate, substantivity and processing conditions. Experience confirms that a considerable improvement in the physical quality of the dyed yarn can be achieved [49]. The increasing trend in package dyeing is towards high-volume pressed packages weighing 1.2–2 kg per package. These can often be used directly, without rewinding, in automatic weaving and knitting machines.

4.5.3 Jig dyeing of woven fabrics

In spite of the outstanding growth in pad–batch dyeing with reactive dyes, jig machines are still widely used for woven cotton. They pose a special problem for reactive dyeing in that marked variations in temperature can exist between the dyebath and the exposed edges of the fabric rolls. Such differences result in 'listed' selvedges that are either paler or off-tone relative to the remainder of the dyed fabric. 'Ending' can also be apparent because the draw roller (initially at ambient temperature) tends to abstract heat from the adjacent layers of fabric. The equilibrium uptake of dye is not greatly affected but the dye–fibre reaction rate is appreciably reduced at lower temperatures.

The use of high-reactivity dyes with medium to high substantivity is the most effective solution to this problem,. Dyebath temperatures of 30–40°C are sufficiently close to ambient conditions, resulting in negligible temperature differentials throughout the goods even under the most adverse conditions. Such dyes exhibit good build-up on the jig at operating liquor ratios in the range 3:1 to 6:1. Pad–jig development gives improved surface appearance and penetration with difficult fabrics. A high pick-up should be avoided to reduce the likelihood of seepage defects. The padded cloth may be passed directly to the jig, set with the full amount of salt, for immediate development. Alternatively, quality can be improved by holding on the turning batching roll for about 30 min before passage to the prepared jig.

4.5.4 Winch and jet dyeing

When reactive dyes were first introduced for dyeing knitted and lightweight woven fabrics suitable for processing in rope form, these materials were dyed at long liquor ratios in the range 20:1 to 30:1 on simple winch machines. These lacked liquor circulation or separate addition tanks and poor reproducibility of liquor ratio and temperature was unavoidable. Particular care was necessary to avoid damage during preparation and dyeing, e.g. abrasion, rope marks, 'crowsfoot' creasing and running streaks. Disadvantages often associated with reactive dyeing on the traditional winch included:

(1) insufficient agitation of the fabric;
(2) variable liquor ratio;
(3) lack of control of temperature rise;
(4) imprecise temperature of fixation;
(5) high energy consumption for dyeing and washing-off;
(6) large amounts of chemicals required;

(7) large volumes of waste dye liquors;
(8) high degree of manual operation.

The introduction of temperature regulation was particularly important for reactive dyeing because it was the first essential step towards adequate control of the process. It led to the decline of high-reactivity dyes in long-liquor dyeing and the development of improved low- and moderate-reactivity ranges of more substantive dyes that followed a more favourable exhaustion–fixation profile.

The discovery and rapid exploitation of the pressure jet dyeing machine for polyester fabrics in the late 1960s led to the introduction of atmospheric jet machines for the reactive dyeing of cotton knitgoods during the next decade. The pump and venturi jet provided effective liquor circulation and these machines were equipped with time–temperature controllers, a separate addition tank and mechanical features to minimise creasing problems. It was possible to operate at lower liquor ratios in the range 8:1 to 12:1 and to achieve improved liquor flow and level dyeing.

These developments promoted liquor exchange so effectively that differences in temperature and concentration within the system became negligible, making it possible to reduce the liquor ratio further and satisfy demands for a more cost-effective process. This reduction of the liquor ratio brought two problems, however: manual addition of the salt to control levelling and manual addition of alkali to bring about fixation [51]. There were restrictions on the addition of salt during running, so the salt-at-start technique became established. The development of metering technology then facilitated accurate control of the reaction at constant temperature. A direct result of short-liquor application is to enhance substantivity at a given salt concentration, or to attain the same substantivity with less salt.

A liquor ratio of 5:1 is regarded as the effective minimum for conventional short-liquor dyeing. It is limited by the solubility of the dye, the levelness attainable and the availability of liquor for dissolving and addition of chemicals. The more rapid and higher exhaustion that occurs at these concentrations brings potential problems of unlevelness, owing to various causes:
(1) Dyebath exhaustion reached too rapidly (uneven uptake).
(2) Excessive exhaustion (inefficient levelling).
(3) Solubility of dye exceeded (uncontrolled surface deposition).

These risks can be countered by improved control of temperature and rate of salt addition, extending the duration of the migration stage before the controlled addition of alkali [52].

In fabric rope-dyeing equipment the decrease in liquor ratio has not stopped at the conventional limit of 5:1. As the development of the Then Airflow and the Thies Rototherm machines demonstrate, liquor ratios as low as 3:1 are attainable by rotating the goods in a dyebath-free chamber using continuous impregnation and recirculation of excess dye liquor leaving this chamber. This method is known as the ultra-low liquor ratio (ULLR) technique.

The dye–fibre reaction thus takes place from a dyestuff concentrate. This implies a high initial rate of fixation and a correspondingly high risk of unlevelness. The ULLR method thus requires a lower starting temperature, low-substantivity dyes, minimum electrolyte levels and pre-buffering to a low pH. Two-stage addition of the salt minimises the risk of precipitation of the dye at the excessive concentration unavoidable in the initial stage. For most reactive systems the economic benefits claimed for the ULLR technique are difficult to confirm [51].

4.5.5 Garment dyeing

This has become increasingly important in recent years. This trend arose in the 1980s because of the greater dependence of retailers on quick change in colours to meet their need for rapid fashion response. Garment dyeing meets these requirements and lead times have been reduced to one week, as against several weeks with other processing routes [53]. Demand for leisurewear garments has grown and such garments are highly colour- and fashion-oriented. Garment dyeing also offers reduced stockholding and improved monitoring of stocks in fashion colours. Four categories of garment dyeing are important:

(1) Fully fashioned garment dyeing.
(2) Cut and sew garments dyed to high fastness.
(3) All-cotton ‘boutique’ garments dyed to relatively low fastness.
(4) Desizing, bleaching and after-washing of yarn-dyed denim.

Traditionally garments were dyed with little agitation and slow liquor interchange in paddle machines at liquor ratios of 25:1 to 40:1. Although suitable for loosely knitted fully fashioned garments these conditions give problems in seams or thick areas of heavier garments. The advent of energy-saving rotary dyeing equipment in the 1970s operating at liquor ratios close to 10:1 eventually allowed the dyeing of a much wider variety of fashionable garment constructions. Modern versions of such machines with integral centrifuging and short processing cycles lend themselves ideally to the quick turnaround times now seen as essential [53–55].

Cotton garment dyeing is particularly suited to the production of the ‘totally relaxed' fashion look associated with leisurewear and the 'distressed' look typical of after-washed denim goods. The last decade has seen periods of high demand for such merchandise. Fashion trends are dynamic, however, and developments have also been undertaken for markets and end uses where a 'neat' or 'pristine' appearance is demanded [53,56].

A notable advantage of machinery incorporating centrifugal action is the efficient rinsing action in a short time. When dyeing cotton with reactive dyes the washing-off stages can be decreased from about 60 to 10 min, drastically reducing overall process time. Control of all machine functions and process parameters may be accurately regulated automatically. Systems are available whereby the dyeing machine may be controlled from a central console, including automatic additions of dyes and chemicals from a central dispensing area.

The requirements of a reactive dye range for cotton garment dyeing include:

(1) good level dyeing properties;
(2) rapid migration and diffusion properties to assist seam penetration;
(3) reproducibility of hue in combination recipes;
(4) suitability for automated rapid processing.

The higher the reactivity of the dye system, the lower the application temperature and the higher the rate of fixation at alkaline pH. The above requirements are met by low-reactivity dyes with a high temperature of fixation so that diffusion and migration are optimised. Linear addition profiles for both dye and alkali additions are preferred to assist level dyeing. Rinsing and soaping are favoured in rotary-drum machines using the hydroextraction facility that greatly improves liquor interchange between rinses.

Problems and faults that may arise in garment dyeing have been outlined [57–59]. These include shrinkage, surface abrasion, peeling or linting, creasing, deformation, unlevel dyeing and poor penetration of seams. Trimmings, buttons, zips and other accessories may give special difficulties. The design of such garments, particularly sportswear and other stretchable constructions, must envisage and provide for the garment dyeing stage. This requires closer links between designers, manufacturers, finishers and retail organisations. The fabric should be designed, manufactured and prepared with processing shrinkage in mind and the inclusion of seams, sewing thread, zips and other accessories planned to minimise potential problems at the dyeing stage.

4.5.6 Dyeing of regenerated cellulosic materials

Exhaustion and fixation of reactive dyes on viscose or modal fibres are normally higher than on cotton or linen, but this is not generally true for polynosic or high-tenacity fibres. The substantivity of individual dyes for these less amorphous regenerated fibres is somewhat more variable. Many reactive dyes show significantly higher fastness to light on viscose than on cotton at equivalent applied depths. The recent development of viscose micro-fibres has brought reflectance values and colour yields closer to those of cotton, improving solidity in blends [60,61].

Lightweight viscose materials can be dyed at relatively low temperatures with high-reactivity dyes using processes that are not much different from corresponding methods for cotton. Yarns and fabrics made from viscose fibres of larger diameter or heavyweight fabric constructions may show poor penetration and surface frostiness under these conditions, however. Dyes of low to moderate reactivity requiring fixation temperatures of 60°C or higher give better results on materials that give inferior levelling or inadequate penetration at lower temperatures.

Salt and alkali requirements are generally lower for reactive dyes on viscose than for the corresponding dyeings on cotton but most turquoise and green hues based on phthalocyanine derivatives are applied according to special recommendations. The pad–jig development process outlined for cotton (section 4.5.3) also gives satisfactory results with woven viscose fabrics. Under alkaline conditions in enclosed machines, viscose tends to give problems of reduction with certain sensitive azo reactive dyes. Addition of a reduction inhibitor from the start of dyeing is essential.

4.5.7 Dyeing of bast fibres

After appropriate preparation, flax yarns and linen fabrics can be dyed by conventional methods developed for cotton. Residual lignin takes up more dye than the cellulosic component, resulting in a speckled appearance and sometimes an off-tone colour. These deeply dyed specks decrease in depth by desorption of the poorly fixed dye during subsequent alkaline fixation and washing treatments. Every effort should be made to remove these impurities as much as possible before dyeing.

In package dyeing flax yarns are more readily penetrated using reactive dyes than by vat dyeing. Dye–fibre reactivity and ultimate fixation efficiency are closer to those of unmercerised rather than mercerised cotton and thus appreciably less than on viscose materials. Careful attention is necessary during the critical levelling and diffusion stage just before and during the addition of alkali.

Causticised linen woven fabrics generally give satisfactory results under normal conditions for cotton. Pad–jig development is regarded as the best approach for the coverage of slubs or other surface irregularities. The pad–batch process is especially attractive for many linen qualities because of the excellent dye diffusion in reasonably short batching times. Careful dye selection is necessary for woven linen that is to be given a crease-resist finish.

Limited amounts of ramie are dyed with reactive dyes by methods similar to those for cotton. Bleached jute is batchwise dyed with reactive dyes using salt and careful additions of soda ash. Jute is somewhat sensitive to alkali and control of alkaline pH and temperature conditions is important. Sisal is sometimes dyed with reactive dyes because of their attractive hues, good light fastness and excellent fastness to water, although poor penetration of certain constructions can present problems. Unsatisfactory results are obtained on coir and other bast fibres, however, owing to their deep natural colours and high content of non-cellulosic impurities.

4.5.8 Developments in automation of reactive dyeing

Considerable progress has been made in reducing the need for manual intervention in batchwise dyeing processes for reactive dyes by automating the marginal operations. Isothermal process cycles based on automated control, compared with conventional techniques involving portionwise additions of dyes and chemicals, have been devised. The dye, salt and alkali may be added according to predetermined profiles over a given time period and additions are controlled from dyeing programmes stored in the microprocessor memory. This type of control contributes to the high degree of reproducibility between repeat batches that is a prerequisite for the market demands of ‘right first time’ production [62–64].

The modern multi-product injection (MPI) dosing systems enable an exact amount of product to be added to a process bath over a certain period of time by means of an electronically controlled system, including intermittent, linear, progressive or exponential rates [65–70]. Thus the dyer can control the dosage of dyes and chemicals as well as temperature and process time, thereby directly influencing the course of the chemical and physical reactions taking place in the dyeing system. Reproducible dyeings can thus be achieved, since dosing always takes place under identical conditions. Liquid and solid dosing equipment can be connected permanently to the dyeing machine, or may be utilised as a portable unit, servicing several machines [71]. In summary, the MPI dosing system offers the following advantages:

(1) Total automation of the dyeing process, saving time and avoiding human errors.
(2) Ensuring that the necessary chemicals are always available.
(3) Increased control and reproducibility of the dyeing process.
(4) Improved levelness of the resulting dyeing.
(5) Reduced risk of dye aggregation or precipitation during short-liquor dyeing of full-depth colours.
(6) More efficient rinsing and washing, since there is less hydrolysis of dye during the process.

Methods of control of parameters relating to the physical characteristics of the material to be dyed, taking into account the influence of mechanical and hydraulic forces exercised by the dyeing machine during the process, are now being introduced [72]. A new generation of process control equipment allows the action of these forces in the dyeing machine to be adjusted, not only for the entire process, but even for each stage of the dyeing cycle. Thus the total energy transmitted to the dyed substrate is reduced, with a consequent improvement in surface appearance because there is less fibre disturbance and abrasion.

In the processing of yarn packages, mechanical and hydraulic influences may impair the physical properties of the yarn. In order to preserve the quality of the yarn, the pump delivery should be reduced to avoid undue turbulence [73]. The consequent risk of unlevel dyeing makes adoption of MPI dosing essential. Only by the controlled addition of dyes and chemicals at a lower liquor throughput can satisfactory dyeing be achieved.

In some instances the turbulence and frictional forces in a jet dyeing machine can adversely affect the surface appearance of the fabric. This reduction in quality can be avoided by reducing the speed of movement of the fabric rope and the rate of liquor flow through the jet nozzle. In doing this there is a risk of unlevel uptake. In order to apply a synchronised dyeing system under jet dyeing conditions [74], it is necessary to determine the kinetics of the dyeing process and to understand the interactions with the following fundamentals of the machine:
(1) Circulation pump (variable flow).
(2) Transporting reel (variable speed control).
(3) Automatic dosing (MPI system).
(4) Machine control (fully automatic microprocessor).

4.6 SEMI- AND FULLY CONTINUOUS APPLICATION

The lower limit of liquor ratio attainable in batchwise dyeing is about 5:1 or, in specially designed ULLR equipment, possibly 3:1. Padding methods extend this further to the range 1:1 to 0.5:1. Thus the advantages of enhanced exhaustion and fixation characteristic of short-liquor exhaust dyeing can be significantly improved by adopting semi- or fully continuous processes. Depending on the reactivity of the dyes selected and the temperature of treatment, fixation times can vary over a wide range. Slow fixation is of particular interest to achieve controlled diffusion, penetration and levelness on certain type of substrate, whilst rapid fixation is of greater relevance to optimal economy and productivity.

In the early days of reactive dyeing it was soon recognised that the excellent solubility, moderate substantivity and versatile reactivity of the various ranges of reactive dyes gave them great potential in continuous dyeing applications. This promise has been fully realised in the extremely wide variety of process sequences and conditions of treatment now available. These include the simpler single-pad methods in which the dye and alkali are applied together, as well as the more elaborate but versatile double-pad sequences where the dye and alkali are padded separately, with or without an intermediate drying step. In addition to the standard processes for woven cotton, linen and viscose fabrics, more specialised routines and equipment have been devised for the pad–batch dyeing of knitgoods and the pad–steam dyeing of narrow fabrics.

The semi-continuous pad–batch process offers a means of producing runs of moderate length to each colour at low capital cost. In effect, this process is an exhaust method at extremely low liquor ratio and ambient temperature in which all the dyebath is entrained within the substrate. The impregnated batch is stored separately from the padding equipment and this allows wide variation of dwell time according to the reactivity of the dyes selected and the pH of the impregnated fabric.

Continuous dyeing represents the highest level of productivity, in which the dwell time after impregnation is reduced to a few seconds or minutes by heating the fabric to a high temperature, but this approach entails much higher capital cost. One of the advantages of reactive dyes is that they possess all the attributes necessary for fully continuous dyeing. This can be achieved without unduly sophisticated machinery, as on the pad mangle, drying cylinders and washing range adopted in the successful trials carried out with the first range of reactive dyes to be marketed [8].

In an early investigation of the substantivity and diffusion properties of selected dichlorotriazine, dichloroquinoxaline, aminochlorotriazine and trichloropyrimidine dyes, the fundamental parameters of padding with reactive dyes were interpreted in terms of these characteristics [75]. Dyes of widely differing characteristics do not behave satisfactorily in combination, neither in exhaust dyeing nor in padding processes. Dyes developed primarily for exhaust dyeing tend to have high substantivity and to diffuse slowly, whereas low-substantivity dyes that diffuse quickly are preferable for application and washing-off continuously.

4.6.1 Pad–batch dyeing

All pad–batch processes follow the following general sequence:

(1) Impregnation of the well-prepared dry fabric in a solution of dye and alkali at ambient temperature.
(2) Uniform squeezing of surplus liquor from the fabric as it passes through the mangle nip.
(3) Wrapping of the batched roll of wet fabric in polythene film and storage at ambient temperature for a specified dwell time (2–24 h, depending on dye reactivity and pH).
(4) Washing-off of unfixed dye.
(5) Drying of the washed dyeing.

The success of this simple but efficient technique is attributable to the low capital cost of the equipment, low consumption of energy and water, excellent reproducibility and scope for selective control of the dye–cellulose and dye–water reaction rates. Batch lengths of 1000–10 000 m per colour, excessive for exhaust dyeing to the same degree of reproducibility but inadequate to justify investment in a fully continuous range, can be processed economically.

With moderate and high-reactivity dyes it is essential to employ a liquor feeding device, to bring dye and alkali streams together immediately before the mixed padding solution contacts the fabric to be dyed. Several reliable systems have been devised for this purpose. The initial approach was a stainless steel pneumatically operated tipping bucket into which solutions of dye and alkali were metered separately and mixed *en route* to the padding trough. More recently, various designs of electrically operated dual metering pumps and valves have been used, whereby the solutions are mixed and delivered to the trough at a known rate of flow [76]. A recent investigation of the use of residual alkali from mercerising to activate the dye solution in the pad–batch dyeing stage was intended to eliminate the need for proportioning pumps and to economise on water consumption by minimising dye hydrolysis [77].

Although high-reactivity dyes may be preferred because they enable dwell times as short as 2–4 h to be used, demands for specific hues, fastness or cost advantages may favour applying low-reactivity dyes at high pH for longer dwell times, possibly 16–24 h or longer. When dyeing viscose or modal fibres, their different swelling behaviour compared with cotton must be taken into account. On such fabrics and certain qualities of mercerised cotton, dye penetration and surface appearance can be improved appreciably using a slower fixation treatment. Recommendations have been given for the pad–batch dyeing of viscose and modal fibres after silicate-free cold-dwell bleaching [78,79].

Tailing effects accompanying many padding processes arise from the selective affinities of the individual dyes for the substrate. A deeper colour at the beginning of a run progressively ‘tails’ (weakens) to a paler, sometimes off-tone, colour as the run continues. Tailing with reactive dyes is troublesome much less often than with direct dyes. In pale depths under unfavourable conditions, however, preferential absorption can occur until a satisfactory equilibrium has been reached by feeding the trough with an adjusted dye solution. When dyes that differ in affinity are used together they can show selective absorption so that changes in both hue and depth will occur unless corrective steps are taken. Substantivity factors and mechanical causes of tailing have been specified and measures necessary to overcome these problems have been explained [80,81].

For single padding processes with reactive dyes, ‘one dip one nip’ is preferable to a multi-dip and multi-squeeze technique. The simpler system minimises tailing and permits the smallest possible pad trough volume consistent with thorough wetting and impregnation. Running conditions that allow a complete change of liquor in the trough every 2–3 min throughout the run are ideal for most purposes. Mangle pressures are set to give a liquor pick-up of 60–80% at ambient temperature. The Bicoflex IFAS (intelligent flexible application system) can be used to control liquor application. The Bicoflex roll allows the squeezing pressure to be adjusted across the width of the fabric to even out variations in liquor pick-up attributable to variations in moisture content or thickness of the fabric [82,83]. If desired, liquor pick-up across the width can be deliberately varied to achieve novel effects. The CVC padding roller with a continuously variable crown and a controlled pressure nip system can be adjusted to give desired profiles of linear pressure across the fabric surface [84].

Tubular-knitted cellulosic fabrics can be dyed on suitably designed equipment by the pad–batch method, although the capital cost of open-width washing ranges has retarded adoption of these techniques in the knitgoods field [85,86]. The problem of folded edge marking and measures to overcome this have been outlined [87]. Specialised impregnation units introduced for pad–batch preparation and dyeing of knitted cellulosics include those of Beau Tech [88], Jawatex [89] and Calator [90]. Substantial savings of energy, water, chemicals and labour requirements, compared with exhaust methods, are claimed.

Convincing reasons can be cited in favour of any of the major reactive systems in pad–batch application [91]. Highly reactive dyes can be fixed in shorter times at lower pH and are often easier to wash off, low-reactivity ranges offer higher stability in the padding liquor and mixed bifunctional systems give highly efficient fixation and excellent fastness performance. Detailed recommendations have been provided for systems of all kinds, including chlorodifluoropyrimidines [92], dichloroquinoxalines [61,93] and aminofluorotriazine–vinylsulphone bifunctional dyes [30,31].

Radiofrequency energy has been evaluated to increase the rate of fixation in pad–batch dyeing trials with sulphatoethylsulphone, bis(aminonicotinotriazine) and aminochlorotriazine–vinylsulphone dyes [94]. The dwell time required was reduced from several hours to about 15 min by heating the impregnated fabric in the radiofrequency field. Colour yields with the monofunctional dyes were lower than under conventional pad–batch conditions but the mixed bifunctional types gave equivalent or superior colour yields and washing fastness after radiofrequency fixation. Bis(aminonicotinotriazine) dyeings applied in this way were equivalent to exhaust dyeings under neutral conditions at 130°C, the appropriate control method in this case.

4.6.2 Pad–dry and pad–dry–bake methods

With skilled organisation and management, fully continuous dyeing methods offer economic advantages when long runs are required in a limited range of colours. Listing and ending are avoidable and excellent reproducibility is possible, with noteworthy savings in handling and labour costs. The minimum length to each colour on large multiple-units ranges is usually estimated at about 10 000 m, depending on local circumstances and avoidance of excessive downtime. The dye–fibre reaction takes place extremely rapidly in the presence of minimal amounts of concentrated alkali at elevated temperature. With highly reactive dyes the dwell times are sufficiently short to permit fixation simply by passing the impregnated fabric through a conventional dryer.

Thorough and uniform preparation of the fabric and presentation to the padding trough and mangle in a crease-free state are crucially important. Where doubt exists about the absorbency of the fabric to be dyed an addition of wetting agent may be necessary. The first pad–dry process originally developed for applying dichlorotriazine dyes together with 10 g l^{-1} sodium bicarbonate is still important with those and other high-reactivity ranges. Urea may also be added to improve the solubility of the dyes in full depths, as well as salt or sodium alginate to minimise migration problems during drying. Fortunately, migration in pale depths (where tailing faults are more prevalent) is rarely severe.

Migration shows itself as either ‘mealiness’ at the fabric surface or side-to-centre colour differences across the width of the fabric. Such effects may be attributable to faulty preparation, a pad bowl fault or excessive local heating in the dryer. Back-to-face colour differences or ‘twosidedness’, where one face of the cloth is paler than the other, may arise from the fabric construction or be caused by movement of the dye solution towards the source of heat owing to uneven distribution of heat above and below the fabric during drying. For optimum colour yield in the pad–dry process using a hot flue dryer, it is necessary to maintain a moisture content not less than 20%, i.e. a high wet-bulb temperature is required. By control of the air extraction system it is possible to ensure the presence of free moisture in the dryer.

Further factors that influence the degree of migration include the swelling behaviour of the substrate, the presence of auxiliaries, the solubility of the dyes and their substantivity and reactivity characteristics. The lower the substantivity of a dye, the greater is the risk of migration. The higher the reactivity of a dye, the lower the migration in the presence of alkali because only unfixed dye molecules are free to migrate. Hence highly substantive dyes containing a high-reactivity system are the least prone to migration problems [95].

Urea is still widely used in continuous dyeing and printing with reactive dyes as a dissolving assistant, a disaggregating agent, a swelling reagent for cellulose and a hygroscopic auxiliary. It is difficult to specify which of these effects is the most important in any given process. Nevertheless, it certainly enhances colour yield, accelerates diffusion and improves the levelness of the dyeing, particularly on viscose fabrics. Although cheap and readily available, urea is not an ideal chemical from the environmental viewpoint and alternatives are being explored with a view to partial or complete replacement of urea by other compounds, such as dicyandiamide [96], trimethyl- or tetramethylurea, or poly(ethyleneglycol) [97].

Soon after the aminochlorotriazine dyes were first introduced, it was recognised that the pad–dry process with bicarbonate, though highly successful for dichlorotriazine types, was totally unsuitable for low-reactivity dyes. Investigation led to the pad–dry–bake sequence, still occasionally of interest where the expensive but more versatile pad–steam range is not available. Typically, the dyes are padded with 10–20 g l^{-1} sodium carbonate and 100–200 g l^{-1} urea. Little fixation takes place during intermediate drying and a baking treatment (e.g. 1 min at 150°C) is necessary to complete the dye–fibre reaction.

Many viscose fabrics show excessive migration and poor diffusion of the dyes, evident as inadequate penetration of colour. These materials can be handled far more satisfactorily by the pad–batch route. A further defect of the pad–dry–bake process is a lack of chlorine fastness from dyes that are normally satisfactory. They become less resistant to chlorine as the severity of the baking treatment increases. The thermal decomposition of urea under dry conditions is the main contributing factor in lowering the fastness of the dyeings to chlorine and also, in some instances, to light.

In recent years there has been considerable interest in applying radiofrequency and microwave methods of heating to the fixation of reactive dyes. Radiofrequency treatment offers rapid fixation, energy saving and no increased risk of migration when compared with conventional hot-air drying [98,99]. In microwave fixation, electrolyte addition and bentonite (added as a migration inhibitor) both improved the colour yield, whilst urea accelerated the rate of drying. Aminochlorotriazine, dichlorotriazine and sulphatoethylsulphone dyes showed satisfactory fixation, sodium bicarbonate giving higher colour yields than sodium carbonate or caustic soda [100].

Simultaneous pad–dry–cure dyeing with reactive dyes and crease-resist finishing with cellulose reactants has been of restricted interest, notably for pale depths, since the early years of reactive dyeing. The main drawback of this approach has been the obvious incompatibility of the latent acid curing conditions required for the resin finish with the alkali needed to fix all types of conventional reactive dye systems. The introduction of the acid-fixing phosphonic acid dyes (section 4.3.1) did not offer an effective solution to this problem but the more recent development of the neutral-fixing bis-(aminonicotinotriazine) dyes has revived interest in combined processes of this kind [101].

4.6.3 Pad–steam and pad–wet fixation methods

In the first practical dyeing method devised for reactive dyes, the fabric was padded in a neutral dye solution and then in a dilute solution of caustic soda in saturated brine, before steaming to complete the dye–fibre reaction. This 'wet-on-wet' sequence presented serious problems of dye 'bleeding' into the alkaline bath even at the maximum salt concentration. Partial hydrolysis of the desorbed dichlorotriazine dye to the chlorohydroxytriazine derivative (Scheme 4.2) resulted in resorption of this inactive species and subsequent loss of fixation.

This unsatisfactory sequence was soon replaced by the 'wet-on-dry' technique, immediately found suitable on the pad–steam equipment already well established for vat dyeing. This process followed the sequence: pad(neutral dye solution)–

dry–pad(caustic soda in brine)–steam–wash. After intermediate drying in a hot flue, highly efficient absorption of the alkali/salt liquor is achieved. Where small-capacity troughs are fitted, few colour-bleed problems are encountered. Recent research has established that vacuum extraction of the padded fabric is a viable alternative to intermediate drying. It restricts bleeding of the dye into the chemical pad solution and the wet vacuumed fabric retains sufficient alkali/salt liquor to give satisfactory fixation at the steaming stage [102].

Several designs of roller-type air-free steamer with a cold water exit seal are suitable. Each commercial range of dyes requires an appropriate set of steaming conditions. It has been claimed that mixed bifunctional reactive dyes of the aminochlorotriazine-sulphatoethylsulphone type are more reproducible than monofunctional systems because they tend to be self-compensating with regard to the changing conditions of treatment on a continuous dyeing range [44,103]. The advantages of the Vald Henriksen Tric-O-Steam pad–steam range for the continuous dyeing of tubular-knitted cotton fabrics with reactive dyes have been described. The Tric-O-Dry tumbler avoids shrinkage by circulating the fabric repeatedly via a current of hot air through a channel where it is compressed and a larger chamber where it relaxes again. The Tric-O-Steam pad–steam–wash sequence is claimed to be particularly suitable for fixation of aminofluorotriazine dyes [104].

Selected sulphatoethylsulphone dyes are suitable for the pad–wet fixation sequence: pad(neutral dye solution)–dry–impregnate(alkali/salt)–wash. This is of particular interest where steaming equipment is unavailable or fully occupied by other requirements. Caustic soda in sodium silicate solution is usually preferred as the chemical development bath, typically for 5–15 s at 95–100°C. A specially designed wet-fixation trough (with indirect heating to avoid dilution via condensation) is recommended for the boiling alkali treatment. A one-bath pad–dry–steam route for these dyes requiring only 1 min steaming time at 100–102°C was recently described, to minimise migration and avoid problems associated with chemical pad methods [105].

4.7 WASHING-OFF AND AFTERTREATMENT

Effective washing after reactive dyeing is crucially important. At this stage the substrate contains unfixed hydrolysed dyes and usually some residual active dyes. The dyeing does not show optimal wet fastness properties until this loose colour is removed or rendered insignificant in amount. It is remarkable that, on average, only about 0.003% dye on weight of substrate will produce a stain equivalent to a grey scale rating of 4. The amount remaining after washing must be sufficiently small to ensure that after migration the fibres on the surface of the material still exhibit acceptable fastness.

During washing the rate of diffusion out of the fibre is retarded by the substantivity forces between dye and cellulose molecules. The smaller the proportion of unfixed dye and the weaker these substantivity forces, the easier is the removal of the unfixed hydrolysed dye remaining. Thus important objectives of the design of reactive dye molecules include a high degree of fixation efficiency and, if practicable, a relatively low or moderate substantivity in the hydrolysed form. Informative reviews of the principles of washing techniques for reactive dyeings are available [106,107].

4.7.1 Batchwise washing processes

All washing processes are essentially techniques for achieving progressive dilution, but the effect of substantivity forces on the rate of removal must always be borne in mind. For example, if an exhaust dyeing of a low-reactivity dye is carried out at a temperature between 80°C and the boil and then given an initial rinse at ambient temperature, this will be inefficient because the dye is more substantive at 20°C than at the dyeing temperature. Hot rinsing at 60–70°C is recommended for optimal desorption of hydrolysed bis(aminochlorotriazine) dyes such as Procion Navy H-ER (Zeneca) (Figure 4.10) from cotton yarn dyed at 80°C [108].

An important function of the initial rinsing steps in a batchwise washing sequence is to lower the total electrolyte concentration by progressive dilution and thus to lower the substantivity of the residual loose dye. This dilution, as well as an increase in temperature to the boil for the first washing stage, will greatly enhance the rate of desorption of loose dye into the washing bath. Reducing the carry-over of entrained liquor between successive steps of the sequence is another highly effective means of increasing the washing efficiency.

Many enclosed dyeing machines operating at atmospheric pressure are incapable of operating close to 100°C without cavitation developing at the pump, which interferes with effective circulation of the wash liquor. The highest temperature attainable within these limitations should always be used at the washing stage, so as to maintain a boiling temperature as consistently as possible. It is usual dyehouse practice to add a small amount of suitable biodegradable anionic or nonionic detergent. Such agents should be low-foaming and insensitive to hard water.

Washing efficiency is often checked using a small sample taken from the dyed material before unloading the machine. This is placed between two layers of white absorbent cotton fabric and pressed with a hot iron. The stain on the interior surfaces of the white adjacents is an approximate indication of the degree of staining likely to arise in wet fastness tests on the finished dyeing. The decision whether further washing is needed to meet target quality depends on this result. This test will prove more reliable if the excess of entrained wash liquor is first removed by mangling or hydroextraction, so that it accurately represents the bulk dyeing just before the final drying.

In a jig vessel only relatively small volumes of wash liquor can be used at each washing step and the only mechanical expression is provided by the heavy ancillary rider roller running on the batch of cloth as it is wound onto the draw roller. In a recent investigation of jig washing conditions, hydrolysed forms of the high-substantivity bis(aminochlorotriazine) dye Procion Red H-E3B (Zeneca) (Figure 4.11; X = chloro) and its much less substantive monofunctional analogue Procion Red H-3B (Zeneca) (Scheme 4.1; CI Reactive Red 3) were compared in terms of characteristic properties and response to process variables such as temperature, liquor ratio and auxiliary additions [109].

In circulating-liquor machines the dyer has to operate blind, except for the sampling of liquor as it is being returned to the expansion tank. Careful development work is necessary to establish an effective washing sequence that can be programmed for automatic control. Electrolyte removal is essential before efficient desorption of unfixed dye can take place. In-to-out flow cycles are favoured, but if flow reversal is adopted, the in-to-out direction is preferable for draining before bath changes. If the machine can be pressurised it is advantageous with highly substantive dyes to soap at temperatures up to 110°C.

The Thermoflush technique was developed by Bayer AG and Thies Maschinenfabrik for the intensive washing-off of reactive dyeings. Once the dyebath has been drained, water is injected without circulation to overflow rinse. A steam treatment then causes unfixed dye to migrate to the surface of the material. By repeating these water/steam injection cycles several times, virtually all the hydrolysed dye diffuses out of the fibres and is rinsed off immediately [110,111]. A further refinement to shorten the process time is the Thies Combined Cooling Rinsing (CCR) system, in which the cooling water passing through the heat exchanger is fed by the liquor pump into the process liquor circulation. The increased liquor volume is taken to drain via an overflow device to maintain a constant liquor level. This combined cooling and rinsing principle may be used when cooling from a hot alkaline fixation step or from a soaping treatment at the boil [64].

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4.7.2 Continuous washing processes

Continuous washing is usually carried out in an open-width washing range. Each vessel has a nip at the exit to minimise the carry-over by the fabric from one bath to the next. The first three boxes of an eight-box range may be used for initial rinsing, the next three for hot soaping and the last two as a final rinse. The concentrations of desorbed dye and electrolyte gradually increase at a rate dependent on the tank volume, the inflow of clean water and the carry-over of contaminated liquor from the preceding vessel. It is necessary to ascertain the degree of dilution of electrolyte by rinsing before the fabric enters the boiling detergent baths, in order to ensure adequate fastness of the finished dyeing.

Vacuum extraction has been evaluated as an alternative technique to assist the continuous removal of unfixed reactive dyes from cotton fabrics, as it offers energy efficiency and other economic benefits. The efficiency of desorption by rinsing the vacuum extraction is dependent on the substantivity of the unfixed dyes present. High temperature and low salt concentration are necessary for effective removal, as in conventional washing processes. Steaming of the wet material permits desorption of unfixed dye into the liquor entrained within the fabric and thus assists removal by the vacuum slot. A procedure based on five warm rinse baths and two steaming treatments prior to vacuum extraction provided a highly effective degree of removal [112,113].

4.7.3 Washing and internal pH

Reactive dyeings that contain monofunctional dyes of the haloheterocyclic type (Scheme 4.2) may be prone to ‘acid bleeding’ of the dyed material. The severity of the effect depends on the structure of the dye in the vicinity of the reactive group. Monofunctional dyes that react by the nucleophilic addition mechanism (Scheme 4.3), on the other hand, form dye–fibre bonds that are less stable under alkaline conditions. It is obvious that such phenomena are dependent on the conditions existing within the fibre phase, especially the pH. This internal pH is related not only to the external pH of the dyebath but also to the electrolyte concentration and the proportion of fixed dye retained within the fibre.

For a given amount of fixed dye, the external dyebath pH is reduced by dilution of the alkali but the internal pH within the fibre is reduced even more by dilution of the electrolyte. The magnitude of the difference between internal and external pH increases with the concentration and degree of sulphonation of the fixed dye. Since this effect is associated with the dilution of electrolytes, the internal pH reached in the later stages of washing will depend on the quality of water supplied. In a dyehouse that uses exceptionally pure water (e.g. from melted snow or ion-exchange treatment) an unusually low internal pH (2–3) may be encountered, compared with normal conditions of about 0.1 g l^{-1} background electrolyte (internal pH about 4–5). If the fibre interior is unusually acidic before drying, exposure to heat will cause serious hydrolysis of dye–fibre bonds and consequent loss of wet fastness of the dyeing.

4.7.4 Effect of trace metal ions on washing performance

If impure rock salt or sea salt is used for reactive dyeing, or if the raw cotton contains an unusually high calcium or magnesium content, this can cause difficulties at the alkaline fixation stage and especially during the washing sequence. Deposits of alkaline earth hydroxides on the surface of the fibres can adsorb dye, causing spotting problems and poor reproducibility of colour [114]. When washing off, hydrolysed reactive dye is more difficult to remove with hard water than with soft water. The fixed dye molecules retain these divalent cations, which then retard the outward diffusion of the hydrolysed dye anions. For these reasons soft water should be used for dyeing and aftertreatment processes wherever possible. Polyacrylate-based sequestrants should be added and washing liquors made slightly alkaline [115].

Washing procedures for reactive-dyed garments that contain metal accessories should take account of the risk of interaction with trace metal ions. Contact of the dyed cotton with press-studs made from polished coppered brass may result in discoloration, since certain *o*-hydroxyazo chromogens will form copper complexes that are significantly different in hue from the unmetallised structure. It is impractical for the fabric dyer to select dyes that are insensitive to this influence, since the use of such press-studs in garment manufacture may not be predictable. Mild detergents should be used in washing and perborates or other oxidative agents should be avoided. The washing instructions for studded garments should reflect these limitations. The acidity of rainwater and water supplies in some areas may aggravate this problem by promoting the dissolution of traces of copper ions from the studs [116].

4.7.5 Aftertreatment of reactive dyeings

When applying reactive dyes in full depths, especially on closely constructed fabrics or on inefficient washing equipment, difficulties may arise in removing the unfixed dyes. In these circumstances it may be found necessary to aftertreat the dyeing with a cationic fixing agent of the type often used on direct dyeings. These agents operate by electrostatic association with sulpho groups in the dye molecules, forming an insoluble dye–agent complex. This is retained by the substrate during washing at temperatures up to 60°C, so that staining of adjacent white material in wet tests is minimised.

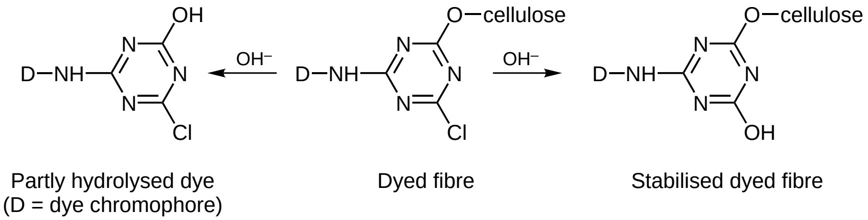
After the most effective washing treatment has been given, the dyeing is aftertreated in a solution of the cationic agent at the optimal temperature for the specific product selected. If a cationic or nonionic softening agent is applied to dyed knitgoods, the dye-fixing agent may be applied from the same bath. Treatment with a cationic agent is not a substitute for thorough washing to remove unfixed dye. Formation of the insoluble dye–agent complex on goods that have not been thoroughly washed will lead to unacceptable fastness to wet rubbing and possibly other deficiencies. Certain reactive dyes exhibit lower fastness to light following a cationic aftertreatment and changes in hue or brightness may occur.

Apart from inadequate washing, another possible cause of staining with dyeings of certain high-reactivity dyes is bleeding under mildly acidic conditions, either during storage in a humid acidic atmosphere or after exposure to a mildly acidic solution. Treatment with an aliphatic polyamine was originally devised to minimise problems of acid hydrolysis on storage of certain sensitive dichlorotriazine dyes such as CI Reactive Red 1 (Scheme 4.1) in medium to full depths. The polyamine is incapable of complex formation with unfixed hydrolysed dye. It is effective only by reacting with a residual active chloro substituent on the triazine ring of the fixed dye molecule. It is not always easy to decide whether unwanted staining, marking-off or bleeding has arisen from inadequate washing or from acid hydrolysis. It may be necessary to counter both possibilities by first applying the polyamine before soaping and then aftertreating with a quaternary fixing agent as described above.

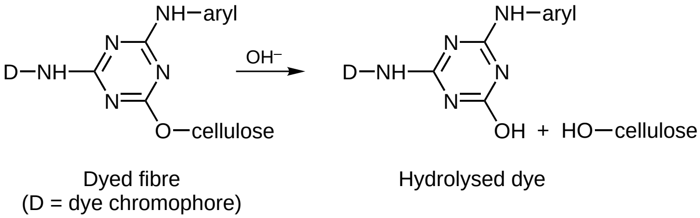
4.8 STABILITY OF DYE–FIBRE BONDS

Since the chromogens used to synthesise reactive dyes exhibit poor wet fastness in the unfixed state, the high wet fastness of reactive dyeings depends almost entirely on the resistance of the dye–fibre bond to the agencies characteristic of wet fastness tests, including pH, temperature, surfactants and oxidants. When the dye–fibre reaction product is formed during the dyeing process (Schemes 4.2 and 4.3), many of the factors responsible for the susceptibility of the reactive system to hydrolysis remain operative and may play a decisive part in determining the wet fastness attainable [8]. Thus when a dichlorotriazine dye reacts with a cellulosate anion, one of the electronegative chloro substituents is replaced by an electron-releasing cellulosyl grouping that is less electronegative but the other electron-attracting chloro and three nitrogen atoms remain, activating the heteroaryl ring to nucleophilic attack by hydroxide ions (Scheme 4.4). This can result in either stabilisation or rupture of the dye–fibre bond.

A somewhat different situation exists for the less reactive aminochlorotriazine dyes. Since amino groups are more strongly electron-releasing than the cellulosyl grouping, the activating influence of the three nitrogen atoms predominates and only the latter grouping is subject to displacement by hydroxide ions (Scheme 4.5). Therefore, this type of dye–fibre linkage will be marginally less stable under alkaline conditions than that formed by reaction of cellulose with a dichlorotriazine dye.



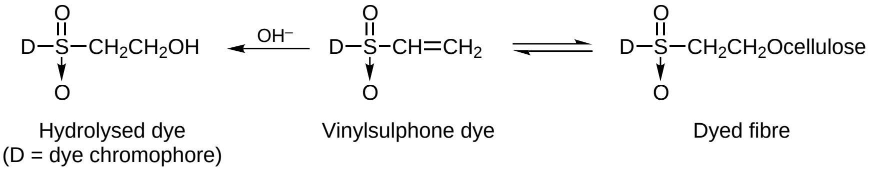
Scheme 4.4



Scheme 4.5

If a pyrimidine ring forms the basis of a chloroheterocyclic reactive system, the effects are similar to those for chlorotriazines but activation by the ring nitrogen atoms is much less and thus the dye–fibre linkage is more stable to alkali than either of the chlorotriazine systems. The rate-determining step for acidic hydrolysis of haloheterocyclic systems is nucleophilic attack of the protonated heterocyclic ring by water molecules. A recent series of quantum mechanical calculations on cellulose dyeings prepared with 12 different reactive systems containing a pyrimidine or *s*-triazine ring yielded rate constants for hydrolysis under acidic and alkaline conditions [117].

When fixation to cellulose is achieved by a nucleophilic addition mechanism (Scheme 4.3), an important factor is the reversibility of formation of the dye–fibre bond. Severe alkaline treatments are capable of rupturing this linkage to regenerate the unsaturated reactive system, which may react again either with cellulose or with water (Scheme 4.6). The presence of a less electronegative activating group than sulphone, as in the vinylsulphonamide dyes, increases the stability of the dye–fibre bond but reduces the reactivity of the dye.



Scheme 4.6

The kinetics of alkaline hydrolysis of a series of fixed vinylsulphone reactive dyeings on cellulose have been investigated at 50°C and pH 11. Bimodal hydrolytic behaviour was observed under these conditions, the reaction rates being rapid at first but becoming slower as the concentration of fixed dye remaining was decreased. These results were attributed to differences in the degree of accessibility of the sites of reaction of the dyes within the cellulose structure [118].

In an interesting recent comparison of dye–fibre bond stabilities over the pH range 3.5–10, cotton dyeings of the aminochlorotriazine-sulphatoethylsulphone bifunctional dye Sumifix Supra Brilliant Red 2BF (NSK) shown in Figure 4.12 were compared with those of the two monofunctional analogues in which, before dyeing, either the aminochlorotriazine group was replaced by aminohydroxytriazine or the sulphatoethylsulphone group was replaced by hydroxyethylsulphone. Under acidic conditions the bifunctional dyeing showed higher stability than the vinylsulphone dyeing, which in turn was more stable than the monofunctional chlorotriazine analogue. At alkaline pH, on the other hand, the chlorotriazine analogue and the bifunctional dyeing were virtually identical in stability, both being markedly more stable than the monofunctional vinylsulphone [29]. For similar reasons, bifunctional reactive dyeings of the aminofluorotriazine-sulphatoethylsulphone type (Figure 4.13) show better all-round stability to acidic and alkaline conditions than analogous monofunctional dyeings based on dichlorotriazine, aminochlorotriazine, aminofluorotriazine or vinylsulphone systems [31].

The hydroxide ion is not the most active nucleophile with which the dye–fibre bonds in reactive dyeings have to contend. Many commercial detergent formulations contain sodium perborate or percarbonate that release peroxy species in washing treatments. The perhydroxide anion (HOO^-) is an exceptionally powerful nucleophile capable of attacking certain types of haloheterocyclic reactive system to give unstable products. Studies of the reaction of alkaline peroxide solutions with dissolved reactive dyes have shown that reactive chloro substituents are readily displaced. Heterocyclic dyes containing other leaving groups, e.g. fluoro, and systems that fix by nucleophilic addition, e.g. vinylsulphone dyes, generally do not show perhydroxide formation.

Surprisingly, however, dyes of the chlorodifluoropyrimidine type (Figure 4.5) readily form a perhydroxide derivative that leads to cumulative damaging effects on dye–fibre bond stability. A comparison between seven different haloheterocyclic systems each attached to the same chromogen (phenylazo H acid) demonstrated several important conclusions [119].

(1) Only dye–fibre linkages that carry on the heterocyclic ring an electronegative substituent that is *ortho* or *para* to the dye–fibre bond show both peroxidation and bond breakage, e.g. 5-chloro-2,4-difluoropyrimidine, 5-cyano-2,4-dichloropyrimidine, 2,4,5-trichloropyrimidine and 2,3-dichloroquinoxaline dyes.

(2) Dye–fibre linkages that carry on the heterocyclic ring an electronegative substituent that is *meta* to the dye–fibre bond may show peroxidation but only slight breakage of bonds, e.g. 2,4-dichloropyrimidine and dichlorotriazine dyes.

(3) Dye–fibre linkages with no electronegative substituents on the heterocyclic ring show neither peroxidation nor bond breakage, e.g. aminochlorotriazine, bis(aminochlorotriazine) and bis(aminonicotinotriazine) dyes.

The relationship between dye–fibre bonding and light fastness was examined for ten sulphatoethylsulphone reactive dyes on cellulose and it was shown that the stronger the bonding between dye and substrate, the more stable was the dyeing when exposed to light [120]. Light-fading studies on cotton dyeings of five trichloropyrimidine reactive dyes revealed that the rate of photodegradation of the cellulose was influenced by the presence of the dye. Compared with an undyed control, the blue dyeing was degraded more rapidly but the yellow, orange, red and green dyes tested exerted a protective effect [121]. Repeated perborate oxidation of dyed cotton and viscose yarns demonstrated increased tendering of dyeings containing metal-complex reactive dyes. Viscose yarns were more significantly affected than cotton, possibly owing to the lower crystallinity, greater accessibility and higher carboxy content of viscose fibres [122].

4.9 REACTIVE DYEING RESIDUES IN WASTE LIQUORS

As already discussed in the introduction, approximately half of the cost of a typical reactive dyeing may be attributed to the washing stage and treatment of the resulting effluent. A central objective of research into novel reactive dyes and dyeing processes has been the improvement of fixation efficiency and minimisation of the proportion of applied dye that is lost by hydrolysis in the dyebath or by absorption, hydrolysis and removal again at the washing stage. The contribution of hydrolysed dye to the overall behaviour of reactive dyes is most evident at the washing stage and in contamination of dyehouse effluent. With dyeings of highly substantive dyes, boiling water treatment is not fully effective in removing all the hydrolysed dye present. If dye concentration and COD values are determined for the successive washing baths, it may be advantageous to separate the waste waters into high- and low-load reservoirs for possible recycling [123,124].

Reactive dye hydrolysates are not easily adsorbed by sewage sludge in a biological clarification plant. It is desirable to decolorise the liquor at source if practicable. A post-scouring step designed specifically to remove hydrolysed dye as effectively as possible offers the possibility of concentrating the waste dye residues into as small a volume as possible, making water treatment of low-load liquors from the rising steps more feasible [125,126].

Studies of washing-off efficiency under batchwise and continuous conditions were carried out on mercerised cotton poplin dyed with two sulphatoethylsulphone dyes, the low-substantivity CI Reactive Red 35 (phenylazo-*N*-acetyl H acid type) and CI Reactive Orange 82 (naphthylazo-*N*-acetyl J acid type) of higher substantivity. The highest efficiency of removal is attainable with low-substantivity dyes at a high temperature, a short liquor ratio and with optimal mechanical washing action to achieve maximum efficiency of liquor interchange [109,127].

Apart from contamination by unfixed reactive dye residues, probably the most serious ecological problem arising from reactive dyeing is the high salt load in the effluent. Dispensing salt in solid form without significant change in liquor ratio offers wider scope for optimising quality and cost effectiveness in the package dyeing of yarns and the jet dyeing of fabrics. Improved dye yield and levelness, shorter process times, lower salt usage and environmental benefits are claimed for this technique [128].

An exceptionally fine grade of Glauber's salt is selected for this application. The electrolyte is transmitted via a screw-type device from a storage tank outside the dyehouse to tanks positioned above the addition vessels, from where it is added to the dyebath at a controlled rate. In this way the transfer problems associated with the large amounts of electrolyte required is also solved. The size of the storage tanks, equipped with special heating units, depends on the dyehouse production. They are periodically refilled from salt-transporting vehicles. The heating avoids caking of the salt grains by condensation of entrapped moisture, since this complicates the transfer and controlled dosing procedures [49].

A more fundamental approach to the objective of minimising contamination of reactive dyeing effluents by excessive salt content is to adjust the dyeing parameters so that only the lowest possible concentration needs to be added at the dyeing stage [129]. There are four main ways in which the salt consumption can be decreased [51]:

(1) Lowering the liquor ratio.
(2) Avoiding high temperatures of dyeing.
(3) Optimising the dye recipe.
(4) Developing novel dyes.

The design of modern batchwise dyeing equipment (section 4.5) takes account of this need to operate at as low a liquor ratio as possible, since this brings many other important technical and economic benefits. The choice of low dyeing temperatures implies a preference for dyes of high reactivity, although these may not be ideal when dyeing substrates that are difficult to penetrate or to dye level. Optimising recipes offers some scope to lower the salt loading and the development of homogeneous dull-hued reactive dyes with high intrinsic substantivity to replace trichromatic mixtures of three bright components is another interesting approach [51]. Several monofunctional sulphatoethylsulphone and bifunctional aminochlorotriazine-sulphatoethylsulphone dyes were assessed recently with regard to the minimum levels of salt required to achieve just acceptable yields in batchwise dyeing. Even under the most favourable circumstances, a concentration of at least 20 g l^{-1} was needed in pale depths at relatively low liquor ratio [130].

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CHAPTER 5

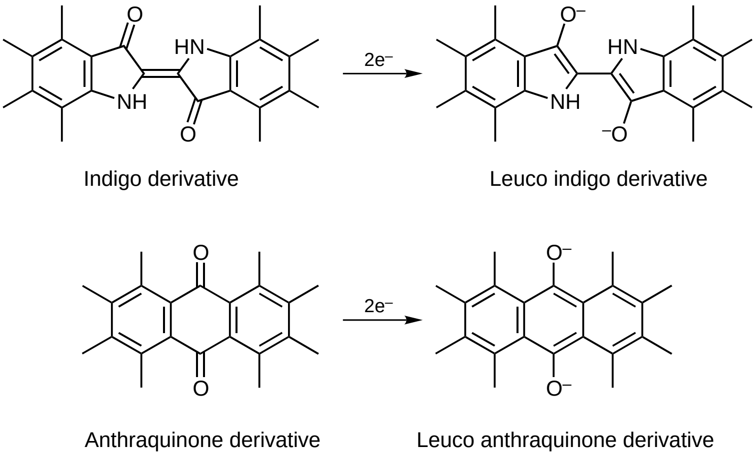
Dyeing with vat dyes

Francis R Latham

5.1 INTRODUCTION

Dyeing with vat dyes is based on the principle of converting a water-insoluble keto-substituted colorant by reduction to a water-soluble enolate leuco compound that is substantive to cellulose (Scheme 5.1). This penetrates into the fibre, where it is reoxidised back to the original insoluble form. All these dyes contain two or more keto (C=O) groups, separated by a conjugated system of double bonds. Many are derived from indigo or anthraquinone but most of the latter derivatives contain highly condensed aromatic ring systems.

Vat dyes are used predominantly for dyeing cellulosic fibres. Although the leuco dyes also have substantivity for wool and nylon, technical reasons (e.g. fibre damage when dyeing wool and the fastness properties on nylon) restrict



Indigo derivative

Leuco indigo derivative

Anthraquinone derivative

Leuco anthraquinone derivative

Scheme 5.1

their commercial significance for these fibres to the dyeing of nylon/cotton blends.

The situation is quite different for the cellulosic fibres, i.e. cotton, regenerated cellulosic and bast fibres. These constitute more than half the quantity of all textile fibres produced, approximately 15–20% of which are dyed with vat dyes. Cellulosic fibres are likely to maintain this leading position, because they are biodegradable and their raw material basis (water, carbon dioxide and solar energy) is not endangered.

The vat dyeing method is of long standing, traditionally carried out using products of natural origin, such as indigo or Tyrian purple, reduced by means of sugars or their products of decomposition. The start of this century saw the synthesis of new vat dyes suitable for application to cellulose and the development of a sufficiently stable reducing agent with the necessary reactivity. Since then, it has been possible to operate the dyeing process reproducibly on an industrial scale. Decisive steps in this direction include firstly the clarification of the structure of indigo and its synthesis, followed by preparation of indanthrone from the alkali melt of 2-aminoanthraquinone. Equally important was the manufacture of a reducing agent with good storage stability, i.e. anhydrous sodium dithionite (often called hydrosulphite or hydros).

5.2 FUNDAMENTAL PRINCIPLES

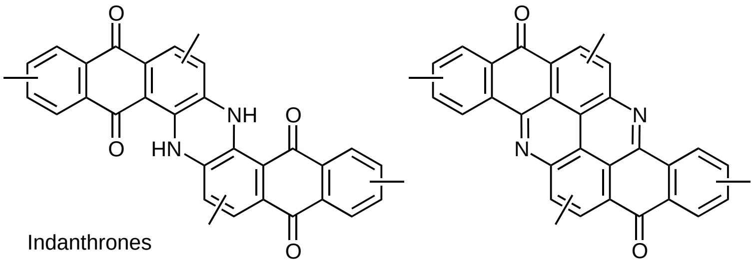
5.2.1 Chemical classification of vat dyes

Apart from indigo, the vat dyes used in dyeing applications are mainly derivatives of anthraquinone and of higher condensed aromatic ring systems with a closed system of conjugated double bonds. They may be homogeneous dyes or mixtures, each usually containing two, four or six reducible keto groups.

The chemical constitution of the dye influences the properties of the leuco enolate form in the dyeing process, e.g. thermal stability in the vat, substantivity, rate of absorption, diffusion into the fibre and levelling properties. It is also a key factor in determining the resultant dyeing characteristics, including colour and fastness properties.

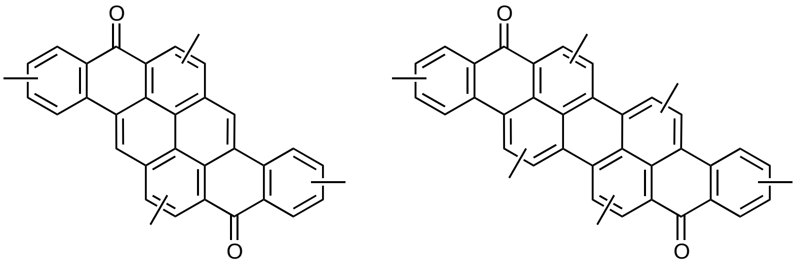
The structural elements of several typical important classes of vat dyes are shown in Figure 5.1. Further groups of vat dye structures have been illustrated in the literature, together with details of their preparation [1–11].

The indanthrones are blue dyes (e.g. CI Vat Blues 4, 6 and 14). Since they are prone to over-reduction and over-oxidation, they can present problems in dyeing. However, because of their attractive colour, excellent fastness and moderate cost



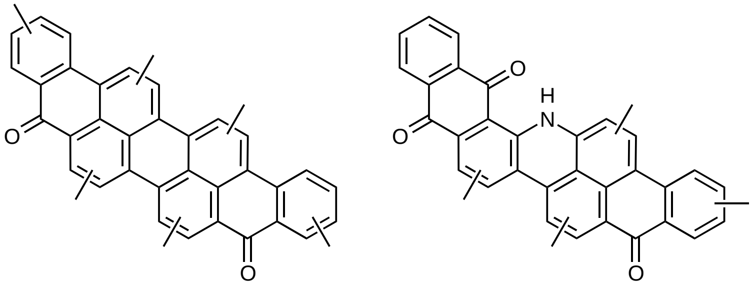
Indanthrones

Flavanthrones



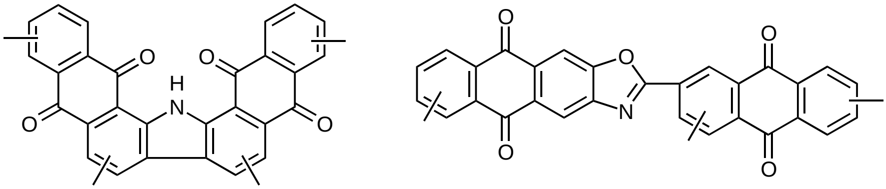
Pyranthrones

Isodibenzanthrones



Dibenzanthrones

Benzanthrone acridones



Anthraquinone carbazoles

Anthraquinone oxazoles

Figure 5.1 Structural elements of some important vat dyes.

they still form one of the most important classes of vat dyes. Flavanthrone (CI Vat Yellow 1) and its derivatives are, in common with the indanthrones, among the oldest synthetic vat dyes. In spite of certain shortcomings (e.g. slow oxidation, lower wash fastness and a tendency to photochromism), this dye is still regarded as important because of its good light fastness.

The same applies to the pyranthrone types (e.g. CI Vat Oranges 2 and 9). Although these dyes also have certain shortcomings (inferior light fastness of the non-brominated product and fibre damage during dyeing) they are still widely used because of their good levelling properties, high colour strength and moderate cost.

The isodibenzanthrone (isoviolanthrone) dyes include some interesting deep violet colours (e.g. CI Vat Violets 1 and 9) that have high colour strength and good fastness to bleaching, but lower fastness to rubbing, hot pressing and water spotting.

The dibenzanthrones (violanthrones) form a particularly large group of dyes, with important examples in the dark blues, navy blues, greens and blacks (e.g. CI Vat Blues 16, 19, 20 and 22, Greens 1, 2 and 9, and Black 9). These dyes suffer from many of the same disadvantages as the isodibenzanthrones, but they have maintained their importance on account of their generally good levelling properties, excellent fastness to light and wet treatments, and because some colours with these properties cannot be produced by any other means.

The benzanthrone acridone types represent another large class, including CI Vat Greens 3 and 13, and Black 25. These are relatively flat olive greens, olives, brown and greys. Although not easy to dye level, they have excellent fastness and provide the fibre with a certain degree of protection against the action of light.

The anthraquinone carbazole class of dyes is of great importance for colours ranging from yellow and orange to brown, khaki and olive (e.g. CI Vat Oranges 11 and 15, Browns 1, 3 and 44, Green 8 and Black 27). In spite of their relatively flat colours, these dyes are extremely important because of their good levelling properties and excellent fastness to light, wet treatments and chlorine.

Finally, also illustrated is the anthraquinone oxazole class. The main representative of this class is CI Vat Red 10, a strong brilliant red that levels well and has excellent fastness.

Other types of vat dyes with important structural elements include:

(1) perylene tetracarboxylic diimide derivatives, e.g. CI Vat Reds 23 and 32;
(2) imidazole derivatives, e.g. CI Vat Yellow 46, which is a bright light-fast yellow;
(3) triazinylaminoanthraquinone derivatives, i.e. reaction products of aminoanthraquinones and cyanuric chloride. CI Vat Blue 66 is an important

> example, with excellent levelling properties and good fastness to chlorine. Furthermore, unlike the indanthrone blue dyes, it is not susceptible to over-reduction.

The leuco potential of all vat dyes, measured with a calomel electrode under standard conditions, lies between –650 and –1000 mV; thus satisfactory vatting (reduction to the enolate leuco form) can only be achieved with reducing agent that has a more negative reduction potential than this.

After it has been synthesised, a vat dye is still not in a suitable state for commercial use, because reduction to the leuco form is normally an extremely slow process at this stage. All vat dyes, therefore, must be converted into a suitable commercial form. This may involve a pretreatment, followed usually by a wet milling process with suitable dispersing agents. The demands placed on colorant formulations have increased considerably, particularly for batchwise pigmentation and semi-pigmentation processes in package equipment and for continuous piece dyeing, where a high standard of control of the particle size distribution is necessary. The top-quality dyes available generally have an average particle size of well below 1 μm.

In a recent study using three vat dyes (CI Vat Red 13, Blue 6 and Brown 1) having mean volume diameters of 0.4–3 μm, the effects of particle size on colour yield, frosting and wash fastness of continuously dyed cotton workwear fabrics were investigated. Colour yield of CI Vat Red 13 decreased with increasing particle size above 0.8 μm but that of Blue 6 was independent of particle size, whereas Brown 1 showed irregular dyeing behaviour [12,13].

Commercially, vat dyes are available in the form of liquids, granules or dedusted powders. In the case of solid brands it is essential that they should disperse readily in water. Apart from particle size, other important properties of all commercial formulations include their storage stability, behaviour during preparation of the dye liquors and the pigmentation process, and their rate of vatting. The vatting rate is determined by the particle size distribution and the crystalline form of the dye.

5.2.2 Types of auxiliaries

Reducing agents

The most important reducing agent in vat dyeing is sodium dithionite, generally referred to as hydrosulphite or hydros. It has a reduction potential that is sufficiently negative for all practical requirements. Other reducing agents can only be used for special purposes, or have not yet been accepted in practice. In this connection reference should be made to the hydroxyalkylsulphinates, which find uses in vat printing and for dyeing at temperatures above 100°C.

Thiourea dioxide is a strong reducing agent but in alkaline solutions it is just as sensitive to atmospheric oxygen as hydrosulphite. Although freshly prepared alkaline solutions of thiourea dioxide appear to be relatively stable, there is rapid formation of formamidinesulphinate. In this form, it is apparently even more readily oxidisable than hydrosulphite [14].

Sodium borohydride reacts too slowly for vat dyeing. From time to time, vatting processes using the readily biodegradable chemical hydroxyacetone have been proposed [15,16].

The properties of hydrosulphite are extremely important for the practical application of vat dyes. Its constitution as sodium dithionite ($Na_2S_2O_4$) has been known since the end of the last century but the erroneous designation hydrosulphite remains popular. The instability of the dithionite anion arises from the presence of the S–S linkage (see Scheme 5.2)

Sodium dithionite (hydrosulphite), $Na_2S_2O_4$
Structure of dithionite ion: $[O_2S{-}SO_2]^{2-}$

(a) Hydrolytic decomposition:
Neutral medium:

$$2Na_2S_2O_4 + H_2O \longrightarrow Na_2S_2O_3 + 2NaHSO_3$$

Alkaline medium

$$2Na_2S_2O_4 + 2NaOH \longrightarrow Na_2S_2O_3 + 2Na_2SO_3 + H_2O$$

(b) Reaction with atmospheric oxygen (alkaline medium):

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

(c) Reaction with hydrogen peroxide (alkaline medium):

$$Na_2S_2O_4 + 3H_2O_2 + 2NaOH \longrightarrow 2Na_2SO_4 + 4H_2O$$

Scheme 5.2

In the anhydrous state the product is quite stable, but in contact with water it forms sodium thiosulphate and sodium bisulphite. The formation of acid products accelerates the decomposition, which proceeds exothermically and may result in spontaneous ignition. The same reactions occur in aqueous solution (without alkali) and both sulphur dioxide and sulphur have been identified as reaction products.

In the absence of air, hydrosulphite is extremely stable in alkaline solutions. Under these conditions it is more stable than hydroxyalkylsulphinates and the formamidinesulphinate that is formed from thiourea dioxide under alkaline conditions. It is only under extreme conditions that sodium dithionite forms the thiosulphate and sulphite as reaction products [17]; at high alkali concentrations and elevated temperatures some sulphide may also be produced [18].

In practice, the important factor is its behaviour in an alkaline solution in the presence of atmospheric oxygen. As shown in Scheme 5.2, sodium sulphite and sodium sulphate are formed. Detailed investigations have shown that, depending on the conditions, more sulphite is formed than sulphate. Apparently the free radical ion ($\cdot SO_2^-$) is the initial transient formed from the dithionite anion ($^-O_2S{-}SO_2^-$). Oxidation with atmospheric oxygen is kinetically 0.5 order in relation to the dithionite concentration. For practical applications it is particularly important to note that sodium hydroxide is consumed in the oxidation. Therefore, it is necessary to ensure that there is sufficient excess present, otherwise the dye liquor will become neutral, or even acid, and enable the above-mentioned hydrolytic decomposition to take place. In the oxidation of vat dyeings with oxidising agents other than atmospheric oxygen, only sulphate (e.g. with hydrogen peroxide) or only sulphite (e.g. with sodium *m*-nitrobenzenesulphonate) are produced from the dithionite.

Since sodium dithionite is sensitive to atmospheric oxygen, an excess of dithionite must always be present. The amount of this excess depends on the application conditions, particularly on the influence of certain factors governing the rate of oxidation [19–21]:

(1) Temperature – given that the other conditions are constant, the rate of oxidation increases with the liquor temperature.

(2) Dithionite concentration – given that the other conditions are constant, a specific amount is oxidised in a given time, i.e. the more concentrated the initial dithionite solution, the longer it takes to become deactivated.

(3) Movement of liquor and air – the greater the agitation of the liquor in the presence of atmospheric oxygen, the more rapidly decomposition proceeds. This is particularly relevant for hank-dyeing machines, winches and jigs.

(4) Specific surface area – the greater the specific surface area of the liquor (i.e. the quotient of the surface area and volume), the more rapidly is the sodium dithionite oxidised. Since the time required for half oxidation is inversely proportional to the specific surface area, oxidation may take many hours in a large vessel with a relatively small surface area. On the other hand, because of

the high specific surface area, a dithionite liquor padded onto a fabric is oxidised within 30–60 s, depending on its concentration and the prevailing conditions.

(5) Presence of dyes – assuming that the other conditions are constant, the reducing agent is oxidised more rapidly in the presence of leuco dyes than when these are absent.

On the other hand, under the conditions normally employed in practice (pH 12–14), oxidation of the sodium dithionite does not appear to depend to any significant extent on the alkali content of the liquor.

Ancillary chemicals

Apart from the reducing agent, other products are necessary to ensure satisfactory dyeing. The most important of these is caustic soda, because these dyes can only be absorbed in the ionised form. To achieve this the liquor must have a pH of 12–13 to prevent formation of the practically insoluble enolic acid leuco compound, which has no substantivity for the fibre. Since caustic soda is consumed in the vatting process, and also by the action of atmospheric oxygen on the vat, a sufficient excess must always be present. In some special cases, caustic soda 27% by weight is replaced by an equal amount of soda ash, e.g. CI Vat Red 32.

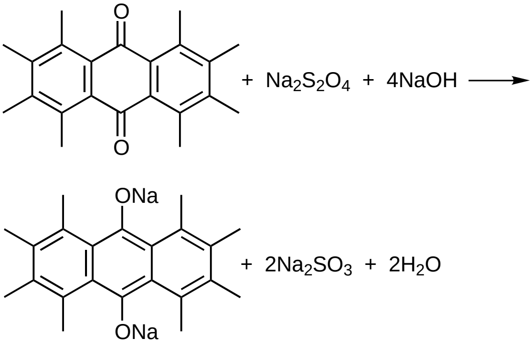
Neutral salts, e.g. sodium sulphate or chloride, can increase the substantivity of the leuco dye for the fibre. Nonionic agents that form complexes with the leuco dyes are used to improve the levelness of the dyeings (e.g. alkoxylated types) or to partially strip faulty dyeings (e.g. polyvinylpyrrolidone).

Wetting, sequestering and dispersing agents help to overcome dyeing problems caused by inadequate pretreatment. For example, a wetting agent is frequently necessary, especially when dyeing loomstate materials, to emulsify the waxes in the grey cotton and to ensure satisfactory penetration of the dye liquor into the substrate. Sequestering agents chelate the alkaline-earth ions contained in the grey cotton and the process water, thus preventing the precipitation of pectins and of the almost insoluble alkaline-earth salts of leuco dyes [22]. The addition of supplementary dispersing agents prevents the aggregation of undissolved particles and is particularly important in the oxidising and washing-off processes.

For continuous dyeing with vat dyes by the pad–steam process with intermediate drying, anionic polymeric inhibitors are necessary to prevent pigment migration in the drying operation [23]. After dyeing, an oxidising agent (e.g. hydrogen peroxide, sodium perborate or sodium *m*-nitrobenzenesulphonate) is required, followed in the subsequent soaping process by an anionic detergent.

5.2.3 Vatting

Before the actual dyeing operation, the water-insoluble dye must be converted into the water-soluble substantive form. This is achieved by vatting, i.e. reaction with a reducing agent – usually sodium dithionite – in the presence of sodium hydroxide to form the sodium enolate leuco compound. In this reaction the dithionite assumes the oxidation number of the sulphite (Scheme 5.3).



Scheme 5.3

The chemical reaction apparently proceeds as a two-electron transfer [24]. The rate of reaction is determined by association of the reducing agent with the oxygen atom in the keto group of the dye. This group is then rapidly split off by the action of the hydroxide ions, leaving the two bonding electrons with the keto oxygen. Finally there is an electron shift to stabilise the dye in the enolate form. These reactions are kinetically first order with regard to both the dye and the reducing agent.

In practice, a heterogeneous system is present, i.e. the dissolved reducing agent attacks the finely dispersed dye particles. In this case the vatting rate is not determined by the chemistry of the reaction but by the diffusion and transport stages [25]. Experiments have shown the following:

(1) Vatting proceeds almost twice as rapidly with an increase in temperature of 10°C.

(2) Above pH 12 the rate of vatting is not dependent on the hydroxide ion concentration.

(3) The higher the concentration of reducing agent and dye, the more rapidly reduction takes place.
(4) The rate of vatting is dependent on the crystalline form and particle size of the dye.

To prepare a satisfactory vat it is necessary to have an adequate amount of reducing agent and caustic soda. The quantity of reducing agent is determined by that necessary for the particular dye (number of reducible groups, relative molecular mass, content of pure dye) together with an excess, the quantity of which depends on the amount of air present in the dyeing process. In certain cases (grey cotton, or fibres damaged by oxidation) dithionite can also be consumed by the substrate. Since sodium hydroxide is consumed both in the vatting process and by the action of atmospheric oxygen, the alkali concentration has also to be so adjusted that the pH of the liquor remains sufficiently high during the dyeing process to prevent formation of the practically insoluble enolic acid leuco compound. Hence the amount of caustic soda required is determined by the number of keto groups that have to be reduced and by the extent of oxidation due to atmospheric oxygen during dyeing. In the latter case, approximately 1 ml caustic soda (27% by weight) is consumed in the oxidation of 1 g hydrosulphite.

5.2.4 Properties of leuco dyes

The leuco dyes are usually present in the dye liquor in a monomolecular form or as aggregates of a few dye molecules. From diffusion measurements, Valkó determined these to be aggregates of between two and four molecules [26]. Absorption spectrophotometric studies have shown that planar molecules, such as the violanthrone derivatives CI Vat Blues 19, 20 and 22, and the perylene tetracarboxylic acid derivatives CI Vat Reds 23 and 32, are present in the vat mainly as single molecules or dimers, depending on concentration and temperature [27,28].

Violanthrone derivatives that do not have a coplanar structure, due to substitution by alkoxy groups in the 16 and 17 positions (CI Vat Greens 1, 2 and 4, and CI Vat Blue 16), are always present in solution as single molecules under dyeing conditions. Evidence from spectrophotometric studies points to interaction between components of binary mixtures of leuco vat dyes in aqueous alkaline solutions and on cellophane film, interaction reaching a maximum at equimolar concentration of the component dyes [29,30].

The substantivity of a dye for the fibre is determined by its constitution and is unaffected by the degree of aggregation. The aggregation can, however, influence the diffusion of the leuco dye within the fibre and thus affect the levelling behaviour. With certain indanthrone derivatives, e.g. CI Vat Blues 4, 6 and 14, vatting usually produces a supersaturated solution that tends to precipitate after a short time, depending on the purity of the dye. In the presence of multivalent cations (e.g. Ca, Mg or Fe) some leuco compounds, e.g. CI Vat Yellow 1, Orange 2 and Blues 4, 6 and 14, form almost insoluble salts that have no substantivity for the fibre; precipitation can be prevented using a sequestering agent.

If there should be too little alkali in the vat, the enolic acid leuco compound may precipitate, resulting in paler dyeings with a lower fastness to rubbing. With the indanthrone dyes CI Vat Blues 4, 6 and 14 this conversion to the acid leuco form can even occur at pH 12, but other dyes need a much lower pH.

Certain leuco dyes, known as tenderers, can damage the fibre when there is frequent alternation between oxidation and reduction during the dyeing process. This can be countered by the addition of pyrocatechol or tannin.

With some leuco dyes, chemical changes may take place in the alkaline medium at high temperatures, such as hydrolysis of carbonamide groups, dehalogenation (e.g. CI Vat Blue 6) or over-reduction with the indanthrone blues. In the latter case oxygen atoms are split off from the molecule at temperatures above 60°C, so that the original dye molecule cannot be re-formed on oxidation. The tendency to over-reduction increases with the concentration of caustic soda and hydrosulphite, and with the temperature and duration of the dyeing process. The hue becomes greener and duller, but this can be prevented by appropriate additions of glucose or sodium nitrite.

5.2.5 Dyeing treatments

Absorption and levelling

When a cellulosic textile is entered into the alkaline dyeing liquor that contains leuco vat dye, the dye exhausts out of the liquor into the fibre until, after a certain time, a state of equilibrium is attained. The higher the substantivity of a dye for the fibre, the higher its concentration in the fibre and the lower in the dye liquor.

It is characteristic of vat dyes that they exhaust rapidly, even at relatively low temperatures. Study of the dyeing kinetics shows that the dye is absorbed in two stages (Figure 5.2). Most of the dye (generally 80–90%) exhausts within about 10 min (stage 1), followed only slowly by the remainder (stage 2).

As a result there is the danger of the substrate being dyed unevenly after the

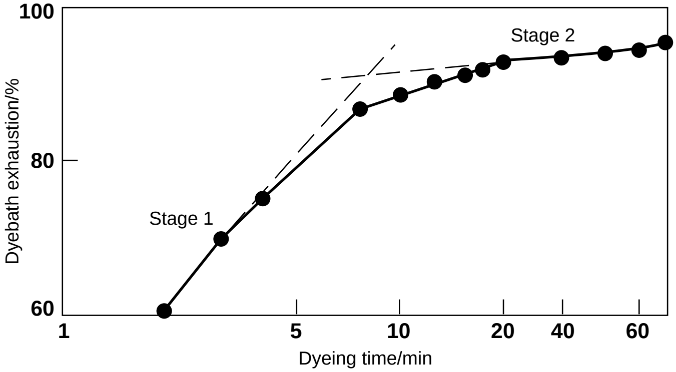


Figure 5.2 Absorption behaviour of a leuco vat dye.

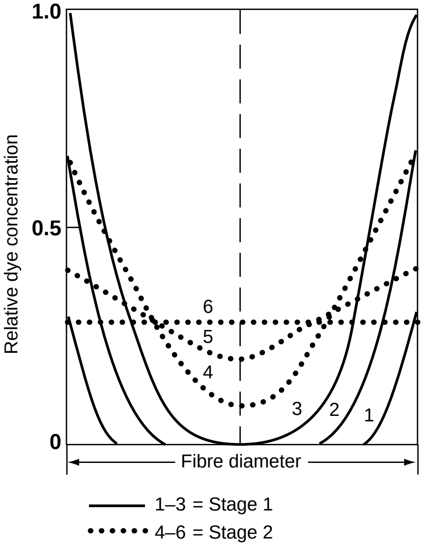


Figure 5.3 Change in concentration in the fibre cross-section during the dyeing process.

first stage, in which the dye is absorbed initially in the outer, more accessible sheath of the fibre, causing ring dyeing.

If the change in dye concentration within an individual fibre is depicted in relation to the dyeing time, it is to be expected that the dye concentration will first increase rapidly in the outer sheath of the fibre (Figure 5.3, curves 1–3) and the bath will be largely exhausted. The second stage is governed by the diffusion of the dye into the interior core of the fibre (curves 4–6). In this stage the dye concentration in the outer sheath of the fibre falls again and only a small amount of dye can be taken up from the bath. This representation has been demonstrated by trials with small rolls of cellophane film [31].

There are thus two stages in the kinetics of the dyeing process, one characterised by rapid exhaustion of the bath, due largely to the substantivity of the leuco dye for the fibre, and a second stage, dominated by diffusion of the dye into the interior of the fibre.

The rate at which the dye exhausts in the first stage is virtually independent of the rate of liquor circulation [32]. It is, on the other hand, influenced to a considerable extent by the textile material, e.g. the greater the surface area of the substrate in contact with the dye liquor, the more rapidly is the first stage completed. Furthermore, trials have shown [31,32] that a rapid initial rate of dyeing is favoured by a low dye concentration, a short liquor ratio and a high dyeing temperature. In practice, the more rapidly the dye exhausts onto the fibre in this initial stage, the greater is the risk of obtaining an unlevel dyeing.

Penetration of the individual fibres takes place in the second stage. The rate at which this proceeds is determined by the diffusion of the leuco dye from the outer sheath to the interior of the fibre. Diffusion behaviour can be characterised by an empirical penetration value [32]. Dyes with good levelling properties have values between six and eleven, whereas those with limited levelling capacity have values of four or less. The rate of diffusion is considerably dependent on dyeing temperature, rising exponentially with increase in temperature. Investigations have shown [28] that dyes with similar constitutions and thus similar substantivity for cellulosic fibres diffuse more slowly if they tend to dimerise in solution (e.g. CI Vat Blue 20 in comparison with CI Vat Green 1). Such dyes also do not level out as readily, i.e. the levelling properties depend not only on the substantivity but also on the rate of diffusion.

A dyeing equilibrium is attained after a certain time when a specific quantity of cellulosic fibre is added to a solution of leuco dye of known concentration and at a constant temperature, i.e. the dye becomes distributed between the solution and the fibre in specific proportion. Dyeing isotherms can be drawn by plotting the equilibrium concentrations in the fibre and the solution for different dyes at different starting concentrations, as illustrated in Figure 5.4. It can be seen that the green dye exhausts much more completely than the two red dyes. In practice the dye uptake rises as the initial dye concentration in the bath, the liquor ratio and the dyeing temperature decrease and as the salt content increases. Exhaustion generally ranges from 85 to 95%.

The substantivity of the dye for the fibre depends on the dye structure and does not appear to be associated with the tendency to form leuco dye aggregates in the liquor, especially since it has been found that dyes which tend to form

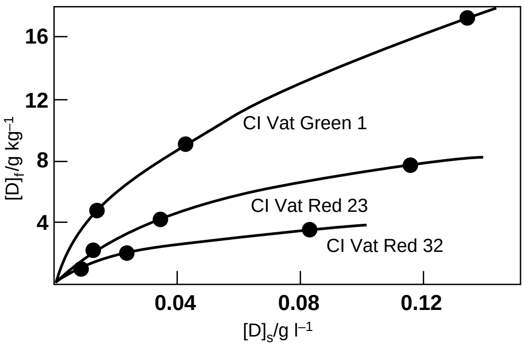


Figure 5.4 Dyeing isotherms of vat dyes.

dimers in solution (e.g. CI Vat Blue 20) are mostly present in the monomolecular form once they have exhausted onto the fibre [27,28,31].

In the absence of nonionic levelling agents the behaviour of the leuco dyes under production conditions is determined by the initial extremely rapid bath exhaustion previously mentioned, with the attendant danger of unlevel dyeings. This danger is particularly great with pale colours, dyeings produced in short liquors or on mercerised cotton, and particularly with regenerated cellulosic fibres. If the bath exhausts too rapidly – even at room temperature – for level dyeings to be obtained, and the other parameters are fixed (i.e. substrate, dyeing equipment, recipe), all that can usually be done is to provide conditions that promote the levelling process. As already stated, the rate at which the dye diffuses within the fibre increases considerably with rise in temperature. At the same time the substantivity diminishes, resulting in an increase of the dye concentration in the liquor. This facilitates the migration of the leuco dye [32], as shown in Figure 5.5.

In these experiments 4% dyeings were treated in a blank vat, together with same amount of undyed material, and the dye content in the dyeing, the white material and the liquor was determined at regular intervals. It is quite clear that although the levelling process accelerates with rise in temperature, much more dye remains in the dye liquor at 90°C than at 60°C (curve 3). For this reason, after the levelling stage, the temperature should be reduced in order to allow the colour to reach its maximum depth.

However, the problem cannot always be solved in this manner, unless long dyeing times are acceptable. Usually, therefore, there is no alternative to using levelling agents capable of complexing with the dyes required. The objective of adding such agents is to shift the absorption equilibrium in favour of the

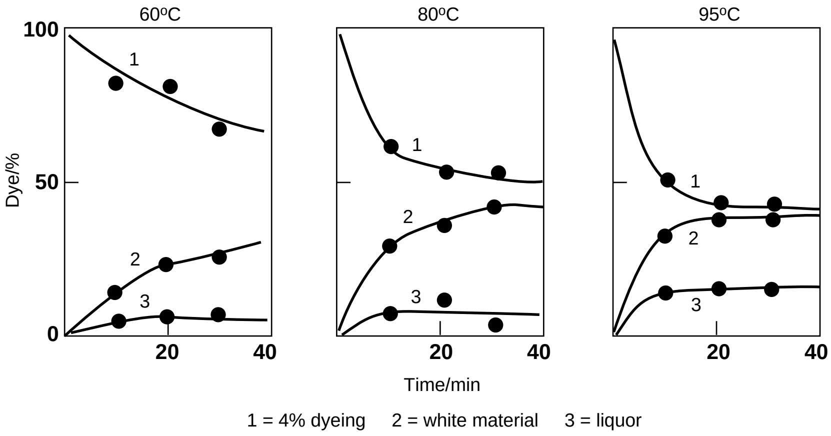


Figure 5.5 Levelling of CI Vat Green 1 at various temperatures.

dyebath, in order to retard the rate of absorption of the dye by the fibre or to promote the migration of dye that has already been absorbed.

These complexing agents include alkylene oxide or imine polymers that are capable of associating with leuco dyes. This interaction normally takes place with the leuco dye in the monomolecular form, even with those dyes that dimerise in aqueous media [27,28,31]. Formation of a dye–agent complex is most likely to be initiated by an ion–dipole attraction between the hydrated dye anion and the polar polymeric chain that is strongly hydrated (analogous to the interaction between a leuco dye and cellulose). These relatively strong forces are responsible for bringing the dye and polymer chain molecules together so that the π–electron system of the dye can interact further with the dipoles of the polymeric agent. These binding forces evidently depend on the size and planarity of the dye molecules.

The strength of the interaction between the dye and agent determines whether the latter functions as a stripping agent (e.g. polyvinylpyrrolidone) or as a levelling agent (e.g. fatty alcohol polyoxyethylene). Because of the similarity in the forces exerted on the dyes by the substrate and agents, the latter usually have a pronounced effect on dyes that have poor levelling properties and high substantivity. Conversely, however, such products have only limited retarding action when used with less substantive dyes having good levelling properties. Consequently these agents can generally be used at higher concentrations when it is particularly necessary, e.g. for dyeing pale colours and at low liquor ratios [31]. If required, the retarding action of the auxiliaries can be diminished by raising the temperature. Their range of action extends from lowering the rate of exhaustion of the dyes (especially in the semi-pigmentation process) to the levelling of uneven dyeings at high temperatures.

Oxidation and aftertreatment

When the exhaustion process is complete, the dyeing is rinsed to remove loose dye and most of the residual reducing agent and alkali. The leuco dye is then reconverted into its original form by oxidation. This is generally carried out with hydrogen peroxide, sodium perborate or sodium *m*-nitrobenzenesulphonate, e.g. Ludigol (BASF). 'Skying' in air, or treatment with alkaline hypochlorite, or with acidified potassium dichromate or sodium chlorite, is now seldom used. In certain cases there can be problems with the indanthrone derivatives (CI Vat Blues 6 and 16, and especially with CI Vat Blue 4) due to over-oxidation, caused particularly by atmospheric oxygen in the presence of high alkali concentration. The yellow-green azine derivative of the dye is formed and the correct colour can then only be obtained by revatting.

Detailed investigations into oxidation with peroxide, perborate or sodium *m*-nitrobenzenesulphonate (Ludigol) have shown that the reaction mechanisms differ in principle. In alkaline media, the peroxy agents react relatively slowly with excess hydrosulphite, whereas Ludigol reacts extremely rapidly. Ludigol also reacts more rapidly with the leuco dyes. The higher the temperature and the lower the pH, the quicker the reactions with the oxidising agents proceed. If oxygen is completely excluded, dyes with an extremely low leuco potential either cannot be oxidised by Ludigol, or can only be oxidised by reducing the pH [14].

After oxidation the dyeings are treated at the boil in an aqueous solution of a surfactant, an operation generally referred to as 'soaping'. This process is very important in vat dyeing. Loose dye is removed and the properties of the dyeing are changed significantly, e.g. the fastness to light and washing may be improved and there may be a change in colour (particularly with mercerised cotton and regenerated cellulose).

It is believed that the forces between the dye molecule and the cellulosic chain are weaker after oxidation than before, and that the dye molecules are aligned mainly parallel to the fibre axis initially [26,33]. In many cases the soaping process produces changes in the absorption spectra and in the dichroism of dyeings on film. From this behaviour it is concluded that the dye molecules associate to form submicroscopic crystals in the fissures of the substrate, and that in these crystals the dye molecules are oriented predominantly at right angles to the fibre axis [33,34]. Valkó [26] has proved, by X-ray examination of extremely deep dyeings on cellophane film, that in certain cases crystallisation takes place on soaping (e.g. with CI Vat Blue 6 and Orange 9). In other cases (e.g. CI Vat Blue 4) X-ray analysis has shown the dye to be amorphous, both before and after soaping. Indigo dyeings were found to contain dye crystals even before they were soaped.

Two factors are important in practice:

(1) The efficiency of the soaping process is determined solely by the temperature and duration of the treatment and is not influenced by the pH.

(2) Dyes that show only a small change in colour are particularly useful for continuous processes, in which only a limited time is available for soaping.

5.2.6 Fastness properties

Dyeings produced with vat dyes on cellulosic fibres have an overall standard of fastness higher than is achieved with other classes of dyes. This applies not only to their fastness in use, e.g. fastness to light and washing, but also to those factors important during fabric processing after yarn dyeing, e.g. fastness to mercerising, soda boiling, chlorite and hypochlorite bleaching. Because of their excellent fastness to these processes, vat dyes are ideal for coloured woven goods such as handkerchiefs, shirting materials and towelling.

If the dye is readily reducible, poor fastness ratings are obtained when the dyeing is washed at the boil in an alkaline medium. This applies to the flavanthrones (e.g. CI Vat Yellow 1) and the pyranthrones (e.g. CI Vat Orange 9). In these cases the fibre itself has a reducing action. The violanthrone dyes (e.g. CI Vat Blue 20) are also sensitive in this respect. Increases in the molecular size and the number of reducible keto groups result in an improved stability to this treatment. The problem can be prevented by adding a mild oxidising agent, e.g. Ludigol.

The indanthrones are sensitive to hypochlorite. In this case over-oxidation leads to the formation of azine groups and the dyeings become greener and duller. CI Vat Blue 4 is more prone to this problem than CI Vat Blue 6.

The light fastness is particularly good with dyes that have a multinuclear ring system with integrated NH groups. However, with certain combinations of yellow with blue or green dyes there can be an adverse action on exposure to light or weathering, resulting in the blue or green component fading more rapidly than anticipated. This effect is commonly referred to as catalytic fading. The behaviour of such combination dyeings is influenced by (a) dye selection, (b) mixing proportions and depth of colour, (c) moisture content of the textile material, (d) u.v. content of the incident light and (e) the substrate itself.

A particular yellow vat dye does not always show the same behaviour towards the different blue or green types with which it may be combined. There is, therefore, no general rule for determining whether a certain yellow dye is suitable for combining with green or blue dyes. Dyeings with a high yellow content are, however, more susceptible than those with a smaller proportion of yellow. The light fastness of such combinations diminishes with an increase in the atmospheric humidity. Hence these light fastness anomalies are hardly shown by textiles that have been given a water-repellent or resin-finishing treatment, because they take up less moisture. Dyeings on mercerised cotton or bright viscose fibres show the effect to a lesser extent than those on unmercerised cotton. However, certain dyes, e.g. CI Vat Green 3, may even have a positive effect on the light fastness of combination dyeings.

On exposure to light, degradation of the cellulosic fibre can occur more rapidly with a vat-dyed substrate than with undyed material, leading to the formation of oxycellulose. The mechanism of this reaction can be explained as reduction of the dye in the fibre by the action of light, followed by its reoxidation by atmospheric oxygen, during which peroxides are formed that degrade the cellulose. This occurs mainly with those vat dyes that absorb radiation of short wavelength (e.g. CI Vat Oranges 2 and 9). Other vat dyes (e.g. CI Vat Green 3, and Blues 4, 6 and 14) have the opposite effect, inhibiting fibre degradation on exposure to light.

5.3 FUNDAMENTAL PROCESSES OF VAT DYEING

5.3.1 Pretreatment for dyeing

Pretreatment for dyeing is very important; it should ensure that the substrate has a high and uniform dye uptake and absorbency, is virtually free of husks, has a sufficiently high standard of whiteness (especially for pale dyeings), but must not cause any significant damage to the cellulose.

The requisite standard of adsorption is achieved by removing the hydrophobic impurities from the cellulose. In the case of cotton the calcium and magnesium ions that are present in the pectin play an important part [22]. Pretreatment is carried out by boiling off in the presence of alkali and dispersing and sequestering agents. Further improvement in the absorbency can be achieved by a treatment with a high concentration of alkali (causticising or mercerising). Prior to dyeing, size is removed from woven fabrics by the usual methods (see Chapter 2).

Since the vat dyeing of cellulosic fibres is carried out in relatively strong alkaline baths, it is also possible – in certain circumstances – to dye grey material.

For example, with suitable auxiliaries grey yarn can be scoured and dyed simultaneously by the high temperature process above 100°C.

The substrate must be whitened sufficiently to obtain a dyeing of the requisite hue and brightness. This is usually achieved by a preliminary oxidative bleaching treatment. As the leuco vat dyes are oxidised with peroxide or perborate after the dyeing process, this also has a certain bleaching action on the substrate, so that an oxidative prebleach may be unnecessary in certain circumstances, e.g. with dyeings in medium- to full-depth colours.

5.3.2 Batchwise dyeing processes

Leuco process

In the leuco process the material to be dyed is entered into a prepared dye liquor that contains the fully vatted dye, alkali (caustic soda) and reducing agent (hydrosulphite), together with various amounts of salt, dispersing agent, sequestering agent and levelling agent, as required.

The amounts of caustic soda, hydrosulphite and salt – and the processing conditions – depend on the liquor ratio, dyeing properties and quantities of the dyes applied. Experience over many years has resulted in dyes with similar dyeing properties being classified into groups:

(1) IK dyes;
(2) IW dyes;
(3) IN dyes;
(4) IN Special dyes;
(5) Dyes that require a special procedure, e.g. CI Vat Red 23 and CI Vat Black 9.

IK dyes have a relatively low substantivity for cellulose and so are dyed at room temperature with a small amount of caustic soda and a high salt concentration. This group of dyes has diminished in importance. IW dyes have a much higher substantivity and are dyed at 45–50°C with somewhat more caustic soda and less salt. Regenerated cellulosic fibres and mercerised cotton are dyed without salt. IN dyes require still more caustic soda and are dyed at 60°C without salt. They have high substantivity for the fibre, as have the IN Special dyes, but the latter differ from the normal IN dyes in requiring even more caustic soda.

The chemical additions required depend on the dye group, liquor ratio and amount of dye applied. Typical amounts range from approximately 5 ml l^{-1} caustic soda (27% by weight), 2 g l^{-1} hydrosulphite and 10 g l^{-1} sodium sulphate for IK dyes in pale depth at 20:1 liquor ratio, up to about

25 ml l^{-1} caustic soda (27% by weight) and 7 g l^{-1} hydros for full depths of IN dyes at 10:1 liquor ratio.

The classification of vat dyes into different groups according to their method of application is also described in the Colour Index [10]. This classification covers three dyeing procedures, methods I, II and III, referring to strong alkali and weak alkali at high temperature, and weak alkali at low temperature respectively.

Normally vatting is carried out in a long liquor for 5–10 min at dyeing temperature. Only concentrated dye preparations that contain little or no dispersing agent are pre-vatted in a highly concentrated stock vat, since vatting takes place more rapidly under these conditions.

With most dyes the dyeing temperature can be raised to 80°C if necessary during the dyeing process to achieve better levelling of any unevenness. It is also usual to raise the temperature to 80°C for shading purposes. If the leuco process is employed at temperatures above 90°C (HT process) it is necessary to use IW and IN dyes that are sufficiently stable at these temperatures, together with a special reducing agent of the hydroxyalkylsulphinate type. Typical chemical additions are 10–20 ml l^{-1} caustic soda (27% by weight) and 5–10 g l^{-1} reducing agent, depending on dye concentration, liquor ratio and temperature. With vat dyes that are sensitive to over-reduction it is necessary to add suitable amounts of inhibitor (e.g. glucose) when the dyeing temperature exceeds 60°C. It should be noted that in the presence of sequestering agents such as ethylenediaminetetraacetic acid, sodium nitrite is not effective for this purpose. The HT process is employed when it is necessary to brighten the substrate while dyeing pale to medium depths (at 115°C) or when there are levelling and penetration problems with certain substrates and dye combinations (at 90–100°C).

Prepigmentation process

In this process the vat dye is distributed in the textile material as evenly as possible in the non-substantive insoluble form, i.e. prior to vatting. Only dyes with a fine particle size distribution are suitable for this method of application. Pigmentation is begun at room temperature and the temperature is then raised slowly to 60–80°C, salt being added, if necessary, to promote exhaustion. This is followed by additions of alkali and hydrosulphite to vat the dye, which is then taken up by the fibre. Dyeing is continued to completion at the usual dyeing temperature, followed by aftertreatment.

Alternatively the HT process can be employed. If a brighter colour is required on a substrate that has not been prebleached, the prepigmentation can be

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combined with a peroxide bleach. The prepigmentation process can be carried out on all types of batchwise dyeing equipment.

Semi-pigmentation process

This process utilises the slower rate of vatting at low temperatures. The dyebath is set with dye and chemicals at 15–20°C and dyeing begun immediately. The temperature is then gradually raised, during which period dye that is not yet vatted becomes distributed in insoluble form in the substrate. Vatting begins simultaneously and the leuco compound formed is taken up by the fibre. With this procedure a more uniform dyeing is obtained from the outset compared with the leuco process, where the leuco dye exhausts extremely rapidly. As in the prepigmentation process, the dyes must have a satisfactory mean particle size distribution.

5.3.3 Semi-continuous dyeing processes

The semi-continuous dyeing methods incorporate at least one continuous operation, i.e. impregnation of the material with the dye dispersion, usually coupled with an intermediate drying treatment. Various batchwise dyeing machines, but most often the jig, can then be used to develop the dyeing, the dye being vatted and taken up by the fibre in the location where it has been applied. The chemical requirements are governed by the amount of dye applied, the liquor ratio and the method used. These processes give well-penetrated dyeings with good levelness.

5.3.4 Continuous dyeing processes

A prerequisite for all continuous dyeing processes with vat dyes is that the fabric should have good absorbency so that it wets out rapidly and uniformly. The continuous dyeing of loomstate fabric or of material that has only been desized is restricted to special cases. Since the differences in substantivity of the leuco dyes have less influence, selection of the dyes is not as limited as in batchwise processes. Highly substantive dyes in the IN and IW groups have proved the most suitable.

The pad–steam process is the most reliable and popular continuous dyeing process for vat dyes. The fabric is padded with the dye dispersion and then dried immediately. In a second padding process alkali and reducing agent (usually hydrosulphite) are applied, after which the fabric is steamed in saturated steam for 40 s at 98°C wet bulb/103°C dry bulb to reduce the dye and fix it on the substrate. This is followed by oxidation, rinsing and soaping on an open-width washer. The consumption of reducing agent depends on the quantity and type of dye applied and on the processing conditions, because a certain proportion of the hydrosulphite is oxidised by atmospheric oxygen during the development process. Typical chemical requirements are about 50–100 ml l^{-1} caustic soda (27% by weight) and 20–50 g l^{-1} hydrosulphite, depending on dye concentration and liquor pick-up.

In the wet-steam process, after pad application of the dye dispersion, the padded material is impregnated wet-on-wet with the requisite chemicals and developed immediately by steaming, thus eliminating the intermediate drying process. The padding trough that contains the chemical liquor can be situated (a) directly in front of the steamer, (b) at the entrance, or (c) inside the unit, immediately behind the entry slot.

The importance of the wet-steam process is restricted to certain qualities (voluminous or heavy unmercerised woven fabrics, such as terry towelling and corduroy). The merits and limitations of this approach have been described [35]. Machines have been developed for dyeing short runs by this procedure, which is particularly economical compared with jig dyeing [36].

5.4 DYEING METHODS

5.4.1 Dyeing of loose stock

Cotton is seldom dyed in the form of loose stock. However, if this procedure is used, dyeing is always carried out by the pack system. The fibrous material is opened up, sprinkled with hot water and loaded into the dyeing vessel, in which it must be packed very tightly and uniformly to prevent channelling during dyeing. The loose stock is not usually pretreated prior to dyeing, which is mostly carried out by the leuco process at high temperature.

5.4.2 Dyeing of sliver

Cotton is dyed in the form of sliver when a large quantity of yarn is required with optimum levelness of colour and a high bulk, or when a fully penetrated dyeing is required on a high-quality yarn. Sliver can be dyed:

(1) wound on beams;
(2) like loose stock, by the pack system;
(3) like wool tops, in the form of wound packages.

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It is usually dyed by the leuco process or by the prepigmentation method with simultaneous bleaching.

5.4.3 Dyeing of wound yarn packages

In package dyeing machines the liquor circulates through the stationary material. Uniformity of liquor flow is particularly important, this being closely related to the resistance of the package, which in turn is determined by the type of fibre, the package density, the type of winding and package centre [37], the pH of the liquor and the dyeing temperature. Yarn that is liable to shrink during dyeing is wound on split or cardboard tubes combined with spring centres. Cotton yarn can be wound more tightly than staple viscose, but uniformity of the winding is the most important factor. Air must be removed from the packages with steam or hot water, using a non-foaming wetting agent, before dyeing is begun.

Cheeses are generally dyed with an alternating liquor flow. In closed machines dyeing can be carried out at temperatures up to 115°C by the leuco, prepigmentation or semi-pigmentation processes already described. A dyeing method based on prepigmentation, followed by controlled metering of a caustic soda/hydroxyacetone mixture and a final addition of hydros, has been described [38]. Alternatively, work has also been done on controlling the rate of reduction by means of metered additions of hydros alone [39–41].

5.4.4 Dyeing of yarn in hank form

In the traditional hank-dyeing procedure, the hanks of yarn rotate in becks containing the stationary liquor. In the spray dyeing machine, however, the liquor is also circulated. The pack system, as used for loose stock, is now seldom employed for hanks, although it has the advantage that even very fine yarns can subsequently be processed without difficulty when dyed in this way.

Hanks dyed in becks are usually dyed by the leuco process. The vat is prepared and raised to the dyeing temperature before the hanks, suspended from rods, are entered and fully immersed. The hanks are then turned, frequently at first, then at longer intervals. On completion of dyeing, the liquor is drained off and the dyeing oxidised and soaped in the usual manner.

Conventional and enclosed hank-dyeing machines are employed for yarn qualities that are usually difficult to dye level, e.g. mercerised ply yarns, knitting yarns and sewing thread. The levelness in circulating-liquor systems is dependent on the uniformity of the liquor flow through the yarn. Careful selection of the dye combinations is important, preferably from the IW group of dyes. The semi-pigmentation process with IN and IW dyes is the most suitable method. Since one-third of the hank is permanently exposed to oxidation by atmospheric oxygen, the hydrosulphite consumption is higher than when dyeing is carried out in becks, so it must be checked constantly. In enclosed machines the consumption of hydrosulphite is only 65–75% of that in conventional hank-dyeing machines.

5.4.5 Dyeing of woven fabrics

Woven fabrics made from cellulosic fibres can be dyed either by batchwise procedures in open-width or rope form, or by semi-continuous or continuous methods. The procedure employed depends on the type of fabric (fibre material, construction), size of dye lot and dyeing equipment available [42].

Batchwise methods

The most important types of dyeing equipment for the batchwise application of vat dyes to woven fabrics are jigs, winches and beam dyeing machines. Jet and overflow machines are increasingly used for dyeing knitgoods (see section 5.4.6).

The most suitable jigs are the covered type, fitted with an automatic reverse mechanism, with the fabric running at a low tension and a constant speed. The fabric must be desized before it is dyed. When the individual pieces and end cloths are sewn together there should be no longitudinal creases, seam marks or projecting selvedges. The more open the fabric construction, the smaller must be the size of the batch. The liquor ratio must not be less than 2:1. Since the fabric is liable to cool the dye liquor initially, it is important to check the liquor temperature carefully during the first pass and to keep it constant. Dyeing can be carried out by any of the batchwise processes already described. The dye liquor on the fabric must always contain sufficient hydrosulphite during the dyeing process to prevent a change in colour taking place at the selvedges because of oxidation by atmospheric oxygen. The concentration of reducing agent must be checked continuously and replenishing additions of reducing agent and caustic soda made as necessary. The recent introduction of reliable metering devices to control the input of alkali and hydrosulphite to the jig trough has greatly improved the level of reproducibility attainable in this long-established process [43].

Enclosed equipment is particularly necessary for winch dyeing to keep the consumption of hydrosulphite to the minimum. The process most frequently employed is the semi-pigmentation method, but the leuco and prepigmentation methods are also used.

In beam dyeing the levelness of the dyeing depends on the uniform flow of liquor through the textile material. The resistance to this flow depends, in turn, on the structure of the material and on the flow rate of the liquor. It is possible to estimate the influence of the fabric structure on liquor flow and to apply this information in the dyeing operation. The most important dyeing methods for woven fabrics in beam dyeing machines are the semi-pigmentation process (for pale and medium depths) and the leuco process (for full depths). On completion of dyeing the liquor is replaced by a cold rinsing liquor and the dyeing is then oxidised and soaped in the usual manner.

Factors affecting the levelness of beam dyeings made with vat dyes have been determined by pumping dye liquor through mercerised cotton knitted fabrics and measuring dye concentrations at the liquor inlet and outlet. Optimum conditions for good levelness in the exhaustion stage can be obtained by coupling pigmentation with control of the rate of vatting [44].

Semi-continuous methods [23]

The most important process in this area is the pad–jig process. The fabric, together with the end-cloth, is impregnated with the dye dispersion in the padder and wound onto a batch. A good wetting agent is necessary, and also a migration inhibitor. If it is not to be dried before development the wet batch must be rotated slowly and continuously, usually wrapped in plastic film.

In jig development insoluble dye is transferred mechanically to the liquor during the first pass. It is therefore advisable to add some pad liquor to the development bath and to allow this to vat before the first pass. A state of equilibrium is quickly reached in the liquor between the insoluble dye that is transferred and the leuco dye that is being absorbed, thus preventing end-to-end shading variations. The quantity of the pad liquor that is necessary depends on the liquor pick-up of the fabric and on the liquor ratio in the jig development stage. The number of ends given is generally from four to six. The state of the vat is checked with vat yellow paper at the selvedge of the fabric before it re-enters the liquor.

Continuous methods

The pad–steam process is the most important continuous dyeing method for vat dyes (see section 5.3.4). The equipment necessary is indicated by the process sequence: padding (dye dispersion) – drying – padding (reducing agent) – steaming – aftertreatment.

In principle, any type of dye padder is suitable, provided it has a uniform squeezing effect. The coverings of both bowls must be of the same hardness (60–70° Shore). Several designs of padders are available that compensate for roller deflection under load. A uniform liquor pick-up is the most important prerequisite for faultless dyeings. This can only be ensured if there is no variation in absorbency across the width and length of the fabric. For this reason the pretreatment processes should also be carried out continuously in open-width. The dye dispersion should have a neutral reaction, and it is advisable to work with as low a liquor pick-up as possible in order to restrict migration of the dyes during drying. The smaller the dye particles, the greater the tendency to migrate [45]. Liquor temperature is preferably below 25°C.

The fabric should be padded and dried in one continuous operation. Drying is usually carried out in two stages. The fabric is first predried to a residual moisture content of 25–30% in one or more i.r. units. Hot flues or cylinder dryers are usually employed for the final drying operation. Stenters are not used for drying fabric that is still wet from the dye padder because of the risks of dye migration and contamination of the stenter chain.

The predrying and final drying of the fabric, padded with the dye dispersion, are operations that can have a decisive influence on the quality of the dyeing. Irregularities in drying can affect the migration of the insoluble dye particles and thus cause two-sided effects or listing, even when the fabric has been uniformly impregnated on the padder. It is advisable to allow the padded material an air passage of 15–20 s between the padder and the first drying unit. During this time some of the water on the surface diffuses into the fibre, thus minimising the migration. The temperature in the first section of a hot flue should be around 100°C with minimum air circulation. Drying can then be carried out in the other sections at higher temperatures (120–140°C) with a higher degree of air circulation. It is advisable that the first six to ten guide rollers be coated with polytetrafluoroethylene (PTFE) to avoid staining.

If intermediate drying is carried out on cylinders, the i.r. predryer stage is essential, otherwise a dye build-up could form on the first cylinders and dye migration would be severe. In order to reduce staining, the first six to eight drying cylinders should be PTFE-coated and temperature control applied to groups of cylinders, the first of which should not exceed 100°C. The risk of two-sided effects is greater at higher temperatures, especially at low processing speeds. Nevertheless cylinder dryers have proved very suitable for smooth fabrics and are much more economical than hot flues.

For the full pad–steam process a conventional padder is usually employed to apply the alkali and reducing agent. The liquor trough must be of small capacity so that the contents are rapidly renewed by the feed liquor. The liquor should be kept cold, preferably below 20°C, and it is advisable to cool the fabric from the preceding drying. The pick-up should be as high as possible. This ensures that there is sufficient liquor available for the dyes and chemicals and that exposed parts of the fabric (e.g. twill lines) are always saturated with sufficient reducing liquor. This gives an improved fabric appearance and prevents frosting.

In the wet-steam process chemical liquor impregnation is carried out so that there is a maximum difference in pick-up between wet fabric entering and leaving the liquor trough. This may be achieved either by applying an unweighted top roller, or by lick-roll application. After leaving the nip or the lick roller, the fabric must pass directly to the steamer without passing over any guide rollers.

Steamers are usually of the tight-strand type with driven top rollers and compensator speed control to maintain correct fabric tension. The fabric capacity is between 15 and 60 m, so that depending on the speed the steaming time is in the range 30–60 s. For fabrics that are to be processed with minimum tension, festoon steamers have proved suitable, provided that precautions are taken to ensure that chemical liquor does not accumulate at the bottom of the loops.

The atmosphere should be saturated steam, at normal atmospheric pressure, and it is imperative that the steam atmosphere should be as free from air as possible, with instruments available for checking this state. Moisture content is as important in the reduction process as temperature. The correct balance is necessary for a successful dyeing operation [46]. The steamer exit must be constructed in the form of a water trap to prevent air from entering the steamer. The water feed should be 3–5 $l\,kg^{-1}$ of material and the temperature in the water trap should not exceed 40°C, otherwise some of the vat dye may be removed. The water should be fed into the water trap across its full width but in such a way that none of it is sprayed on the fabric. The water drains by overflow, again across the whole width. The design of the steamer must prevent condensation drops from the steamer roof and from the steamer throat entry.

The air passage between the padder and the steamer entry is critical and must be as short as possible in order to avoid decomposition of the hydrosulphite (see section 5.2.2). Likewise the air passage between the steamer water trap exit and the first wash box should be kept short; this applies especially to blue indanthrone dyes that are susceptible to over-oxidation by atmospheric oxygen at high alkali concentrations, forming the dull yellow-green azine derivative.

Aftertreatments consist of rinsing, oxidising, soaping and final rinsing, and are carried out continuously immediately after steaming. The most suitable equipment is an open-width washer, preferably with eight compartments. The fabric capacity of each compartment is approximately 15 m, although this depends on the speed of processing. Efficient oxidation and especially soaping depend on the processing time and concentration of chemicals, so the fabric capacity of these compartments should be proportional to the processing speed. Oxidation is by peroxide or perborate maintained at pH 8–9 and 50°C. The fastness of the dyeing and the final hue are affected by the soaping process. In the presence of water at an elevated temperature a change takes place in the state of the reoxidised dye on the fibre that is accompanied by a hue change. Dyes selected for continuous processing should be relatively insensitive in this respect, since it is essential for the final hue to be attained within the time available for soaping [45,47].

Two factors are decisive for the treatment: the time should be not less than 30 s and the temperature should be 95–100°C. To ensure good reproducibility of the dyeings, rinsing water and chemical additions should be controlled by flowmeters and specific temperatures maintained by automatic controllers.

5.4.6 Dyeing of knitgoods [42,48]

Vat dyes are being used increasingly to meet higher fastness requirements on cotton knitwear. This development has been facilitated by the use of jet and overflow dyeing machines, in which the dyeing conditions can be defined more precisely than in winches due to the rapid liquor circulation and uniform temperature [49,50].

Knitgoods have only a low dimensional stability to mechanical stress. Dyeing must therefore be carried out at the least possible tension to ensure that the finished fabric has a low shrinkage on subsequent washing. Cotton knitgoods were formerly dyed mainly in rope form on winches, or on beams after slitting. They are now dyed successfully in jet and overflow dyeing machines. Warp-knitted fabrics are dyed mainly in beam dyeing equipment.

The semi- and prepigmentation processes are the main ones used for winch dyeing, the former having proved particularly suitable, e.g. for dyeing interlock qualities in pale to medium depths. The hydrosulphite content of the liquor must be carefully checked and replenished when necessary. It is advisable to increase the dyeing temperature to 70–75°C with IW or IN dyes to promote migration. In the prepigmentation process the hydrosulphite consumption can be reduced by extending the pigmentation stage and shortening the dyeing stage.

In jet and overflow machines the fabric is transported mainly by the liquor flow. Since products that tend to foam will cause problems in machines that are only partially flooded, care is necessary in the selection of the auxiliaries used. This restriction does not apply to fully flooded jet dyeing machines because no foam can develop. In the case of machines that are not fully flooded, the atmospheric oxygen in the machine consumes a certain amount of hydrosulphite. Experience has shown that the oxygen in 1 m^3 air consumes 1.7 kg hydrosulphite and 1.7 l caustic soda (27% by weight), which must then be replaced. To improve the brightness of pale colours the material can be bleached oxidatively during soaping without undue extension of the processing time.

The increasing use of metered dosing equipment has resulted in the development of a one-bath dyeing/oxidation method [38]. In this process the caustic soda, hydros and auxiliary products are added first at the dyeing temperature. The dye dispersion is metered in over 10–20 min and run for 40–60 min, followed by an addition of a mixture of hydrogen peroxide and sodium *m*-nitrobenzenesulphonate (Ludigol). This is run for 20 min, drained and soaped. The advantage of this process is that it eliminates the difficulties associated with intermediate rinsing.

5.4.7 Correction of faulty dyeings

Faulty dyeings can be corrected by levelling, stripping or over-dyeing. Levelling is carried out at 80–90°C, on the winch or jig, or even above the boil in package-dyeing machines. In addition to caustic soda, reducing agent and other auxiliaries, the liquor must contain a sufficient amount of nonionic levelling agent. For stripping the dyeing is treated at 80–90°C in a liquor that contains caustic soda and hydrosulphite, together with polyvinylpyrrolidone (PVP) as a stripping agent. This complexes more readily with the leuco dye than does the levelling agent, rapidly forming soluble leuco dye polymer complexes in the liquor. The concentration of caustic soda should not exceed 20–30 ml l^{-1} (27% by weight), with a maximum of 1 g l^{-1} PVP and a treatment time of 30 min (repeated if necessary).

5.4.8 Dyeing of regenerated cellulosic fibres

Viscose fibres swell to a greater extent than cotton in the presence of alkali. This swelling action – and its effect on the strength and handle of the material – is less pronounced with more tightly spun yarns and woven fabrics. Better stabilisation is achieved by fibre blending. For example, viscose can be dyed with vat dyes without difficulty when they are blended with polyester or cotton.

Polynosic fibres or high wet modulus (HWM) fibres are more stable to alkali than conventional viscose. Cotton/polynosic blends form an alkali-stable substrate that can be mercerised. Although the HWM fibres are more sensitive to alkali, they are sufficiently stable to be dyed with vat dyes.

The strong swelling of viscose results in an increase in the diameter of the fibre. Particular attention must be paid to this in the dyeing of wound packages, since it increases the resistance to liquor flow. For this reason, packages of viscose staple yarn must be wound at a lower tension than cotton yarn. Since leuco dyes have higher substantivity for regenerated cellulosic fibres than for cotton, there is a greater risk of obtaining unlevel dyeings; this can be counteracted by increasing the quantity of levelling agent used.

Regenerated cellulosic yarns are dyed in package or hank form by the leuco or prepigmentation process. Dyeing at as high a temperature as possible minimises swelling of the fibre and promotes levelling. On completion of dyeing the material must be thoroughly acidified because alkali is only removed slowly from these fibres by rinsing.

Since woven viscose staple fabrics are readily deformed in the wet state, care must be taken not to stretch the material during dyeing. They can be dyed (a) batchwise in low-tension jigs, beam dyeing machines and on the winch, (b) semi-continuously by the pad–jig process or (c) continuously, by the methods just described.

5.4.9 Dyeing of linen

After retting, in addition to the bundles of cellulosic fibres, bast fibres still contain portions of the epidermis, the cortical cells and the woody zone, i.e. an amorphous binding substance composed of lignin and hemicellulose [17]. This binding substance must not be removed during the dyeing process because it gives the linen its distinctive handle.

The material is therefore only pretreated and bleached when it is to be dyed in pale depths, since all alkaline treatments remove the non-cellulosic substances present and thus result in an undesirable loss in weight. Dyeing at 60–80°C produces a loss in weight of 5–10%, but an alkali treatment under high-temperature conditions followed by a reductive bleach can produce a weight loss of 20%. In package dyeing it is difficult to achieve good penetration of the yarn and the crossover points, particularly in the case of conical packages on rigid tubes. Hence it is best to use flexible springs, together with dyes giving good levelling performance and a sufficient quantity of levelling agent. All the dyeing processes described for cotton yarn may be used for linen. The only problem in dyeing linen fabrics is that of achieving satisfactory penetration. In this respect the best results are obtained by beam dyeing at high temperatures. The pad–jig and cold pad–batch processes are also suitable.

5.4.10 Dyeing with indigo

Jeans made from blue denim have been popular over a longer period than any other item of apparel. They are inexpensive, durable, versatile and socially egalitarian. The blue-dyed warps wash down to an attractive blue without staining the white weft.

Leuco indigo has only low substantivity for cellulose, hence only pale depths are obtainable by exhaust dyeing procedures. Indigo is therefore applied in a series of 'dips', with intermediate squeezing and atmospheric oxidation. By repeating the process, dye is applied to the substrate 'layer on layer' to give deep dyeings with a relatively low rubbing fastness. On cotton, indigo dyeings have a light fastness rating of 3 at standard depth. Yellow decomposition products are formed on exposure, the dyeing becoming greener and duller. Since these yellow products are water-soluble the original bright blue colour is restored on washing. When reassessed after washing a light fastness rating of 6 is obtained.

Indigo is usually dyed from a caustic soda and hydrosulphite vat. Cotton is dyed with indigo in the form of ball warps, warp beams or in fabric form, usually continuously. The batchwise dyeing of hanks of yarn is carried out in becks with repeated short dips, followed by squeezing and atmospheric oxidation. Wound packages cannot be dyed in full depths with indigo. Piece goods can be dyed on the jig but the batchwise dyeing of indigo is of little importance.

In the continuous indigo dyeing of warp yarn, the yarn is in the form of a full-width warp beam or a cable the thickness of a thumb (ball warp), containing 300–400 individual threads. It passes through several vats, each followed by an air passage for oxidation. The processing speed is 20–30 m/min with an immersion time of 20–30 s in each vat. On leaving the vat the material is squeezed to a liquor pick-up of approximately 100%, after which the dyeing requires around 2 min for oxidation before it passes into the next vat. Rinsing at ambient temperature in two or three rinsing baths after oxidation is normally adequate. At least 3–4 $\mathrm{l\,kg^{-1}}$ of water per rinsing beck is sprayed with force against the warp yarn [51]. To ensure that the dyebath composition is exactly the same in all the multiple dip tanks, they are coupled together with distribution pipes and pumps, including a feed tank to continuously replenish the dye, caustic and hydrosulphite consumed. Good volumes of flow with minimum turbulence is essential to ensure uniformity [52].

A typical recipe for a dye liquor would be:

(1) caustic soda (27% by weight), 5 ml l^{-1};
(2) hydrosulphite, 1.5 g l^{-1};
(3) stock vat, 62.5 ml l^{-1}.

The stock vat is composed of:

(1) Indigo Pure (BASF CI Vat Blue 1), 80 g l^{-1};
(2) dispersing agent, 4 g l^{-1};
(3) wetting agent, 1 g l^{-1};
(4) caustic soda (27% by weight), 130 ml l^{-1};
(5) hydrosulphite, 60 g l^{-1}.

Apart from the stock vat replenishing addition, it is also necessary during the dyeing process to add hydrosulphite and caustic soda in amounts that depend on the prevailing conditions. The content of reducing agent and alkali must be checked at regular intervals to determine what quantities are necessary.

Careful buffering of the dyebath pH can be an effective means of conserving indigo and achieving more reproducible dyeings [53,54]. Depending on dyebath pH, reduced indigo can exist in three forms: as the nonionic enolic acid leuco compound, the mono-enolate anion or the bis-enolate anion. Colour yield correlates closely with the fractional amount of singly charged mono-enolate ions present in the dyebath, reaching a maximum at pH 10.5–11.5. This moiety is much more soluble than the acid leuco form and more substantive than the doubly charged bis-enolate [54,55].

Several techniques are available for imparting the desired ‘stressed’ look to denim garments before sale. The abrasion, wear and damage to trims and sewing threads caused by conventional aqueous pumice stonewashing have been compared with dry stonewashing, which causes less damage [56]. Acid washing involves aftertreatment with potassium permanganate but residual manganese can cause subsequent yellowing if not removed by a sequestering treatment with ethylenediaminetetraacetic acid [57]. White (or snow) washing is a further modification, where stones soaked in alkaline hypochlorite or acidic permanganate are tumbled with the dyed garments [58].

Enzyme treatment has major advantages over stonewashing methods in that the machinery does not suffer the same wear and there is less degradation of the garment while achieving the worn and faded look [59]. A two-stage enzyme sequence is recommended [60]: desizing first using a conventional amylase, followed by a neutral or acid cellulase/glucanase formulation. Neutral cellulases are preferred because of reduced backstaining of pockets and less stringent pH control requirements [61].

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CHAPTER 6

Dyeing with sulphur dyes

Colin Senior

6.1 COMMERCIAL POSITION

The first sulphur dye to be discovered was Cachou de Laval, a brownish khaki colour obtained by heating organic wastes such as sawdust with sodium polysulphide [1]. Since that time there has been a steady improvement in dyeing and fastness properties, together with the development of different product types, in a range covering all colours except a true red. Sulphur dyes still constitute the largest class of dyes in terms of quantity with an estimated worldwide production of more than 80×10^3 tonnes p.a., even though a different picture emerges if unit price is used as the basis of calculation.

When reactive dyes were introduced in the 1950s, it was widely expected that this class would capture a major share of the existing market for sulphur, direct and vat dyes, but this has not occurred, as Table 6.1 shows. Although it is impossible to give an exact relationship between the different tinctorial strengths and production quantities of the various forms of sulphur dyes from the various producers, the figures do show very clearly that sulphur dyes are a major class of colorant in world terms.

Sulphur dyes are important for black, navy, brown, olive and green colours in medium to heavy depths, being relatively inexpensive. The liquid brands are ideally suitable for continuous dyeing in long runs. Their fastness properties vary markedly throughout the range, e.g. light fastness increases from yellow at about 3 to black at 7. Fastness to wet treatments in general is good, although fastness to bleaching is poor with certain notable exceptions, such as CI Sulphur Reds 10 and 14, Green 14 and Black 11.

Sulphur dyes are widely used on cellulosic fibres and their blends, especially with polyester, but also with nylon and acrylic. Cotton and polyester/cotton drill and corduroy are dyed continuously or on the jig, whilst cotton/nylon and cotton/acrylic knitted and pile fabrics are winch- or jet-dyed. Since 1985 fashion changes have demanded greater usage of sulphur black in denim fabrics. Yarn

Table 6.1 Share of the world dye market held by different types of colorants [2]

Consumption on cellulosic fibres		Consumption on all fibres	
Colorant class	(%)	Colorant class	(%)
Sulphur dyes	29.0	Sulphur dyes	18.0
Direct dyes	27.4	Direct dyes	17.0
Vat dyes	19.4	Disperse dyes	16.5
Reactive dyes	9.7	Acid dyes	16.0
Azoic dyes	8.1	Vat dyes	12.0
Pigments	6.4	Reactive dyes	6.0
		Azoic dyes	6.0
		Basic dyes	4.5
		Pigments	4.0

dyeing is carried out in warp, hank or package form, mainly as navy or black. Loose stock is dyed in circulating-liquor machines of various kinds. Sulphur dyes are also applied in limited quantities to paper and silk, and more widely to leather.

6.2 CONSTITUTION OF SULPHUR DYES

Sulphur dyes were first made from organic compounds of known constitution in the 1890s. Various black dyes could be obtained by melting certain nitro-substituted phenols and arylamines with sulphur and sodium sulphide. In 1899 a particularly economical black was discovered by refluxing an aqueous mixture of 2,4-dinitrophenol and sodium polysulphide. The high quality, excellent fastness and low cost of this dye (CI Sulphur Black 1) still keep it in place as the most important black dye for the textile industry.

In spite of their long-established use, surprisingly little is known of the detailed constitution of sulphur dyes. They are normally distinguished in terms of the organic intermediates from which they are derived and the process of sulphurisation used in their manufacture.

Many yellow, orange and brown sulphur dyes are made by dry baking of intermediates such as 2,4-diaminotoluene (Figure 6.1) with sulphur above 160°C. The colour produced is considered to be attributable to the formation of the thiazole chromophore, as in CI Sulphur Orange 1, for example (Figure 6.1).

An aqueous reflux method is used for the production of CI Sulphur Black 1

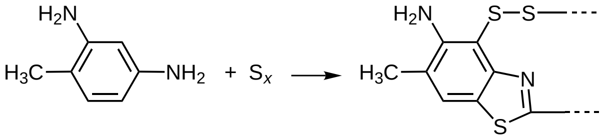

Figure 6.1

and other black, blue-green and violet dyes derived from indophenols or the more stable leuco indophenol intermediates. Indamines, capable of forming phenazones, are also included in this group; on thionation they produce reddish brown to bordeaux dyes. All these intermediates give rise to thiazine-type sulphur dyes (Figure 6.2).

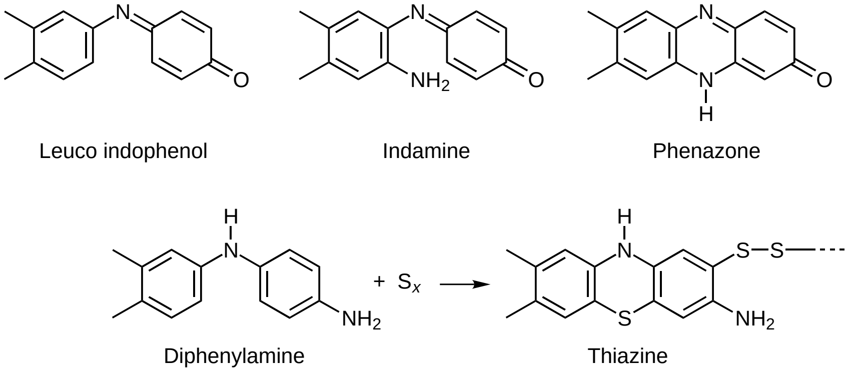

Figure 6.2

The patents relating to the preparation of sulphur dyes are numerous and the products obtained are varied in properties, especially regarding hue and solubility. It is therefore not surprising that structural concepts also vary [3]. The products resulting from thionation processes are varied and complex mixtures, the common features being essentially benzenoid nuclei linked by heterocyclic rings such as thiazole, thiazine or phenazine, as well as the disulphide linkages that enable the dyes to be reduced to the soluble leuco form.

6.3 CLASSIFICATION AND COMMERCIAL FORMS

6.3.1 Colour Index classification [4]

The classification of sulphur dyes in the Colour Index has become somewhat confusing owing to deletions from and additions to ranges and newly developed product types, although the main subdivisions are still clear. The four subdivisions are:

(1) CI Sulphur dyes;
(2) CI Leuco Sulphur dyes;
(3) CI Solubilised Sulphur dyes;
(4) CI Condense Sulphur dyes.

The definition of a sulphur dye (group 1) is a water-insoluble dye, containing sulphur both as an integral part of the chromophore and in attached polysulphide chains, normally applied in the alkaline reduced (leuco) form from a sodium sulphide solution and subsequently oxidised to the insoluble form on the fibre. Sulphur dyes differ from vat dyes in being easier to reduce, but more difficult to reoxidise, different oxidants producing variations in hue and fastness properties.

As well as the traditional water-insoluble powder forms, this group includes the black grains types, which contain some sodium sulphide and possess limited substantivity, but require additional reducing agent for dyeing, and the dispersed sulphur dyes that are available in powder and paste forms and are non-substantive. To complicate the issue, however, some dispersed products are of the so-called sulphur vat type, e.g. CI Vat Blue 43 and CI Vat Green 7, that require caustic soda/sodium dithionite reduction.

A leuco sulphur dye (group 2) has the same CI constitution number as the parent sulphur dye (group 1) but is a powder or liquid brand containing the soluble leuco form of the parent dye and reducing agent, usually sodium sulphide or hydrosulphide, in sufficient quantity to make the dye suitable for application either directly or with the addition of only a small amount of extra reducing agent. Compared with the parent sulphur dye (group 1), a typical pre-reduced leuco sulphur formulation has a dye content in the region of 25 to 50% [5].

A solubilised sulphur dye (group 3) has a different constitution number because chemically it is the thiosulphuric acid derivative of the parent dye, non-substantive to cellulose but converted to the substantive alkali-soluble thiol form during dyeing.

The condense sulphur dyes (group 4) are sodium *S*-alkyl- or *S*-arylthiosulphates. Although they contain sulphur, their constitution and method of manufacture bear little resemblance to those of traditional sulphur dyes. They do require sodium sulphide or polysulphide for dyeing, but conventional sulphur dyeing methods are unsuitable for the condense sulphur dyes.

The so-called sulphur vat dyes are not classified separately in the Colour Index, but are a collection of dyes from both the CI Sulphur and CI Vat classes that possess superior wet fastness properties and better resistance to bleaching than traditional sulphur dyes. They are often applied using caustic soda/sodium dithionite reduction and the range includes CI Vat Blues 42 and 43, CI Vat Greens 7 and 20, and CI Sulphur Red 10, Brown 96 and Black 11. The various commercial forms of sulphur and sulphur vat dyes currently available have been reviewed with reference to the specific applications for which they are intended [6].

6.3.2 Commercial forms

Powders

Unmodified powders were traditionally the principal form in which sulphur dyes were sold. They are now mainly of interest where high-strength dyes have to be transported over long distances. In general they are made from the dried presscake, finely ground and standardised with common salt or sodium sulphate, together with soda ash. They are prepared for dyeing by making a paste with water, which is dissolved by boiling with the necessary amount of reducing agent and further addition of water.

Pre-reduced powders

These are usually made from presscake paste, to which a reducing agent such as sodium sulphide, hydrosulphide or dithionite has been added to form the leuco dye. Before drying, the dye paste may be mixed with dispersing and stabilising agents to aid application.

Grains

Grains are pre-reduced, the quantities of sodium sulphide or hydrosulphide and electrolyte being adjusted to give a granular product when the paste slurry is dried on a steam-heated drum dryer. Grains offer the advantage of having non-dusting properties.

Dispersed powders

The principal use of dispersed powders is in pad–dry–chemical-pad–steam dyeing. They are normally made from presscake by ball or bead milling to microparticle size in the presence of a dispersing system. The drying is strictly controlled and is carried out in the presence of anticoagulants to prevent aggregation of the dispersed dye particles.

Dispersed pastes

The milled pastes vary in strength, but for ease of handling the consistency of the dispersed pastes generally permits pouring from the container. Since no drying costs are involved they are usually cheaper than the dispersed powder brand.

Liquids

During dye manufacture some liquid formulations are made directly from the thionation melt by additions of caustic soda and sodium hydrosulphide. Hydrotropic substances are sometimes added, either at the initial thionation melt stage or after the polysulphide process is completed in order to keep the reduced dye in solution. Partially reduced liquids are usually more concentrated than fully reduced liquids, thus saving packaging and transportation costs. They require a further addition of reducing agent to the dyebath to enable the full colour value to be obtained, but this need not be a sulphide. Glucose or dithionite may be used in order to minimise the sulphide content of the effluent. Fully reduced liquids are ready to use, since the amount of reducing agent for each dye has been carefully controlled to give maximum stability on storage and maximum colour yield in use. The ready-to-use liquid brands clearly predominate for continuous dyeing owing to their ease of handling [5]. Unlike the dispersed pastes, they are not affected by low temperatures.

Water-soluble brands

Solubilised sulphur dyes can be prepared as powders or liquids, the latter being cheaper to produce since no drying costs are involved [3]. These dyes are the Bunte salts or thiosulphuric acid derivatives of the sulphur dyes. They are made by warming the polysulphide-free pastes with sodium sulphite or bisulphite until they dissolve. They are salted out from solution or isolated by drum or spray drying of the liquor. Aqueous solutions of these dyes show little or no substantivity for cellulosic fibres until a reducing agent has been added. This assists the penetration of tightly woven materials. These dyes give more level dyeings with less tendency to bronziness. They are widely used, particularly where effluent pollution may be a problem and especially by small and medium-sized firms, or on speciality goods.

6.4 AUXILIARIES

6.4.1 Reducing agents

The two most important reducing agents for sulphur dyes are sodium sulphide

(Na_2S) and sodium hydrosulphide (NaHS). These products are commercially available in different forms at various concentrations.

Sodium sulphide

The traditional reducing agent for sulphur dyes is sodium sulphide, available as crystals (30–35%) or flakes (usually 60–62%, but may be as low as 50% in some parts of the world).

The quantity of sodium sulphide required is dependent on the particular dyes being used and is usually directly proportional to dye weight, except in the case of pale colours when a minimum concentration in the region of 2.5–5 g l^{-1} sodium sulphide flakes (60%) is used, the higher amount being recommended for yellow, orange, brown and khaki dyes.

Particularly when dissolving the water-insoluble types, it is essential that at least 20 g l^{-1} sodium sulphide flakes (60%) are present during dissolution and that sufficient of this solution is used to dissolve the dye fully. When dyeing very heavy depths at low liquor ratios it may be necessary to use the full dyebath volume to dissolve the dye. The amount of sodium sulphide required varies markedly for different dyes, and the details given by the manufacturer should be followed to obtain optimum results. However, it should be borne in mind that the normal recommendations are for jig or package dyeing, so that abnormal conditions of use, e.g. excessive oxidation, may require some modification of the standard recommendations.

Sodium hydrosulphide (sodium sulphydrate, sodium hydrogen sulphide)

Sodium hydrosulphide is now widely used in place of sodium sulphide and is available at several different concentrations in liquid and powder form. Usage is as for sodium sulphide, but the amount of sodium hydrosulphide (35%) recommended is approximately equal to that of sodium sulphide flakes (60%) under similar circumstances, and an addition of alkali is necessary (10 g sodium carbonate or 5 g sodium hydroxide per 20 g sodium hydrosulphide 35%).

This product is available from many sources, including the manufacturers of paper and viscose fibres. Although the quality varies, in some parts of the world it may be better than that of available sodium sulphide.

Caustic soda/sodium dithionite (hydrosulphite)

For many years this was the only sulphide-free dyeing system available for sulphur dyes, although it was never universally popular. The system is difficult to control and tends to give inconsistent results. The chief exception is with certain sulphur vat dyes (CI Vat Blues 42 and 43, and CI Sulphur Black 11), which can be dyed satisfactorily in a caustic soda/dithionite bath. However, a mixed system of sodium sulphide/caustic soda and sodium dithionite may be preferred in jig dyeing.

Typical recipes for package dyeing at 10:1 liquor ratio would range from 3.5 g l^{-1} caustic soda flake and 2.5 g l^{-1} sodium dithionite for a 1% dyeing to 7.5 g l^{-1} caustic soda flake and 7 g l^{-1} sodium dithionite for a 6% dyeing. These concentrations would be decreased (for example, by 30–40% at 20:1) or increased (correspondingly at 5:1) according to liquor ratio.

Traditional water-insoluble sulphur dyes reduced by this system have been used in warp dyeing of yarn for denims by the dye–dry–size system. Better colour yield is obtained than when using sulphide-reduced baths.

Sodium carbonate/sodium dithionite

This is really only suitable for the water-soluble sulphur dyes as it is too weakly alkaline for the water-insoluble types and requires careful control if over-reduction and consequent low colour yield are to be avoided. Some dyes, for example CI Solubilised Sulphur Red 6, Browns 12 and 15, and Greens 3 and 26, are not suitable for reduction with sodium dithionite, the colour being gradually destroyed. On the other hand, there are a few dyes that give a better yield in the presence of dithionite than they do with sodium sulphide or hydrosulphide. These are special products such as CI Solubilised Sulphur Red 11, CI Sulphur Red 12 and Brown 93 [5].

Water-soluble black and blue sulphur dyes are well suited to this reduction system, and it is particularly useful for dyeing the flame-retardant viscose fibres that are sensitive to strong alkalis (e.g. Evlan FR). The flame-retardant properties are still satisfactory after this dyeing process (at 60–70°C), which is not the case with reduction systems employing caustic alkali.

The various dye manufacturers publish detailed information on the requirements of their dye ranges. Typically 0.5–1.5 g sodium carbonate and 0.25–0.75 g sodium dithionite are recommended per gram of solubilised sulphur dye.

Glucose (dextrose monohydrate)

Together with sodium carbonate, caustic soda or a mixture of both, glucose is in increasing use where environmental considerations prevent the use of sulphide-based reduction systems, although it does present some problems of its own. Jig dyeing presents particular problems, where not all dyes are satisfactorily reduced, because it is difficult to ensure a consistently high temperature.

Glucose may be used as additional reducing agent for the pre-reduced or partially reduced liquid brands, either in place of sodium sulphide or hydrosulphide in order to lower the total sulphide content of the dyeing system, or together with sodium sulphide or sodium polysulphide when applying the water-insoluble types. Sodium polysulphide varies in composition between Na_2S_2 and Na_2S_4. It acts as an antioxidant and greatly assists in overcoming bronzing of the dyeing and premature oxidation of the dyebath. Sodium borohydride ($NaBH_4$) additions are also effective in preventing selvedge bronzing when dyeing sulphur blacks [3].

With the water-soluble dyes glucose may be used either as the total reducing system, i.e. a sulphide-free dye liquor, or together with sodium polysulphide to give improved dye yields [5], especially in continuous pad–steam systems (Figure 6.3). The optimal pH is 11–12 for the glucose–polysulphide method [7].

In package dyeing systems the use of a caustic soda/sodium carbonate/glucose system has been found to give more consistent results than using either alkali alone. As glucose-based dyeing systems are dependent on both pH and temperature, the combination of alkalis may well be buffering the system. At liquor ratios between 10:1 and 20:1 typical recommended concentrations are 3–8 g l^{-1} glucose, 4–10 g l^{-1} sodium carbonate and 2–6 g l^{-1} caustic soda flake, depending on applied depth.

When first evaluated for exhaust dyeing, glucose gave unsatisfactory results, especially in open dyeing machines like jigs and winches. This was because the redox potential and hence the dye yield with glucose is highly dependent on

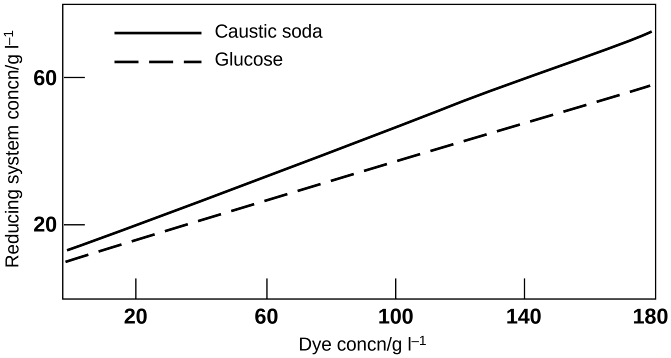

Figure 6.3 Amounts of glucose and caustic soda required in the one-bath pad–steam process for applying solubilised sulphur dyes, in the presence of 7.5 ml l^{-1} sodium polysulphide.

temperature [5]. In all batchwise dyeing systems using glucose it is essential to maintain a temperature of 90–95°C for optimum results, regardless of the alkali selected. Considerable problems have been experienced on jigs. The system has a characteristic odour (of burning sugar) that some consider preferable to the odour of a sulphide-reduced dyebath, although others dislike it, finding it too sweet and nauseous.

Thioglycol (2-mercaptoethanol)

This product has been examined for use with solubilised sulphur dyes, both by exhaust dyeing and by one-bath pad–steam processes. In combination with caustic soda, thioglycol may be used in the application of most solubilised sulphur dyes although the colour yield is lower than from sulphide-reduced systems. The advantage with thioglycol is that there is no sulphide in the effluent and no significant odour from the dyebath. The main drawback is that the dyeing method is more costly overall. Many of the water-insoluble dyes do not dissolve completely and the sulphur vat types are not applicable from a thioglycol-reduced dye liquor [5].

Hydroxyacetone

This product has been suggested for sulphur dyeing, but as with thioglycol, the colour yield is lower than with sulphide, the cost is higher and the product is also flammable. These dyebaths have a characteristic odour similar to acetone. Like thioglycol, the effluent is free from sulphide when used with solubilised sulphur dyes.

Thiourea dioxide

Together with caustic soda, this has been used with limited success in the dyeing of solubilised sulphur black on packages. However, although consistent results may be obtained under laboratory conditions, results in bulk have not proved as successful. Unlike glucose, this product gives effluent with a relatively low COD/BOD, of the same order as caustic/dithionite dyebaths.

6.4.2 Antioxidants

Sodium polysulphide is widely used as an antioxidant in dyebaths reduced with sodium sulphide, hydrosulphide or glucose. It is not compatible with sodium dithionite, however. It inhibits premature oxidation of the sulphide reducing agent, thereby promoting better dyebath stability, especially under adverse dyeing conditions, e.g. winch, jet or jig machines. This lessens the risks of bronzing, poor rubbing fastness and dark selvedges.

Sodium borohydride has been used in dyebaths reduced with glucose, or with dithionite, and appears to act in a similar manner in these dyebaths to that of sodium polysulphide in sulphide/hydrosulphide dyebaths.

6.4.3 Sequestering agents

Sequestering agents based on sodium hexametaphosphate or the sodium salt of ethylenediaminetetraacetic acid (EDTA) are widely used in dyeing with sulphur dyes where the water quality is low or variable. The presence of multivalent metal ions in the dye liquor or in the substrate will usually lead to poor rub fastness or unlevelness; many dyers regard sequestering agents as essential insurance against these problems.

Increasing use of irrigation and crop spraying by the growers has led to an increase in the content of calcium and magnesium salts in the raw cotton. Rapid preparation methods may not fully remove such salts and require sequestering agents to be used more regularly.

6.4.4 Wetting agents

The majority of sulphur dyes are unaffected by most wetting agents, but several dyes, notably CI Sulphur Red 10 and Blue 13, are adversely affected by some products, which either inhibit the dye uptake in exhaust dyeing or precipitate the dye as a tarry leuco product. These are usually nonionic surfactants and should be avoided, both in prescouring and in the dyebath itself.

6.4.5 Rinsing and soaping

Thorough rinsing before oxidation is essential with sulphur dyes if good fastness to rubbing is to be obtained. It is most important that all loose colour should be removed before the acidic oxidation stage, which precipitates any unfixed dye on the surface of the fabric (or on the outside of a package), giving a bronzy dyeing with low fastness to wet rubbing.

Heavy-depth dyeings, but not usually pale to medium depths, are soaped after oxidation. This gives an increase in brightness, together with improved fastness to washing in respect of change in colour of the dyeing. There is considerable difference of opinion on the relative merits of soap or synthetic detergent. The latter is undoubtedly preferable in hard water, but whichever is used an addition of soda ash is recommended. Thus 1–3 g l^{-1} soap or detergent and 2 g l^{-1} soda ash for 15–20 min at 90–95°C could be a typical recommendation for batchwise processing, whilst 5–10 g l^{-1} soap or detergent and 2–5 g l^{-1} soda ash for 30–60 s at the boil would be suitable for continuous processing.

6.4.6 Oxidising agents

Sodium dichromate/acetic acid

Traditionally this is the preferred system for oxidising sulphur dyeings. Chromium (VI) compounds oxidise all reduced sulphur dyes rapidly and completely. Colour yields and fastness properties are good and are taken as the standard. Nevertheless, it is being criticised increasingly on environmental grounds, being banned or restricted by many water authorities, and for its adverse effects on handle and sewability, especially with sulphur blacks. Hence dichromate oxidation is usually avoided when dyeing in yarn form.

For batchwise methods treatment in 0.25–1.0 g l^{-1} sodium dichromate and 0.8–1.2 g l^{-1} acetic acid for 15–20 min at 60°C is usually recommended. In continuous dyeing 5 g l^{-1} sodium dichromate and 6 g l^{-1} acetic acid is the usual starting bath at 60–70°C, with dwell times varying in the range 20–40 s.

Whilst the system is quite tolerant to variation in sodium dichromate concentration, better economy is achieved with close control and for optimal oxidation it is essential to maintain pH 4.5–5.5. The addition of a dispersant and a sequestering agent to the oxidation bath has been recommended to improve rub fastness. Better fastness to washing is obtained if the goods are subsequently soaped.

Copper sulphate with sodium dichromate/acetic acid

The addition of 1 g l^{-1} copper sulphate to batchwise oxidation baths of sodium dichromate and acetic acid improves the light fastness of sulphur dyeings by up to one grey-scale unit. When carrying out this treatment it is essential that the copper sulphate is not added to the bath until all residual sodium sulphide has been destroyed and the pH is below 6. This avoids precipitation of copper as hydroxide or sulphide.

The improvement is most marked on yellow, orange, brown and khaki colours, traditionally those of low light fastness. The treatment has a dulling effect, however, and gives a significantly harsher handle. It is not recommended for sulphur blacks, where the presence of copper promotes acid tendering. The copper is leached out by successive wet treatments and the effect is thereby diminished or lost altogether.

Potassium iodate/acetic acid

The legislation governing the concentration of chromium compounds permissible in effluents has now become so strict that in future it will no longer be possible to continue to oxidise with dichromate. The introduction of iodate systems in the USA was possibly the first substitute for dichromate. Although a reasonable technical alternative, iodates have since been replaced by a new generation of oxidants on environmental, economical and operational grounds.

Sodium bromate

Although this product alone, or even with acetic acid, is ineffective as an oxidant for sulphur dyes, it has been found that the addition of sodium metavanadate in catalytic amounts produces an oxidation system with properties approaching those of sodium dichromate and acetic acid. This system has replaced potassium iodate where the use of sodium dichromate is no longer permissible.

Proprietary formulations of the catalyst-activated sodium bromate are available, e.g. Dyetone (Olin), and are used at either 1–2 g l^{-1} (batchwise) or 5–7 g l^{-1} (continuous) at 60–65°C. The pH should be maintained at 4–4.5 with acetic acid for optimal oxidation. The fastness of dyeings oxidised with this system is similar to that from sodium dichromate or potassium iodate oxidation. Unfortunately, pollution by metavanadate as a catalyst is now also being investigated by some water authorities in the UK.

Hydrogen peroxide and peroxy compounds

The use of 1 ml l^{-1} hydrogen peroxide (130 vol.) or 1 g l^{-1} sodium perborate at pH 9 and 40°C for 10–20 min to give a brighter colour, especially with sulphur blues, is well known. However, the wet fastness of the dyeing may be lowered by one or more grey-scale units in respect of staining of adjacents, by comparison with sodium dichromate treatment. The treatment is also widely used in the oxidation of sulphur black, giving a bluer or brighter hue of marginally decreased wet fastness.

Under alkaline conditions the vigorously active peroxide causes overoxidation of the disulphide groups in the dye molecule, forming ionisable sulpho groups and hence impairing wet fastness [7]. Hydrogen peroxide under mildly acidic conditions gives a somewhat slower rate of oxidation, perhaps too slow for some red-browns, notably CI Sulphur Red 10, but a combination of 1 ml l^{-1} hydrogen peroxide (130 vol.) and 0.8 g l^{-1} acetic acid for 15–20 min at 50–60°C is widely used for the oxidation of package-dyed yarn.

The potassium and ammonium salts of peroxydisulphuric acid are slightly more energetic in an acetic acid medium than hydrogen peroxide. However, the activity is not high enough for satisfactory oxidation of CI Sulphur Red 10. Many blue dyes give slightly duller and weaker dyeings than when oxidised with dichromate [5].

Sodium chlorite

This is the active constituent in several proprietary oxidising agents, e.g. Oxidurit SK (CAS), Protegal OD (Protex) or Rewin SW (CHT), the oxidation being carried out at alkaline pH (using sodium carbonate) at temperatures close to the boil. This type of formulation contains, in addition to sodium chlorite, a stabiliser, a sequestering agent and a detergent. It is claimed that EDTA (section 6.4.3) is essential to give the fully oxidised hue with optimum yield and levelness.

Chlorite oxidation gives dyeings with good wet fastness and soft handle, but does not give complete oxidation with some red-brown sulphur dyes, such as CI Sulphur Red 10. For batchwise processing a typical oxidation bath would be 2–3 g l^{-1} Protegal OD and 5 g l^{-1} sodium carbonate for 15–20 min at 90–95°C. Typical continuous conditions are 5–10 g l^{-1} Protegal OD and 5–10 g l^{-1} sodium carbonate for 1–2 min at 90–95°C.

Other oxidants

The effect of five different oxidising systems on the hue obtained with typical sulphur dyes on cellulosic fibres has been investigated recently. The best results with regard to stabilisation of hue were achieved using Chloramine T or hydrogen peroxide [8].

It has been claimed that the sodium salt of *N*-chloro-*p*-toluenesulphonamide (Chloramine T) can be used in package dyeing to achieve complete oxidation, at a concentration of 2 g l^{-1} for 10 min at 40°C.

The sodium salt of *m*-nitrobenzenesulphonate gives uniformly complete oxidation on jet machines and winches. Typical amounts are in the range 2–4 g l^{-1} in the presence of 2 g l^{-1} sodium carbonate at pH 9.5–10.5 and 40°C for 20 min.

In conjunction with sulphuric acid, sodium nitrite is an oxidant for sulphur dyes, but the risk of oxidative degradation of cellulosic fibres under these conditions far outweighs any advantages.

6.4.7 Fixation additives

Alkylating agents based on epichlorohydrin give dyeings of markedly improved fastness to severe washing treatments that use detergent/perborate formulations, such as are now standard usage in domestic washing. The alkylation treatment of the leuco dye also effectively oxidises the dyeing and so may replace a normal oxidation treatment, except for those containing quinoneimine groups that have a marked yellow leuco colour, e.g. CI Vat Blue 43 or CI Sulphur Blue 7, which should be given a mild oxidation treatment with hydrogen peroxide or sodium perborate to give an olive green colour before alkylation [5].

A typical product is Solidogen IH (CAS), which is applied at 2–3% o.w.f. with 1–2% sodium carbonate to give pH 10, beginning the treatment at 30–40°C (to ensure uniform uptake) then raising to 90–95°C for 10–15 min (to ensure complete reaction).

The light fastness of the dyeing may be decreased by one point on the blue wool standard scale. In the event of the dyeing needing subsequent correction, alkylated sulphur dyeings are difficult to strip and attempted removal will often entail destruction of the dye chromogen.

6.4.8 Crease-resist finishing

Crease-resist finishing may increase the fastness to wet treatments of sulphur dyeings by up to one grey-scale unit, whilst the light fastness is either unaffected or marginally improved. The effect on the colour of the dyeing is usually towards a redder and duller tone.

6.5 APPLICATION METHODS

6.5.1 Introduction

The leuco potentials of some typical sulphur dyes have been studied recently. The dependence of the leuco potential on the temperature and pH of the leuco dye solution was examined. The dyeability of cotton fibres was discussed in terms of the redox potential of the leuco dyebath [9].

The substantivity of sulphur dyes for cellulosic fibres differs according to the particular substrate. Thus mercerised cotton and viscose fibres are dyed more heavily than unmercerised cotton. Substantivity varies from dye to dye and between brands of the same dye. Dye liquors prepared from the liquid brands containing the leuco form, being virtually electrolyte-free, are exhausted to a much lower extent than dye liquors prepared from the traditional powders, which invariably contain electrolyte added during dye standardisation. The quantity of diluent added in this way, however, is insufficient to give optimum exhaustion under batchwise dyeing conditions.

The rate of exhaustion of sulphur dyes is slow at low temperatures, but some dyeing can be expected to occur even at 45–50°C. In the case of liquid brands of leuco dyes this is only slight until electrolyte has been added. The rate of exhaustion may be controlled by temperature or by the gradual addition of electrolyte. It is standard practice to add electrolytes to the dyebath, usually sodium chloride or sulphate, to promote dye uptake. It is essential to use good grades of these products, avoiding those containing calcium or magnesium salts. These tend to precipitate the dye and reducing agent as insoluble salts and thus lower the rub fastness of the resultant dyeing, as do iron salts from rusty water pipes or damaged machinery.

The addition of electrolyte to the dyebath in batchwise dyeing processes may be made either at the start or on reaching the top temperature; opinions vary as to which gives the best results. Where additions can be made with relative ease, e.g. on the jig, the addition of electrolyte at dyeing temperature is preferred because some uptake of dye occurs during the heating stage. On equipment where addition is difficult, incorporating the salt at the start of the dyeing and gradually raising the temperature to control exhaustion is preferred.

For pale depths it may be preferable to forgo the electrolyte addition to reduce the possibility of an uneven dyeing. In pale to medium depths an addition of 5–10 g l^{-1} salt is normally adequate, adding 10–20 g l^{-1} salt in medium to heavy depths where there is less risk of unevenness.

In continuous dyeing, however, the presence of electrolyte may promote tailing, hence the preferred use of the pre-reduced liquid brands, which contain the leuco dye and minimal electrolyte, at padding temperatures as low as possible consistent with good absorption of pad liquor. This is often a compromise between what would be ideal and what is realistic, but for continuous dyeing, fabric preparation should always produce a substrate with high and uniform absorbency.

Solubilised sulphur dyes may be used in pad–dry–chemical-pad–steam dyeing, with an intermediate drying stage such as is often necessary for mercerised cotton fabrics [5]. They are not substantive to cellulose, hence tailing should not be a problem even at elevated temperatures.

6.5.2 Preparation

For special effects or fashion requirements minimal or even zero preparation may give the desired results, but to obtain high quality and reproducibility thorough preparation is essential. Yarn is often given a light scour only, but may be bleached for pale or brighter colours. Fabric should be desized and scoured to give good absorbency, especially for continuous dyeing, and may be bleached for brighter colours.

6.5.3 Dissolution procedures

Dissolving sulphur dyes, especially the water-insoluble types, is generally considered to be the most important factor in obtaining a satisfactory dyeing. The water-soluble and dispersed brands are much easier to prepare for dyeing, whilst the liquid formulations are already in solution and should present no problem at all to the dyer.

Water-insoluble dyes

These types are dissolved either by boiling for several minutes in a reducing solution (e.g. sodium sulphide) or by vatting with caustic soda and sodium dithionite in a similar manner to vat dyes.

In the first method the dyes are pasted with water and a suitable wetting agent, to which is added the required amount of sodium sulphide (or sodium hydrosulphide/caustic soda) and sufficient water (approximately 30–50 ml per gram of dye) to give a concentration of 20–30 g l^{-1} dye. This is the limiting range of concentration below which most sulphur dyes readily dissolve. Notable dyes outside this range are CI Sulphur Black 1, which is normally soluble to 80–100 g l^{-1} and CI Sulphur Blue 13, which has a solubility of only 5–10 g l^{-1}.

The dye liquor should be thoroughly stirred, heated to the boil and allowed to simmer for 2–5 min with occasional agitation to ensure complete dissolution. When dissolving small amounts of dye it is essential to ensure that a minimum concentration of 20 g l^{-1} sodium sulphide flakes (60%) is present. Conversely, when dissolving large quantities of dye it is necessary to ensure that the solubility limit of the dye is not exceeded.

Traditionally a small amount of sodium carbonate was added to the dyebath to neutralise acidity; nowadays this is more often to counteract hardness of water. Alternatively a sequestering agent may be added. The dye liquor is then diluted to full dyebath volume at the required starting temperature.

In the alternative method the dyes are pasted with water and a suitable wetting agent, then 30–50 ml water per gram of dye are added, followed by the required amount of caustic soda. This liquor is heated to vatting temperature (60–70°C) and the sodium dithionite added. After stirring gently for 10–15 min to ensure complete dissolution, the leuco solution is added to the dyebath, which has been set with a small quantity of caustic soda and sodium dithionite.

Dispersed powders or pastes

These are simply sprinkled onto warm water with vigorous stirring, preferably mechanical, to ensure uniform dispersion of the dye, which is then ready to use, either directly as a pad or pigmentation bath, or after reduction to a solution of the leuco form. Pale depths may require the addition of 1–2 g l^{-1} dispersing agent to maintain a satisfactory dyebath condition. When dyeing by a pad–dry–reduction method a migration inhibitor should be added to the pad liquor after the dye.

Liquid dyes

These do not require heating as they are already in solution. However, some care is needed in the preparation of the dyebath and the following procedure is recommended:

(1) Set the dyebath at 50–70% of its final volume.
(2) Add sequestering agent where required.
(3) Add any required alkali: most yellow, orange and yellow-brown dyes require an addition of 1–3 g l^{-1} caustic soda flake for optimum hue and yield.
(4) Add any required reducing agent: pale depths require an extra addition of reducing agent, 1–5 g l^{-1} sodium hydrosulphide (35%), to maintain good dyebath reduction.
(5) Add the dyes.
(6) Add the wetting agent and adjust to full volume.

The various dye manufacturers may recommend specific additions to individual dyes and the appropriate literature should always be consulted.

Water-soluble dyes

These dyes should be dissolved by sprinkling into warm water (approximately 20–50 ml per gram of dye) containing the wetting agent and any sequestering agent needed. After stirring vigorously, the liquor is heated to the boil and allowed to simmer for 1–2 min to ensure complete dissolution, before dilution to full dyebath volume.

6.5.4 Yarn dyeing

In dyeing any form of wound package, be it cone, cheese or beam, thorough wetting out is essential. The most common method is a scour using sodium carbonate, a sequestering agent and a wetting agent or detergent, although some dyers prefer acetic acid instead of sodium carbonate when the yarn is known to contain calcium or magnesium salts. In either case, treatment for 15–20 min at 80–90°C should be sufficient.

Package dyeing

The most suitable dyes are either the water-soluble sulphur dyes, which are applied in a non-substantive form to obtain uniform penetration of the package, followed by reduction, or the pre-reduced liquid brands, which require no pre-boiling and may be more easily added to the vessel, in portions if desired. Whenever possible, soft water should be used in all package dyeing operations.

The preparation of packages suitable for dyeing is quite critical. For package dyeing the essential requirement is for consistent winding, as variation in tightness of packages within a dye lot will lead to channelling and uneven dyeing. Whilst soft packages are undoubtedly easier to dye, many dyehouses process hard packages quite satisfactorily using equipment capable of providing a good rate of flow of dye liquor.

For beam dyeing uniform density of winding is essential. If the beam is too soft or contains too few ends it will be more prone to ‘bursting’, i.e. dye liquor breaking through the mass of yarn and effectively ruining any chance of obtaining a level result.

A typical method for the pre-reduced brands, after wetting out or scouring, would be as follows:

(1) Set the bath at 40°C with 1 g l^{-1} sodium sulphide flakes (60%), 1 g l^{-1} sequestering agent and 1 ml l^{-1} antioxidant and then circulate for 10 min.

(2) Add the dye in one to four portions over 10 min, then raise to 75–90°C and circulate for 10 min.

(3) Add 5–20 g l^{-1} salt slowly over 20 min and run for a further 10 min.

Throughout dyeing the flow direction should be changed every 5 min. Rinsing should be by overflow until clear, then rinse hot and oxidise. Heavy depths may be soaped after oxidation.

Blacks should always be finished with an alkaline rinse containing 2–5 g l^{-1} sodium carbonate or 5–10 g l^{-1} sodium acetate to prevent possible tendering problems.

A typical method for the water-soluble brands would be as follows:

(1) Dissolve the dye by boiling for 30–60 s and circulate for 10–15 min at 35–40°C, then add the reducing agent and circulate for 10–15 min.
(2) Raise to 75–90°C and run for 10 min.
(3) Add 5–20 g l^{-1} salt over 20 min and run for a further 10 min.

The frequency of flow change, rinsing and oxidation stages are as for the liquid brands.

Sulphur dyes may be applied at 120°C with consequent savings in time and, it is claimed, some improvement in levelness. Dyebaths should be cooled to 70–80°C, however, before rinsing by overflow and oxidation as for conventional dyeings.

Beam dyeing

Beam dyeing machines may be vertical or horizontal; in the latter design the beam is only partially immersed in the dye liquor and hence the flow is entirely in-to-out. Even on fully immersed beams the flow may be maintained in-to-out to avoid disturbance to the package and attendant risk of bursting of the beam. The following method would be suitable for dyeing with the pre-reduced liquid brands:

(1) Set the bath at 20–30°C with 3–6 ml l^{-1} sodium hydrosulphide (35%), 0.5 g l^{-1} caustic soda flake, 1–2 ml l^{-1} sequestering agent, 10–20 g l^{-1} salt and then circulate the liquor for 10 min.
(2) Add the dyes and circulate for a further 10 min.
(3) Raise the temperature to 80–90°C over 40–45 min and continue dyeing at 80–90°C for a further 30–45 min.

Rinsing is by overflow without dropping the bath until the rinse water is clear. The bath is then dropped and the material is given one cold rinse before oxidising as for package dyeing.

Continuous dyeing of warps

The yarn in the form of a web or sheet, or sometimes in cable form (ball warps), is passed successively through vessels containing wetting agent and soda ash, dyes, rinse water and oxidant solution, and then receives further rinsing (and possibly soaping). The process may be repeated when dyeing deep colours in order to build up the required depth. When the desired colour has been achieved, the yarn is passed through a bath containing fibre lubricant, wax, softener and (perhaps) size in order to facilitate the weaving operation, before finally drying.

This dyeing method was widespread until the 1960s, but now is used in only a small number of dyehouses in its traditional form. However, the indigo dyeing range and dyeing in the 'slasher' or size box are regarded as developments of warp dyeing; sulphur dyes may be applied in both systems.

In the indigo dyeing machine cotton yarn is passed successively through tanks containing wetting agent and caustic alkali at the boil, four or five tanks containing indigo dye reduced with caustic soda and sodium dithionite (with airing passages between each tank), rinsing water and finally drying cans. In order to dye more economically, some dyers add CI Leuco Sulphur Black 1 (or Blue 7 or 20) at a relatively low concentration to the preparation tank before applying the much more expensive indigo.

Some dyers claim, however, that carryover of sodium sulphide into the indigo tanks can adversely affect the chemical balance of the reducing system, lowering the colour yield. They prefer to apply the sulphur dye after the indigo in the last tank before rinsing. In this case a sulphur blue should be used, as black dulls the colour to an unacceptable degree.

Dyeing in the slasher is a simple method of warp dyeing, widely used in dyeing warp yarns for the denim trade, where the process is pad(dye)–dry–pad(size)–dry. Although not ideal for the process as usually practised, sulphur dyes are used in some areas of the world to produce 'coloured denim', i.e. colours other than indigo blue. Pre-reduced liquid brands (CI Leuco Sulphur liquids) may be applied by padding at 40°C, followed by a short air passage and drying. The yarn then enters the size box, which contains acetic acid to neutralise residual alkali and give some degree of oxidation in the drying stage.

Improved colour yields are obtained from the water-insoluble brands reduced with caustic soda and sodium dithionite, which are reoxidised much more readily than the sodium sulphide reduction system used in most leuco sulphur liquid dyes. After a short air passage and drying, the acetic acid in the size box neutralises the residual alkali, and the full depth and yield of the dyeing is attained.

The history of warp dyeing with sulphur vat dyes in the sizing machine for the manufacture of blue denim jeans has been reviewed recently. Stonewashing techniques have been developed to confer the ‘distressed’ appearance to garments yarn-dyed in this way. The worn look can also be simulated by partial bleaching with sodium dithionite or alkaline hypochlorite, or by surface degradation using cellulase enzyme treatments. Recipes for snowwashing treatments of this kind are suggested [10].

6.5.5 Batchwise dyeing of knitted fabrics

Virtually all knitted fabrics can be dyed in black, blue and brown colours in winches or jet machines, usually after a light scour with detergent and sodium carbonate, although some fabrics may require more severe pretreatment incorporating solvent in order to obtain a satisfactory dyeing.

Winch dyeing

In general, the heavier the fabric, the better the result: lightweight fabrics are more difficult to process since they are more prone to float in the dyebath, leading to local oxidation and the possibility of bronzy patches. In addition, such fabrics carry less dye liquor over the winch reel and hence tend to reoxidise more rapidly than the heavier fabrics. Addition to the dyebath of an antioxidant based on sodium polysulphide is essential in winch dyeing to prevent premature oxidation of the reducing agent.

The leuco sulphur or the solubilised sulphur dyes are preferred. A typical recipe for a black on knitted cotton at a liquor ratio of 20:1 would be:

(1) CI Leuco Sulphur Black 1, 15–20%;
(2) caustic soda flake, 0.5–1.0 g l^{-1};
(3) sodium hydrosulphide (35%), 2–4 g l^{-1};
(4) antioxidant, 2–5 ml l^{-1};
(5) salt, 10–20 g l^{-1}.

After scouring and rinsing, set the bath at 40–45°C with all the chemicals, including the salt, and run for 10 min before adding the dye. Run for a further 10 min before raising the temperature to 90–95°C over 30–45 min. Continue dyeing for 30 min before rinsing by overflow until clear. The temperature should then be adjusted as required for oxidation, e.g. to 40–45°C for oxidation with 1–2 ml l^{-1} hydrogen peroxide over 15–20 min. The goods are then rinsed and finished in a bath containing lubricant and softener, bearing in mind that all sulphur blacks should be finished on the alkaline side with 2–3 g l^{-1} sodium carbonate.

The following recipe has been suggested for solubilised sulphur dyes. After scouring and rinsing, set the dyebath at 40–45°C with a suitable wetting agent, add the dissolved dye and run the winch for 10 min. Add the required quantity of reducing agent, together with 2–5 ml l^{-1} antioxidant (sodium polysulphide) and raise the temperature to 80–90°C over 30–45 min. Then add 10–20 g l^{-1} salt over 15–20 min and continue dyeing for 20–30 min before rinsing and oxidising, using hydrogen peroxide and acetic acid, catalyst-activated sodium bromate and acetic acid, or sodium chlorite in alkaline solution (section 6.4.6).

In some winch vessels it is impossible to maintain a temperature of 90–95°C throughout the machine. In these circumstances glucose-based reduction systems are likely to give unsatisfactory results since a minimum temperature of 90°C is essential to maintain full reduction.

Jet dyeing

The first high-temperature jet machines to be produced were largely unsuitable for dyeing sulphur colours because the turbulence created in the dye liquor effectively oxidised the reducing agents so rapidly that antioxidants were ineffective.

Modern softflow machines, however, are generally quite suitable for sulphur dyes and give better results than winch dyeing, especially when glucose-based reduction systems are involved, as the required temperature of 90–95°C is easily maintained. In addition, the enclosed conditions of the jet dyeing vessel minimise the problems of reoxidation that adversely affect winch dyeing with sulphur dyes.

The following recipe is typical of the application of a leuco sulphur black on a jet or overflow machine. Set the bath (after scouring and rinsing the fabric) at 40–45°C with:

(1) caustic soda flake, 0.25–0.5 g l^{-1};
(2) sodium hydrosulphide (35%), 1–2 g l^{-1};
(3) antioxidant (sodium polysulphide), 1–2 ml l^{-1};
(4) defoamer (if required);
(5) salt, 10–20 g l^{-1};

and run for 15 min. Add the dye and run for a further 15 min before raising the temperature to 80–90°C over 30–45 min and run for 20–30 min. Rinse by pumping in clean water and running the dye liquor to drain, until the wash water is clear, then reoxidise as for winch dyeing.

The sulphur-free reducing system based on glucose is ideal for jet dyeing because many dyehouses operating jet machines are situated in areas where sulphur dyes were seldom or never used. Hence permission to pass sulphides into the sewerage system is difficult, if not impossible, to obtain.

High-temperature dyeing machinery is more suited to sulphur dyes than atmospheric equipment, even when dyeing at 90–95°C, as foaming tends to be a greater problem at atmospheric pressure. It can be controlled by defoaming agents, the fatty alcohol types (e.g. nonyl alcohol) having been found by experience to give the best results with sulphur dyes. As with all foaming problems, it is usually easier to prevent foam forming than to destroy it once it has formed.

The following procedure has been recommended for dyeing with CI Solubilised Sulphur Black 1 on a jet machine using caustic soda, sodium carbonate and glucose. In addition to being sulphide-free, this reduction system also has the virtue of leaving the dyeing machinery in a particularly clean condition, whereas sulphide-based systems and certain other classes of dyes usually require some cleaning down following the dyeing of full black shades:

(1) CI Solubilised Sulphur Black 1, 10–15%;
(2) caustic soda flake, 2–4 g l^{-1};
(3) sodium carbonate, 4–8 g l^{-1};
(4) glucose, 3–6 g l^{-1};
(5) defoamer (if required);
(6) salt, 15–20 g l^{-1}.

After scouring and rinsing, set the bath at 40–45°C with the dissolved dye and run for 15 min. Add the predissolved alkali and glucose (glucose dissolves readily in dilute alkaline solution) and run for a further 15 min before raising the temperature to 90–95°C. Run for 10 min before adding the salt over 15 min and continue for a further 20–30 min at 90–95°C. Rinse by flooding until clear, before oxidising with 1–2 ml l^{-1} hydrogen peroxide (130 vol.) for 15 min at 40–45°C. Rinse and finish with softener (the final rinse should contain 2–5 g l^{-1} sodium carbonate to prevent any possibility of tendering).

This procedure could also be used in the dyeing of blues and browns using appropriate solubilised sulphur dyes. However, it should be noted that blue and green sulphur dyes are critical in their requirement of the reducing agent for optimum results, an excess leading to very poor colour yield.

6.5.6 Garment dyeing

Some garments are dyed in Dytex machines, which are very similar to the drums used for dry cleaning. If possible, the dry goods are entered into the prepared dye liquor in order to achieve good penetration of the seams, which is invariably difficult. Often, however, the goods must be prescoured with detergent and alkali to obtain a satisfactory ground for dyeing. Leuco liquid or solubilised sulphur dyes are recommended [11], dyeing methods being suggested for liquor ratios of 10:1 or 15:1.

For leuco liquid dyes the dyebath is set at 40°C with:

(1) sodium hydrosulphide (35%), 3–6 ml l^{-1};
(2) antioxidant, 2–3 ml l^{-1};
(3) caustic soda flake, 0.5–1 g l^{-1};
(4) wetting agent, 1 g l^{-1};
(5) dyes, x%.

Enter the goods and run for 15 min. Raise to 90°C over 20–30 min before adding 10–20 g l^{-1} salt over 10–15 min and running for a further 20–30 min. Rinse cold by overflow until clear, then oxidise and finally rinse.

For solubilised sulphur dyes set the dyebath at 40°C with the required predissolved dyes and 1 ml l^{-1} wetting agent, enter the goods and run for 15 min. Add the required reducing agent and run for 15 min before raising the temperature to 90–95°C over 20–30 min. Add 10–20 g l^{-1} salt over 10–15 min and run for a further 20–30 min before rinsing by overflow until clear, oxidising and finally rinsing.

6.5.7 Batchwise dyeing of woven fabrics

Sulphur dyes are widely applied on jigs, ranging in batch size from 200 to 1500 m and in width from 75 to 300 cm. Complete removal of all contaminants such as size, fats and waxes is essential to obtain satisfactory results.

A thorough desize using an enzyme, followed by a caustic scour (and bleaching if necessary for brighter colours) or a combined caustic/peroxide scour–desize and bleach system may be employed. The fabric may be prepared on the jig immediately prior to dyeing, or alternatively on a pad–batch, pad–roll or continuous preparation range. Whichever system is employed, regular checks on starch and wax content should be made to ensure that a consistent quality of preparation is being achieved (Chapter 2).

Jig dyeing

The essential requirement in jig dyeing is a constant rate of uptake of dye, since there is little or no possibility for subsequent levelling. The dye liquor is normally divided into portions, two-thirds being added at the start and the remainder after the first end. All the chemicals, apart from any reducing agent necessary for the second portion, are added at the start. This is simple in theory, but much more difficult in practice, especially when dyeing medium to heavy depths with the insoluble powder brands, since the limited solubility may necessitate dissolving the dyes in the jig trough. In these circumstances the jig roll should be 'swung' whilst the second portion is being prepared. The liquid brands may simply be divided into two portions and added over two ends with no need to stop the jig. Electrolyte is also added over two ends, a typical dyeing procedure (20–32 ends) being as follows:

(1) Add dyes over two ends and run two ends.
(2) Add salt over two ends and run two to four ends.
(3) Rinse cold over four to six ends and hot over two ends.
(4) Oxidise over two to four ends and rinse over two to four ends.
(5) Soap over two ends and rinse over two to four ends.

With the steadily increasing size of jigs and batch sizes, the length of one end may be 20–30 min and the above sequence becomes impracticable and uneconomic. A shorter process is required and so modern jigs are equipped with spray bars for increased rinsing efficiency. The following modified process (14–18 ends) is increasingly in use:

(1) Add dyes over two ends and salt over two ends.
(2) Run two ends and rinse cold over two to four ends.
(3) Oxidise over two ends and rinse hot over two ends.
(4) Soap (synthetic detergent) over two ends and rinse over two ends.

Proprietary oxidising formulations containing detergents are available; these permit reoxidation and soaping in one step. The addition of a nonionic detergent to dichromate/acetic acid oxidation baths has been recommended.

Although the use of a glucose reduction system gives satisfactory results by jet or package methods, it has proved unsatisfactory on jig, giving inconsistent results and poor colour yield.

Bronzing of blacks and navies, due to premature oxidation of dye or precipitation by metals such as calcium, magnesium or iron is a well-known problem. It can be minimised or overcome by the addition of an antioxidant such as sodium polysulphide, or a sequestering agent. Lower dyeing temperatures (60–65°C) have been found to be beneficial in dyeing blue and navy colours.

Pad–jig

The solubilised and dispersed sulphur dyes are the most suitable for application by this method owing to their lack of substantivity during impregnation [12]. After padding, the goods may be stored on a rotating batch or run directly into the jig already set with reducing agent and salt at 80–90°C, and then run for four to six ends before rinsing and oxidising.

Some dyers use the leuco liquid brands by this method, especially when heavyweight or tightly woven fabrics are being processed, in order to obtain better penetration. In this case the padded goods are run directly on to the jig set with a small quantity of reducing agent (1–2 ml l^{-1}) and 10–20 g l^{-1} salt at 80–90°C, and then run for four to six ends before rinsing and oxidising.

In all pad–jig processing an addition to the jig of 10–20 ml l^{-1} pad liquor is recommended in order to achieve equilibrium conditions more rapidly in the jig development stage.

The pad–jig method is particularly useful in the dyeing of mercerised cotton or viscose fabrics, where the rapid strike onto the fibre makes subsequent uniform penetration of the fabric more difficult.

Pad–batch

This process was originally developed for the application of reactive dyes and has been used with limited success for sulphur dyes. The leuco liquid brands are preferred; extra reducing agent and antioxidant are added to the pad liquor to compensate for oxidation during the batching operation.

The additions required are 3–12 g l^{-1} sodium hydrosulphide (35%) and 4–6 ml l^{-1} antioxidant (sodium polysulphide), using the higher quantities for lower dye concentrations, together with a suitable wetting agent (5 ml l^{-1}). For heavier depths 10–15 g l^{-1} anhydrous sodium sulphate gives improved fixation.

A minimum of 3 h batching at room temperature is recommended. If large batches are being processed it may be convenient to store them overnight. A pad liquor temperature of 40°C with a pick-up of 80–100% is suitable, with rinsing and oxidation sequences as for pad–steam processing (see below).

6.5.8 Continuous dyeing

Greater quantities of sulphur dyes are applied by continuous dyeing than by all other sulphur dyeing methods put together. Traditionally cotton pile fabrics have been a major sector for sulphur dyeing. Corduroy is generally dyed in muted hues, such as dark brown, olive, navy and black, colours for which sulphur dyes are the least expensive class. The one-bath pad–steam method without intermediate drying is especially suitable for this purpose since it produces a particularly good appearance by avoiding migration [13].

To produce good results in continuous dyeing it is essential to prepare to a consistently high level of absorbency. This can only be achieved by close quality control of the continuous fabric preparation range. Any variation in residual starch or wax content will lead to variation in dye uptake and subsequent unlevelness, which is almost impossible to correct at the dyeing stage.

Cotton fabrics are often mercerised before continuous dyeing for reasons of economy in dye consumption rather than any increase in lustre. Close control of the mercerising process is also essential if variations in dyeability along the warp threads and from selvedge to selvedge are to be avoided.

Pad–steam

The achievement of level dyeings is dependent on many factors, e.g. the pad mangle, air-free steam and efficient washing. Possibly the most important is fabric preparation. The fabric must be highly and uniformly absorbent so that padding may take place at as low a temperature as possible in order to minimise tailing effects. Information is available relating to feed ratios, i.e. the dye concentrations in the feed liquor relative to those in the pad liquor at the start, but this is only a guide as the pretreatment of the fabric, running speed and dwell time in the pad all vary widely.

Machinery requirements for pad–steam dyeing are simple to state but more difficult to achieve in practice and may be summarised briefly as follows. The pad trough should be as small as possible, equipped with an efficient constant-level device fed from one of two mixing tanks (the second being recharged to ensure a constant flow of dye liquor for continuous running). The mixing tanks should be equipped with good temperature control to maintain the required pad liquor temperature, stirrers and water supply to facilitate rapid rinsing down. The pad mangle should be of high quality since uneven application of dye liquor will give uneven dyeings, there being no migration in a pad–steam dyeing system. For 100% cotton the pick-up will normally be 60–80%, whilst for polyester/cotton it might be 50–70%.

The steamer should be airtight and supplied with air-free saturated steam at 102–105°C, the design being such as to prevent condensation spots and provide a steaming time of 30–60 s at the desired running speeds. Typically these may be

30–100 m min^{-1} in Europe but up to 180 m min^{-1} in the USA. Air in the steamer may lead to premature oxidation of the dyeing, giving bronzing, poor rubbing fastness and possibly unlevelness, if air is drawn across the fabric causing local cooling and/or oxidation. It is usually quite easy to seal the exit via a water trough, but the entry seal is more difficult to achieve; machinery manufacturers adopt different approaches.

Thorough rinsing before chemical oxidation is vital to the attainment of satisfactory fastness. To this end the water seal at the steamer exit and the first wash box especially should have a very good water supply to give a high rate of liquor exchange. Subsequent wash boxes should also be well supplied and the counter-current principle may be employed.

Oxidation may proceed in one or two boxes, depending on the particular system in use. Soaping off is preferable, especially with heavy depths, but regrettably some pad–steam ranges have insufficient boxes to enable this operation to be carried out. The variation between washing ranges is wide, from as few as 4 to as many as 14 boxes, and running speeds also vary from 20 up to 150 m min^{-1}.

A typical pad–steam process, using an eight-box washing range, is as follows:

(1) Padding with:
  leuco sulphur liquid dye, x g l^{-1},
  reducing agent, y g l^{-1},
  wetting agent, 5 ml l^{-1},
  temperature 40°C, pick-up 60–80%.
(2) Steaming:
  1 min at 102–105°C.
(3) Aftertreatment:
  Box 1 – cold water,
  Box 2 – warm water 40–50°C,
  Box 3 – hot water 60°C,
  Box 4 – oxidation,
  Box 5 – hot water 60°C,
  Box 6 – soaping 90°C,
  Box 7 – hot water 60°C,
  Box 8 – cold water 20–30°C.

Up to 5 ml l^{-1} reducing agent would be added for pale depths, whilst many corduroy dyers add 10–20 ml l^{-1} sodium hydrosulphide (35%) to all pad liquors to counteract the oxidation caused by air trapped within the pile.

Pad–sky

The process sequence is identical to that for pad–steam, but the steaming stage is replaced by a simple air passage of 30–60 s duration, followed by rinsing and oxidation as for pad–steam.

This approach is really only suitable for relatively pale colours as heavier depths give poor colour yield and inferior fastness to washing and rubbing. The method has been used for speciality requirements, such as washdown effects, where the desired result is obtained as a consequence of the decreased fastness characteristics.

Pad–dry–bake

In recent years various suggestions have been made for avoiding the steaming route, using dry heat fixation with or without an intermediate drying. For example, Hoechst recommended the following process for solubilised sulphur dyes in pale to medium depths only; the rub fastness is unsatisfactory in heavy depths. Dissolve x g l^{-1} dye and add 30–50 g l^{-1} urea, 25–50 g l^{-1} Hydrosol Fixer KT (HOE) as a solution, 5 g l^{-1} Cassapret P Conc (HOE) and 3–5 ml l^{-1} wetting agent. Pad at 20–30°C, dry at 120°C, fix for 1 min at 150–175°C. The dyeings are said to need only rinsing, no oxidation being necessary.

Pad–dry–chemical-pad–steam

This sequence is claimed to give a much better surface appearance to mercerised cotton fabrics, although it does have disadvantages for cotton since it involves an intermediate drying stage. It is applicable to polyester/cotton blends by the inclusion of a thermofixation stage for the disperse dyes after drying.

Solubilised sulphur dyes may be used for cotton, with a chemical-pad reduction using any of the reducing agents mentioned in section 6.4.1. Alternatively, the dispersed sulphur dyes (section 6.3.2) may be used, probably with a caustic/dithionite reduction stage.

A third possibility is to use the pre-reduced liquid brands and to reduce again with sodium sulphide or hydrosulphide at the chemical pad. This is claimed to give better surface appearance than the direct pad–steam process. The drying stage does give rise to more unpleasant fumes than from the other dye types. It is not suitable for sulphur blacks. The subsequent rinsing and oxidation stages are similar to pad–steam processing.

Typical formulations for a black would be 100 g l^{-1} CI Solubilised Sulphur

Black 1, 5 ml l^{-1} wetting agent and 10–20 ml l^{-1} migration inhibitor padded at 20–30°C, 60% pick-up and dried for 1 min at 120°C. This would be followed by 100 g l^{-1} sodium sulphide flakes (60%), 2 ml l^{-1} wetting agent and 10–20 ml l^{-1} dye liquor padded at 30–40°C, 70–80% pick-up; steaming would be for 30–60 s at 102–105°C.

The addition of some dye liquor to the chemical pad helps to establish a state of equilibrium by minimising initial bleed-off of dye from the fabric into the chemical pad. Electrolyte may also be added to the chemical pad to increase the fixation when dyeing medium to heavy depths; a concentration of 10–15 g l^{-1} anhydrous sodium sulphate is recommended.

The dispersed sulphur dyes are applied in a similar manner. However, some of them are not dyeable from a sulphide reduction liquor, so a combination of 20–30 g l^{-1} caustic soda flake and 40–60 g l^{-1} sodium dithionite provides more suitable reducing conditions.

Leuco liquid dyes may be applied by the following method, bearing in mind that CI Sulphur Black 1 does not give satisfactory results. Pad x g l^{-1} dye, 1–3 g l^{-1} sodium hexametaphosphate and 5 ml l^{-1} wetting agent at 40°C and dry for 1 min at 105–120°C. Then pad 30–100 g l^{-1} sodium sulphide flakes (60%) or sodium hydrosulphide (35%) and 10–20 g l^{-1} electrolyte, steam for 1 min at 102–105°C. Rinsing and oxidation are as for pad–steam dyeing.

6.5.9 Non-reductive dyeing systems

CI Solubilised Sulphur dyes may be dyed on cellulosic materials that have been given a cationic pretreatment. The pretreatment is being increasingly used on garments, and knitted and woven fabrics. The fastness is typically slightly lower than by conventional dyeing, but is judged to be adequate, especially where wash-down effects are required.

The material is treated with 2–8% suitable cationic resin such as Jarofix 391 (JR), Sandofix TPS (S) or Precat 3001 (CHT), for 20–30 min, raising the temperature from 25 to 60°C, and subsequently rinsed. Increased depth is achieved if caustic soda is included in the pretreatment bath, but this also incurs greater risk of uneven dyeings.

The dyeing is carried out with x% dye by raising the temperature from 40 to 95°C. Depending on the depth, other additions may be unnecessary, but with pale shades a levelling agent such as Jarolev 593 (JR) or Lyocol O (S), and with medium to heavy shades, acid donor salts such as ammonium acetate, or even acetic acid, together with 5–20 g l^{-1} salt may be required to promote exhaustion. Fibre lubricants may also be added to the dyebath.

Exhaustion of pale to medium shades is virtually complete, but heavy depths may not be achievable, especially with sulphur blacks.

Selection of the cationic product may be critical, depending on the application, as some products promote levelness at the expense of depth, and vice versa.

The cationic fixation process may be applied continuously by a pad–dry–pad–steam system. Intermediate rinsing is preferable, but may not be essential depending on the particular requirements.

6.6 EFFLUENT TREATMENT

Unless alternative reducing systems are used, the effluent arising from sulphur dyeing processes contains sulphides, the concentration of which depends on the dyeing method, applied depth and the dyes used. The discharge of sulphides to drain is not normally permissible because of the danger to life or damage to the sewer structure from the bacterial oxidation of liberated hydrogen sulphide to sulphuric acid. The leather industry has installed air-oxidation sulphide treatment plants at tanneries and similar methods are suitable and effective for the treatment of sulphur dye effluent, even when it contains relatively large amounts of sulphides.

Air oxidation can be accomplished by diffused aeration, surface aeration, ejectors or by coarse bubbles from sparge pipes. Design of the equipment for aeration is varied, e.g. floating rotary blade beater motors and vertical helix columns through which compressed air is passed or alternatively dissipated through venturi pipes. By such means, approximately 10–12% of the oxygen in the air can be effectively utilised in the degradation of the sulphide dye waste that is usually rendered acceptable to municipal sewage treatment plants.

Diffused aeration is achieved by generating fine bubbles from activated-sludge dome diffusers, which are set at one 20 cm diffuser per 1000 cm^2 cross-sectional area of treatment tank to achieve the best effect. Each diffuser requires 30–35 $l\ min^{-1}$ of air and sulphide removal rates of up to 750 $mg\ l^{-1}\ h^{-1}$ have been achieved. Diffusers suffer from suck-back and have to be removed regularly for cleaning.

Helixor modules are considerably more expensive per unit than diffusers, but fewer are required and they are relatively maintenance-free. Each helixor requires 1100–1250 $l\ min^{-1}$ of air for maximum efficiency, and again rates of sulphide removal as high as 750 $mg\ l^{-1}\ h^{-1}$ have been achieved. Operating units in the leather industry are utilising up to 65% of the available oxygen in treatment tanks of 6 m working depth. This rate falls to 15–30% utilisation in sulphur dye treatment tanks of 4 m working depth. A sulphide removal rate of 400 $mg\ l^{-1}\ h^{-1}$ is regarded as a reasonable rate at such depths.

Typically 1 kg of sulphide requires about 1.1 kg of oxygen for complete removal, indicating that the sulphate arises from further oxidation of the thiosulphate formed initially (Scheme 6.1).

$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

$$Na_2S_2O_3 + 2NaOH + 2O_2 \longrightarrow 2Na_2SO_4 + H_2O$$

Scheme 6.1

The oxidation of sulphide is difficult to drive to completion without a catalyst. The use of catalysts such as manganese sulphate, anthraquinone-1,2-disulphonic acid, hydroquinone, ferric chloride, copper sulphate or chrome either alone or in mixtures is useful in the oxidation of sulphides, but less so when sulphur dyes are present in the effluent. Presumably small amounts of sulphur dyes act as reaction promoters through a redox mechanism. During oxidation the pH gradually falls from 12 to about 10, often marked by a slight increase just before the reaction is complete. It is absolutely essential that the pH is not allowed to fall below 9 during aeration, otherwise hydrogen sulphide is evolved. The oxidation of sulphide is exothermic; although the reaction proceeds more rapidly at elevated temperatures it is not necessary to raise the temperature by heating. The restrictions on the discharge of sulphate to sewer require that aeration should cease when all the sulphide has reacted, since excessive oxidation converts thiosulphate to sulphate.

Whilst air oxidation is ideal for treating large amounts of sulphide, the technique has been applied in small dyehouses where batch liquors have been collected and treated either separately or after bulking together. For small quantities the use of either hydrogen peroxide or sodium hypochlorite is also very effective. With peroxide below pH 8.5 the reaction shown in Scheme 6.2 predominates, but in more alkaline effluent the reaction gives sulphate (Scheme 6.3); hypochlorite also oxidises sulphide to sulphate.

Precipitation and settling using ferrous sulphate and alum is a technique that is also employed on a large scale.

Sulphide can be determined in two ways. The first method involves titration with ammoniacal copper sulphate solution using a platinum measuring electrode

Scheme 6.2

$$H_2O_2 + H_2S \longrightarrow S + 2H_2O$$

Scheme 6.3

$$4H_2O_2 + S^{2-} \longrightarrow 4H_2O + SO_4^{2-}$$

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and calomel reference electrode. This method is easy to operate but gives unreliable results below about 150 mg l^{-1} sulphide. In the alternative method, zinc acetate is added to the sample and the zinc sulphide separated by filtration; iodine and hydrochloric acid are then added and the excess iodine titrated with sodium thiosulphate.

Sulphide concentrations vary considerably depending on colour and application method. The following examples are typical of manufacturing experience:

(1) In pad–steam processing a full black was dyed with CI Leuco Sulphur Black 1. The pad liquor contained 13 900 mg l^{-1} sulphide and the discharges were 380 mg l^{-1} sulphide from the first wash box and 28 mg l^{-1} from the second.

(2) A full blue was dyed on the jig and had a final sulphide concentration of 1300 mg l^{-1} while a similar pale depth had only 600 mg l^{-1}.

(3) The spent dyebath after dyeing a black on the beam contained 3400 mg l^{-1} sulphide. This was air blown sulphide-free in 8 h at 5°C. The chemical oxidation demand fell from 4550 to 2600 mg l^{-1}. In general, a reduction of up to one-third in the sulphide concentration can be expected after dyeing.

6.7 FASTNESS PERFORMANCE

The fastness characteristics of sulphur dyes, as a class, fall between those of direct dyes and vat dyes. As with most ranges the fastness varies from dye to dye but those of higher fastness, e.g. CI Sulphur Green 14 and Black 11, behave similarly to those vat dyes having the least impressive fastness performance.

Sulphur dyes are, of course, considerably cheaper than most vat dyes and are much in demand for medium to heavy depths, especially black, blue and brown, of reasonably good fastness at an economical price.

6.7.1 Fastness to light

The fastness to light (BS 1006: 1990, test method B02 xenon arc) increases throughout the range from lowest in the yellows and oranges to highest in blacks and navy blues, although there are exceptions to this rule, e.g. the yellow-browns: CI Sulphur Brown 10 fades much more quickly than Brown 51 or 60.

Pale depths generally show quite low light fastness, particularly yellow, orange and brown, although medium to heavy colours in most brown and khaki hues can be dyed to a light fastness of 5, whilst CI Sulphur Black 1 gives a rating of 5 even in relatively pale depths.

Blues and navies reach standard 5–6 or 6, as do most dark olive and green dyeings, and a full black dyed with CI Sulphur Black 1 will reach standard 7.

6.7.2 Fastness to wet treatments

Washing

Sulphur dyeings in general exhibit good fastness to washing tests based on soap (tests C01–C05), but are less resistant to laundering with detergents and perborate (C06, A2–D2), although even here the fastness to washing is reasonable at temperatures not exceeding 50°C (i.e. tests C06, A2 and B2). Some older green and red-brown dyes are not as fast to washing as newer types, e.g. CI Sulphur Red 10 and Green 14 are much superior to Red 6 and Green 3 respectively.

The use of alkylating agents based on epichlorohydrin adducts will normally give improved fastness to severe washing treatments.

Perspiration

The fastness to perspiration (test E04), especially at pH 5.5, is particularly good. Alkaline perspiration is generally good to excellent, some exceptions being CI Sulphur Red 6, Blue 15 and Green 3.

Bleaching

Most sulphur colours are destroyed by sodium hypochlorite (test N01), the exceptions being CI Sulphur Reds 10 and 14, Green 14 and Black 11 and the so-called sulphur vat dyes CI Vat Blues 42 and 43, all of which have some resistance to bleaching with sodium hypochlorite. Some yellow, orange and brown dyes are only partially bleached, although the hue is usually considerably affected.

The effect of peroxide bleaching (test N02) is not quite as severe as hypochlorite. Nevertheless most sulphur dyes lose considerable depth in peroxide bleaching, the exceptions being the same as for hypochlorite bleaching.

Mercerising

Although fabric to be dyed with sulphur dyes would normally be mercerised where necessary before dyeing, occasionally yarns dyed with sulphur dyes may be subjected to mercerising after weaving into fabric. The fastness (test X04) is good, with some apparent increase in depth, usually only marginal hue change and slight staining of adjacent undyed cotton.

Rubbing

The fastness to rubbing (test method X12) is so greatly dependent on the fabric itself, its preparation and the dyeing process, especially the efficiency of rinsing before oxidation, that absolute rubbing fastness ratings cannot be quoted. The fastness to dry rubbing is normally quite good. Even in heavy depths ratings of 4–5 for transfer to adjacents are readily attainable. Fastness to wet rubbing in heavy depths is not usually as good and stain ratings of 2–3 are quite common on dark navy and black dyeings. In order to obtain the maximum rub fastness it is essential that the dyes should be completely in solution throughout, with a sequestering agent and antioxidant present as necessary. The dyeing should also be thoroughly rinsed to remove as much unfixed dye as possible before the oxidation stage is reached.

Tables 6.2 and 6.3 show the fastness to light, washing and perspiration of a short range of dyes selected to illustrate some of the points made in sections 6.7.1 and 6.7.2.

Table 6.2 Comparative washing fastness ratings of some sulphur dyes (1/1 depth)

	C03			C06 (C2)		
		Staining of			Staining of	
CI Sulphur	Change in colour	Cotton	Wool	Change in colour	Cotton	Viscose
Black 1	4–5	4–5	5	4	4	4–5
Blue 5	4–5	4	4–5	3–4	3	3–4
Blue 13	4–5	4–5	4	4	4	4–5
Brown 10	4–5	4	4–5	4	4–5	4–5
Brown 51	4–5	4	4–5	4	4	4–5
Green 3	4	3–4	4	3–4	3–4	4–5
Green 14	4–5	5	5	3–4	4–5	4–5
Red 6	4	3–4	4–5	3–4	2	3
Red 10	4–5	4–5	4–5	4	4	4–5
Yellow 9	4–5	4–5	5	4	3–4	4

Table 6.3 Comparative light and perspiration fastness ratings of some sulphur dyes

CI Sulphur	Light fastness (2/1 depth)	Perspiration fastness (alkaline)		
		Change in colour	Staining of	
			Cotton	Wool
Black 1	7	4–5	5	5
Blue 5	6–7	4–5	4–5	5
Blue 13	5–6	5	4–5	5
Brown 10	4	4–5	5	5
Brown 51	6	4–5	5	5
Green 3	5–6	5	4	4–5
Green 14	6–7	5	5	5
Red 6	4–5	3–4	2–3	4
Red 10	6	4–5	4–5	5
Yellow 9	3–4	4–5	4–5	5

6.7.3 Acid tendering of sulphur dyeings

The phenomenon of tendering of sulphur black dyeings is well known; they all produce sulphuric acid under adverse storage conditions (high humidity and temperature). This problem may be alleviated or even eliminated by thorough washing before oxidation and alkaline rinsing as the final stage of processing. Resin finishing is claimed to inhibit the tendering of sulphur blacks [14]. A proprietary cationic fibre-protective agent has been marketed by Hoechst as a more durable inhibitor than buffering with alkali.

No evidence has been reported of sulphuric acid damage by other sulphur dyes and the incidence of reports of tendering with sulphur blacks is now infrequent, even though the production of these dyes has increased. Apparently dyers are well aware of the problem and have adopted the necessary preventative measures.

6.8 COMMON FAULTS

When a dyeing is found to be faulty, the dyer is invariably held responsible and he or she in turn usually blames the dyestuffs, although often the problem originated in preparation or by some operation being carried out incorrectly.

6.8.1 Yarn dyeing

The problems here are usually unlevelness, either within the package or from package to package. The fault may be bronzing on the outside or a deposit on the inside of the package, as it is an efficient filter. Light spots from crossover marks or from entrapped bubbles of air may also be evident.

Variation in permeability from package to package is a winding problem caused by inconsistent tension during the winding of the packages on to dyeing centres, leading to different rates of flow through the packages. This can be corrected by rewinding the packages at constant tension and treating them in a blank bath of reducing agent, e.g. 10 g l^{-1} sodium sulphide flakes (60%), at as high a temperature as possible to partially strip the dyeing, before redyeing to shade. Variation within a package also requires a blank bath treatment at a high temperature; severe cases may need bleaching and redyeing.

A blank bath containing 7.5–15 g l^{-1} sodium sulphide flakes (60%) together with 2–3 ml l^{-1} sequestering agent at 90–95°C will strip off 10–20% dye, whilst the use of caustic, dithionite and a stripping agent such as polyvinylpyrrolidone will remove a further 10–20%. It is essential to redye from a fresh bath when using polyvinylpyrrolidone as this will prevent exhaustion when further dye is applied.

Bronzing is usually attributable to premature reoxidation of the dyeing before the initial rinsing stage. This can be avoided by overflow rinsing until clear. A correction routine would be the same as for unlevel dyeings in general.

Causes of unlevel dyeings include:

(1) beginning dyeing at too high a temperature;
(2) raising the temperature too quickly at a slow rate of flow;
(3) packages wound too tightly;
(4) addition of electrolyte too quickly or too early in the dye cycle;
(5) cavitation in the pump;
(6) inadequate rinsing before oxidation (fastness may also be poor).

6.8.2 Jig dyeing

The most common jig dyeing problems are ending (variation from one end of the jig roll to the other), listing (variation from selvedge to selvedge or centre to selvedge) and poor fastness to rubbing.

Ending may be caused by adding all the dyes and auxiliaries in the first end, starting dyeing at too high a temperature or adding excessive quantities of electrolyte early in the dyeing cycle. Variations across the fabric width may arise from differences in temperature across the roll, possibly exacerbated by the selection of a combination of dyes that do not all have the same optimum dyeing temperature, e.g. yellow or orange with green. The use of an antioxidant is often helpful in such a case, as well as where light or dark selvedges result from poor batching of the jig roll. Poor rubbing fastness may be attributed to poor preparation, since residual size or wax prevents full penetration and fixation of the dyes. The presence of metal ions such as calcium, magnesium or iron may interfere with dye solubility, penetration and fastness. Increasingly, these impurities are to be found in raw cotton as a result of changes in the cultivation of the cotton crop.

Correction of all these faults involves treatment in a blank bath of reducing agent, e.g. 20–30 g l^{-1} sodium sulphide flakes (60%), for 30–60 min at 90–95°C with the addition of a sequestering agent. Where a more severe treatment is required, the use of caustic soda and sodium dithionite will usually strip off 20–30% dye. However, because of the low liquor ratios involved, stripping is rather inefficient and the treatment may need to be repeated to obtain satisfactory results before redyeing.

6.8.3 Knitted fabric on jet or winch

The most common faults are streakiness, possibly with bronzing, and rope or running marks. Streakiness and bronzing are often caused by premature oxidation while passing over a winch reel or floating in the winch beck. Streakiness is minimised by an addition of antioxidant, whereas bronzing due to floating may require the addition of a wetting or deaerating agent to promote sinking of the fabric into the dye liquor.

6.8.4 Continuous processing

Common problems in pad–steam dyeing are tailing, water or colour spotting, streakiness and skitteriness. It is usually impossible to correct faults on continuously dyed fabrics by a continuous process, and batchwise treatment on a jig or jet machine is normally necessary.

Traditionally, tailing was taken into consideration by diluting the initial pad bath by 10–20%, thereby topping up the pad trough with a stronger feed liquor. This procedure is inadequate under conditions of rigorous quality control. Information from manufacturers allows the adjustment of feed liquors to take account of the properties of the particular dye combinations being used [15]. Tailing is further reduced by padding from a small-capacity trough at a low liquor temperature and a high running speed, all of which require high-quality preparation of the fabric.

Water spotting is a steamer problem, caused by condensed water droplets falling from the steamer roof onto the fabric. This fault may vary in severity from a virtually undyed spot to one only slightly weaker than the rest of the fabric. In the former case it may be necessary either to bleach and redye or to overdye to a much darker colour (usually black). Slight water spotting may be corrected simply by a batchwise treatment in a blank bath of reducing agent. Heating the upper surfaces of the steamer, together with efficient lagging, should be sufficient to prevent the fault occurring, however.

Spots that are heavier in depth than the rest of the dyeing may be caused by foam picked up from the surface of the pad liquor or by insoluble dye particles in the solution. The latter cause is unlikely when pre-reduced liquid sulphur dyes are being used, unless an incompatible auxiliary is inducing dye precipitation. Low-foam wetting agents and antifoams may reduce the incidence or prevent entirely the production of foam.

Streakiness may result from poor penetration, or a build-up of lint or other deposits on rollers in the pad mangle or steamer, whilst a skittery dyeing is invariably caused by poor preparation. If the cause is poor preparation, this should be corrected at source if at all possible, although the use of a more efficient wetting agent may be tried if the problem is only a marginal one. However, any change of auxiliary should be thoroughly evaluated beforehand in the laboratory to ensure that it does not create fresh problems.

It cannot be emphasised often enough that in all continuous processing, thorough and uniform preparation, to give a highly absorbent fabric by consistent removal of size and wax, is essential. Only by this means can high-quality reproducible dyeing be achieved, with minimal problems or substandard material.

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CHAPTER 7

Dyeing with azoic components

John Shore

7.1 INTRODUCTION

Azoic components are defined in the Colour Index as those used to produce ‘insoluble azo dyes in situ, usually on a textile substrate’ [1]. Nowadays the substrate is almost always cotton; corresponding azoic components were formerly available for dyeing the ester fibres [2] but these are now obsolete because of environmental hazards and time-consuming application methods [3]. Azoic coupling components are mostly naphthols and azoic diazo components are primary amines or stabilised diazonium compounds, often called fast bases or salts, respectively. So-called azoic compositions are described in the Colour Index as ‘mechanical mixtures of an azoic coupling component and an azoic diazo component’.

The normal procedure for azoic dyeing includes application of the naphthol, removal of excess liquor, development in a solution of the diazonium compound and aftertreatment to achieve satisfactory fastness. In the first stage the material is impregnated with an alkaline solution of naphthol in a batchwise or continuous process. The intermediate stage may consist merely of removal of water by hydroextraction or an intermediate rinsing with a solution of common salt; for fabrics, a drying stage is introduced. Development is achieved by simple immersion in a solution of the diazonium salt, which is prepared by diazotisation of a base or simply by dissolving a stabilised diazonium salt. Aftertreatment is important and is carried out by soaping at the highest temperature attainable, followed by rinsing and drying. Except in continuous dyeing it is usual to soap twice, first at 60°C to remove loosely held dye and then at 80–90°C to achieve maximum fastness.

The first patent for the production of insoluble azo dyes on cotton was granted in 1880 to Thomas and Robert Holliday of Read, Holliday & Co., for the preparation and coupling of 2-naphthol with diazotised naphthylamines to obtain red or bordeaux colours [4]. In 1889 Gallois and Ulrich of MLB recommended the use of 2-naphthol coupled with diazotised 4-nitroaniline to produce Para Red, which was important over a long period for dyeing and printing [5].

The use of 2-naphthol and the derived BON acid (3-hydroxy-2-naphthoic acid) was followed by the introduction in 1911 of the anilide of BON acid, the first substantive azoic coupling component. Use of a red pigment derived from BON acid in the printing of metal foil revealed a light fastness problem that was solved by Winter, Laska and Zitscher of Griesheim Elektron, who replaced it by the analogous azo pigment made from the anilide of BON acid [6]. This coupling component was marketed as Naphtol AS (HOE, CI Azoic Coupling Component 2). With diazotised 2-nitro-4-methylaniline (Fast Red GL Base, CI Azoic Diazo Component 8) it gave the so-called Griesheim Red. Subsequently many other coupling components have been marketed, at least three-quarters of them being anilides of BON acid.

The advantages of azoic dyeing are the following:

(1) They are particularly strong in the orange, red and bordeaux sectors, but the range also includes dark blue and black.
(2) Dyeings can be produced in certain bright full depths not always attainable with other classes of dyes.
(3) Materials can be dyed in many forms on various machines.
(4) Dyeings have excellent reproducibility.
(5) In general, the standard of fastness is high.
(6) Most combinations are dischargeable.
(7) They are economically viable.

The main disadvantages of this dyeing method include the following:

(1) Difficulties of handling the component chemicals under typical dyehouse conditions, particularly the diazotising of arylamine fast bases.
(2) Complicated and time-consuming application procedures.
(3) The limitations of hue selection imposed by the need to avoid the cross-coupling that occurs if more than one azoic combination is applied.

The world consumption of azoic components in textile dyeing fell from *c.* 35 × 10^3 tonnes per annum in about 1970 to *c.* 22 × 10^3 tonnes in 1981 [7] and their use has continued to decline since then.

7.2 CHEMICAL CONSTITUTION AND HUES OBTAINABLE [8]

Table 7.1 indicates the hue range obtainable by azoic dyeing and the types of coupling component and base required. The hue range extends from yellow to black; most variation is obtainable in the red and bordeaux sectors, whilst there are gaps in greens and bright blues.

Table 7.1 Colours obtainable using azoic components

Colour	Coupling components (naphthols)	Diazo components (fast colour bases or salts)
Yellow	Amides of acetoacetic acid (yellow naphthols)	Aniline derivatives (fast yellow, orange, scarlet and red bases or salts)
Red	Arylamides of BON acid (red naphthols)	
Bordeaux	Arylamides of 7-methoxy-3-hydroxy-2-naphthoic acid (bordeaux naphthols)	
	Arylamides of BON acid (red naphthols)	Aminoazobenzene derivatives (fast bordeaux, garnet and corinth bases or salts)
Violet and blue	Arylamides of BON acid (red naphthols)	Substituted 4-benzoylamino-anilines, 4-amino-diphenylamines and other compounds (fast violet and blue bases or salts)
Green	3-Hydroxy-2-anthroic acid 2-toluidide (green naphthol)	
Brown	Arylamides of heterocyclic 3-hydroxyaryl-2-carboxylic acids (brown naphthols)	Various fast colour bases or salts
Black	Arylamides of BON acid (red naphthols)	Substituted aminoazobenzenes, polynuclear aromatic diamines and other compounds (fast black bases or salts)
	Arylamides of 3′-hydroxy-1,2-benzocarbazole-2′-carboxylic acid (black naphthols)	Aniline derivatives (fast red bases or salts)

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7.2.1 Yellow

Yellows are unobtainable with arylamides of BON acid and require the so-called yellow naphthols, which are bis-acetoacetyl derivatives of aryldiamines and are not derived from 2-naphthol; various simple arylamines can be used as bases.

7.2.2 Red

Practically all red naphthols are arylamides of BON acid. As will be seen from Table 7.1, in principle the amines used as diazo components are the same as those for yellows. Naturally the constitution of the diazo component exerts a marked influence on hue: orange, scarlet and red bases on red naphthols give the corresponding colours, whereas the so-called yellow bases and naphthols give yellows only.

7.2.3 Bordeaux

Two different possibilities exist in the bordeaux sector. The older method is based on the so-called red naphthols, together with bordeaux, garnet and corinth bases; the hue change to bordeaux derives from the bathochromic effect of the diazo component. In many cases such diazo components contain an azo group, so that a disazo dye is obtained on coupling. The other route to bordeaux is to use the so-called bordeaux naphthols, in which a 7-methoxy group has been introduced into the arylamides of BON acids. As will be seen from Table 7.1, these components yield bordeaux hues with orange, scarlet and red bases.

7.2.4 Violet and blue

Violet and blue bases are substituted 4-benzoylaminoanilines, diphenylamines or other compounds. The so-called red naphthols are used as coupling components for violets and blues. Bright greenish blues of the phthalocyanine type are unobtainable and the hues produced are indigo and navy blue (Variamine Blues).

7.2.5 Green

The green naphthol in the anthracene range gives dull greens when coupled with the blue bases. It is also possible to produce bright greens with azoic dyes of excellent light fastness. CI Azoic Coupling Component 108 is a condensation product of a copper phthalocyanine sulphochloride and an aminophenylpyrazolone, i.e. a blue phthalocyanine combined with a yellow azopyrazolone chromophore after coupling with a diazotised base. This green naphthol has very low substantivity for cellulosic fibres and is only applicable by continuous dyeing or printing [9]. A further possibility is to use CI Azoic Diazo Component 118, another combination of blue and yellow components in one molecule; blue-green hues are obtainable on red naphthols and scarlet hues on yellow naphthols.

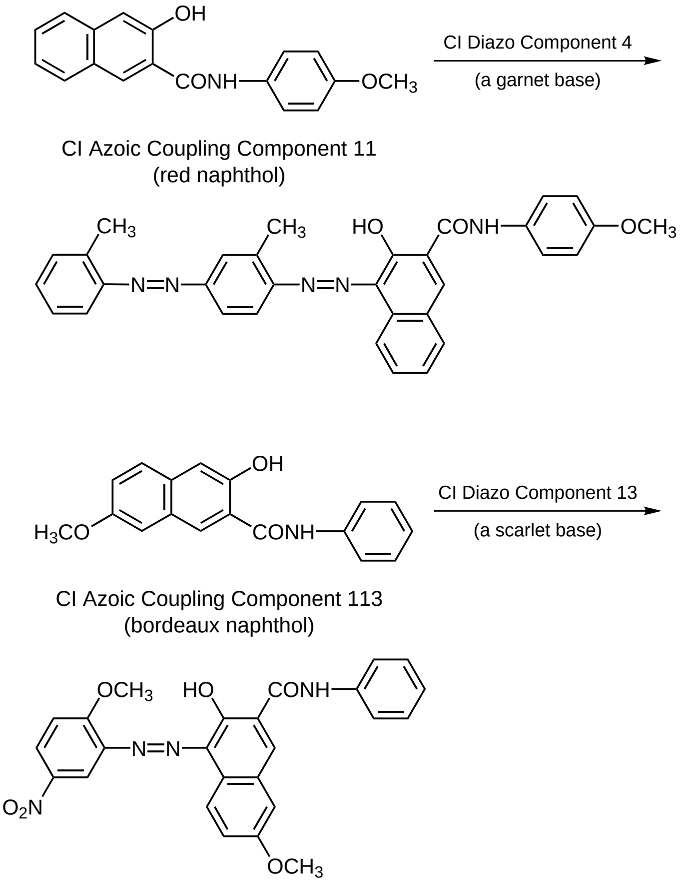
7.2.6 Brown

To obtain brown azoic colours it is necessary to use arylamides of heterocyclic 3-hydroxyaryl-2-carboxylic acids, derivatives of carbazole or dibenzofuran, as coupling components. As the brown naphthols are highly substantive to cellulose, a batchwise process is preferred. Various fast colour bases or salts can be used as diazo components.

7.2.7 Black

As in the case of bordeaux, there are two main methods of producing blacks. Various red naphthols are suitable for continuous dyeing or printing with diazotised bases and salts, the naphthol-prepared fabric being dried before application of the diazo component. As will be seen from Table 7.1, blacks are usually obtained with diazotised bases or salts derived from aminoazobenzene (similar to fast corinth bases) or multinuclear aryldiamines containing azo groups. Alternatively, blacks of high fastness are obtainable by batchwise application of a black naphthol (arylamide of 3′-hydroxy-1,2-benzocarbazole-2′-carboxylic acid) followed by development with a red diazotised base.

The chemical constitutions of both naphthol and diazotised base affect the hue obtained on coupling. An example is given in Scheme 7.1, showing the reactions of CI Azoic Coupling Component 11 (a red naphthol) and CI Azoic Coupling Component 113 (a bordeaux naphthol), which have closely similar structures, both being anilides of BON acid containing a methoxy substituent. The red naphthol is a 4-methoxyanilide, whereas the bordeaux naphthol has a 7-methoxynaphthoic anilide grouping. Virtually the same hue is produced when either the red naphthol is coupled with Fast Garnet GBC Base (CI Azoic Diazo Component 4) or the bordeaux naphthol is coupled with Fast Scarlet RC Base (CI Azoic Diazo Component 13). In the first case a disazo dye is formed and in the second a monoazo dye. The 7-methoxy group in the bordeaux naphthol, therefore, has the same bathochromic effect as a second azo group in the diazo component. Alkoxy groups in the 7-position of the naphthoic anilide residue give a significant increase in substantivity. CI Azoic Coupling Component 11 exhibits



Scheme 7.1

poor substantivity as a coupling component, whereas CI Azoic Coupling Component 113 has moderate substantivity.

7.3 TREATMENT WITH NAPHTHOLS

Unless specifically mentioned, the following recommendations refer to cotton as the most important substrate for azoic dyeing. Special precautions are necessary when other natural or regenerated cellulosic fibres are dyed.

7.3.1 Preparation of naphtholate solutions

Naphthols are insoluble in water, but their sodium salts (naphtholates) are water-soluble or can be prepared as a stable dispersion. Both cold and hot methods of dissolving naphtholates can be used.

Cold-dissolving method

The naphthol is converted to its naphtholate with alkali and dissolved in aqueous industrial alcohol. The naphthol can be pasted with industrial alcohol and warm water and then converted to the naphtholate by adding caustic soda. Alternatively, a mixture of water, caustic soda and methylated spirit can be poured over the naphthol, which is brought into solution by stirring. Dark brown to olive green solutions are produced that are highly concentrated and tend to crystallise unless diluted. Where necessary, formaldehyde and a dispersant are added to the concentrated solution before dilution to form the application liquor ready for immediate use.

Hot-dissolving method

A hot solution of dispersant is poured over the naphthol. After a brief boil, the required quantity of hot caustic soda liquor is added, usually forming a clear solution that is ready for use. In the case of naphtholates of low solubility the alkaline solution must be given a further brief boil before application.

Several naphthols of low to moderate substantivity, normally difficult to dissolve, are marketed in a special form that dissolves easily and quickly. In the hot-dissolving method these products can be strewn directly into the application bath already prepared with alkaline dispersant solution. After stirring briefly, a clear liquor is obtained that is ready to use for padding.

The cold-dissolving process is used when preparing naphtholate solutions for batchwise application. The hot-dissolving method is preferable for padding processes at temperatures near the boil, in contrast to batchwise processes carried out at room temperature. The simplest method of preparing naphtholate solutions is to use liquid brands of naphthols.

7.3.2 Selection and application of naphthols

When cotton is immersed in the naphtholate solution, exhaustion begins according to the substantivity of the naphtholate anion. Equilibrium absorption of the naphtholate is soon attained; treatment for 30 min is usually adequate for satisfactory levelling under bulk-scale conditions. Naphthols of low substantivity are mainly used in continuous dyeing where high substantivity is not required. Their use in batchwise dyeing with the addition of salt is limited.

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Naphthols of moderate substantivity can be applied either by continuous methods, suppressing substantivity by increasing the padding temperature and running speed, or by batchwise techniques with electrolyte addition to increase the absorption.

Naphthols of high substantivity are particularly suitable for batchwise techniques. With such products the concentration remaining in the exhausted bath is low, so that dyeings with good fastness to rubbing are obtained. If highly substantive naphthols are applied continuously, the undesired substantivity must be controlled by setting the initial concentration in the padding trough lower than the concentration used for making additions. With such naphthols it is necessary to use a high temperature and running speed in padding and to maintain a low liquor level in the padding trough, so that the absorbed solution is quickly replaced with fresh padding liquor.

7.3.3 Strengths of azoic dyeings

The depth of an azoic dyeing is controlled by the amount of applied naphthol; dyeings are defined by the quantity of naphthol fixed on the substrate and designated as ‘g kg^{-1} naphthol’. In batchwise techniques the depth of dyeing obtained with an individual naphthol and an individual diazotised base is dependent on the material used, concentration of the naphthol solution, liquor ratio and concentration of added salt, if any. For this reason the depth of a particular azoic dyeing cannot be specified by ‘g l^{-1} naphthol’ only, and both liquor ratio and salt addition must be noted. In continuous processes the depth achieved is dependent on the concentration of the naphthol added to the liquor and on the liquor retention of the fabric. Manufacturers supply graphs and tables to indicate the concentration of naphthol for batchwise application at a specified liquor ratio to obtain the required depth (expressed in terms of grams of naphthol per kilogram of substrate). In padding processes, applied concentration (g l^{-1}) can be calculated from the desired depth (g kg^{-1}) by taking into account the liquor retention.

7.3.4 Additions to the naphtholate solution

Water

Soft water should be used wherever possible for naphtholate application. If this is unavailable a sequestrant should be added: sodium hexametaphosphate, nitrilotriacetic acid or ethylenediaminetetraacetic acid can be used.

Surfactants

Addition of a stabiliser ensures that the naphtholate remains in dispersion and the addition of a wetting agent ensures rapid wetting-out of the material. Certain auxiliaries, such as Turkey red oil, combine these two functions but sulphoricinoleates of this type form insoluble soaps with alkaline-earth metal ions present in hard water, so they should only be used in soft water.

Dispersion stabilisers can be classified into three groups:

(1) Purified sulphite cellulose waste liquors (salts of lignosulphonic acids).
(2) Protein–fatty acid condensates.
(3) Adducts of formaldehyde and sodium naphthalenesulphonates.

Wetting agents are necessary when using the batchwise technique; usually sodium salts of alkylnaphthalenesulphonates are suitable. When padding with naphtholate solution, the high temperature employed facilitates wetting-out of the fabric.

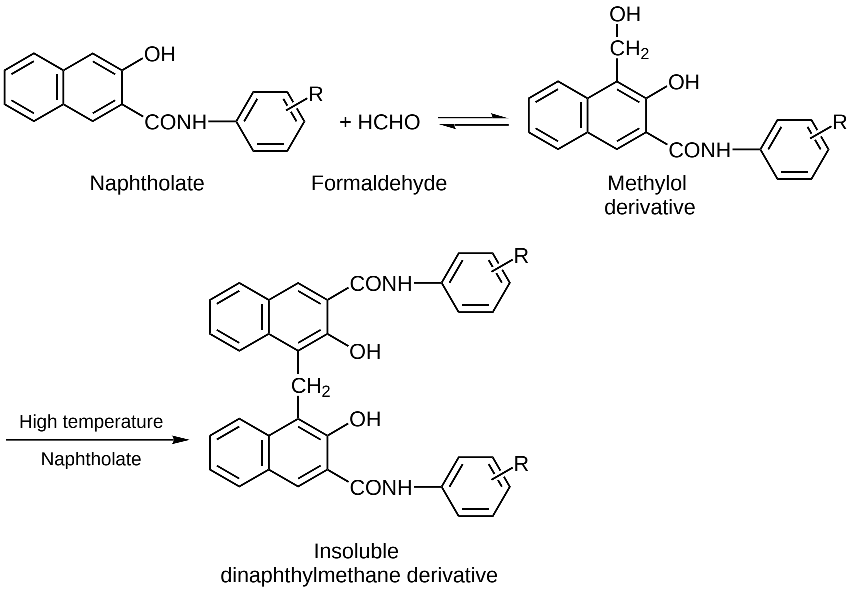
Caustic soda

As already mentioned in section 7.3.1, it is necessary to convert the water-insoluble naphthol to the soluble naphtholate. Naphtholate solutions, whether prepared by the cold- or the hot-dissolving method, contain an appreciable excess of caustic soda. Hence the naphtholate tends to hydrolyse, both in solution and on the fibre. Formation of the free acid form of the naphthol must be prevented as it will not couple in this state. The amount of caustic soda absorbed by the material during naphthol application must be taken into account when calculating the quantity of alkali binder required.

Formaldehyde

Conversion of the dissolved naphtholate back to the insoluble free naphthol form can occur on exposure to atmospheric carbon dioxide and to a marked degree in acid steam. The presence of the formaldehyde together with excess of caustic soda provides good protection against formation of free naphthol while the treated fabrics are hydroextracted or batched; methylol compounds of the naphtholate are produced.

Addition of formaldehyde is recommended when applying most naphthols by batchwise techniques, with the cold-dissolving method for preparation of the naphtholate solution being used. The protective action of the formaldehyde is brought about at 40–50°C by reversible formation of a methylol derivative from the naphtholate and formaldehyde. At temperatures above 50°C the methylol derivative combines with another molecule of naphtholate to give a dinaphthylmethane derivative that will no longer couple (see Scheme 7.2). Formaldehyde must therefore be omitted from the hot naphtholate solutions used in padding processes.



Scheme 7.2

The addition of formaldehyde produces a slight increase in the absorption of red naphthols, whereas in the case of bordeaux, brown, green and black naphthols the absorption is either unaffected or decreased. With black naphthols addition of formaldehyde improves the stability of the naphtholate solution. Formaldehyde must be omitted from solutions of yellow naphthols, however, otherwise less coupling will take place.

Common salt and Glauber's salt

Electrolyte addition increases the exhaustion of naphthols and is thus recommended for long-liquor application but not in padding processes, where high substantivity is undesirable. Improved rubbing fastness can be obtained by adding common salt in package-dyeing machines or jigs to minimise the residual naphthol in the exhaust bath. At short liquor ratios, with fabrics difficult to penetrate, naphthol application should be started without salt, which can be added later. The amount of common salt required (10–40 g l^{-1}) depends on the individual naphthol; it can be replaced by twice the amount of Glauber's salt.

7.3.5 Temperature of naphtholate application

The exhaustion of naphthols decreases with increase of temperature, so batchwise treatment is normally carried out at 20–30°C. Only when improved wetting or penetration is necessary should the temperature be raised, and 50°C should not be exceeded if addition of formaldehyde is required. The temperature should be reduced to 30°C for the final 10–12 min in order to obtain adequate absorption.

Padding with naphthols should be carried out at higher temperatures (80–95°C) without formaldehyde.

7.3.6 Stability of naphtholate solutions

Naphtholate solutions are essentially dispersions of limited stability, agglomeration occurring on standing, particularly when electrolytes are present. Furthermore the labile monomethylolnaphthol may be converted, on standing, to the stable dinaphthylmethane derivative (see Scheme 7.2) that will no longer couple. The best procedure is to prepare the naphtholate solution just before use. Fresh baths are particularly advisable when using naphthols that have high or moderate substantivity so that good reproducibility from batch to batch and good rubbing fastness can be obtained.

7.4 INTERMEDIATE TREATMENTS

In batchwise techniques an equilibrium between absorbed and residual naphthol is obtained, usually after about 30 min. The treated substrate contains absorbed naphtholate and further naphtholate solution retained in the interstices of the material. The degree of absorption depends on the substantivity of the naphtholate, the amount applied and the liquor ratio. The retained naphtholate couples with the diazonium compound in a similar manner to that absorbed, but this loose azoic dye is produced only on the fibre surface and impairs the fastness, particularly to rubbing and washing. Although most of the surface deposition is removed subsequently, it should be kept to a minimum in order to achieve dyeings of maximum fastness. The amount of loosely retained naphtholate can be decreased by hydroextraction but complete removal requires intermediate drying and this is only applicable with fabric.

7.4.1 Removal of retained liquor

Hydroextraction is the most efficient method of removing liquor and under optimum conditions can reduce the liquor content to 40% of the weight of cotton. Other methods comprise suction, squeezing or wringing, and their use depends on the form of the material.

7.4.2 Rinsing

Rinsing is customary with fabrics prepared on jigs or yarn treated in package-dyeing machines, in order to reduce the final concentration of naphthol on the material. It comprises treatment with 10–50 g l^{-1} common salt and 1–2 ml l^{-1} caustic soda (27%) for 5–10 min; 10–30 g l^{-1} of common salt is used with highly substantive naphthols and 30–50 g l^{-1} with naphthols of low to moderate substantivity. If possible the rinsed material should be suction-extracted prior to development.

7.4.3 Drying

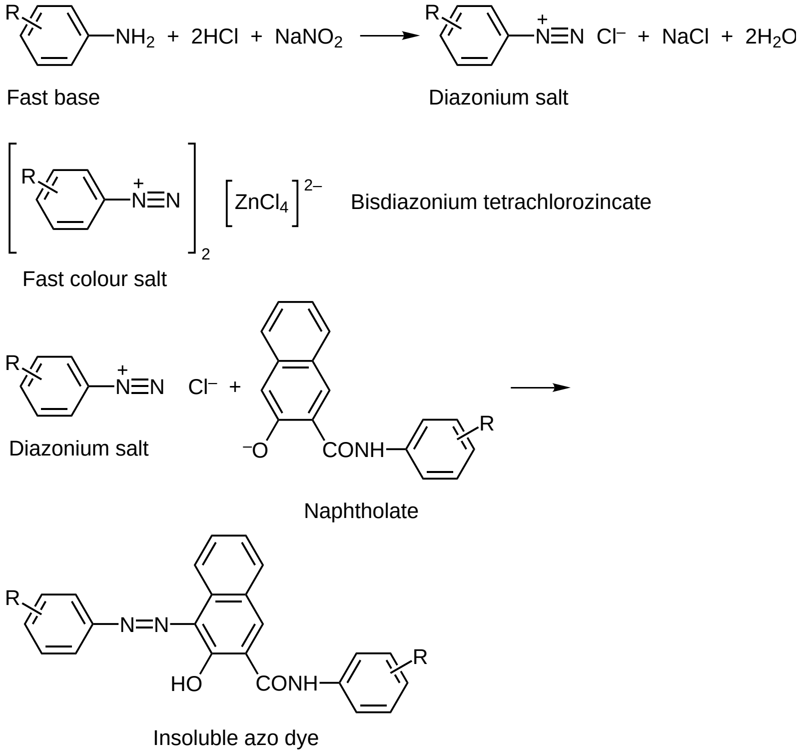
In continuous dyeing it is advantageous to express the water on a pad mangle and then pass the fabric into a hot-flue dryer. Care must be taken to prevent sudden drying, as this can lead to over-saturation of the residual liquor and absorption of the naphtholate can no longer be controlled, so that surface deposition occurs. The most appropriate drying temperature is between 90 and 110°C. It is important to ensure that the material is not overdried and with cotton a residual moisture content of 9–12% is desirable. This is achieved by suitable regulation of the rate of passage of the fabric through the dryer.

7.4.4 Sensitivity to light

The naphtholated substrate is affected by light, giving brownish areas on the yellowish background, the effect depending on the intensity of the incident light. On subsequent development, dyeings are obtained that are unlevel or differ in hue from the standard. The most marked effects are caused by exposure to direct sunlight, although prolonged exposure to diffuse light can also cause changes. Naphthol-prepared and dried fabric can be rolled up, covered with other dry material or stored in wagons that are likewise covered. If suitably protected in this way, dry naphthol-prepared fabrics can be stored for some weeks prior to further treatment, without damage occurring.

7.5 DEVELOPMENT

After naphtholation and intermediate treatment the material is passed into the development bath containing a dilute solution of a diazonium salt. This is produced either by diazotisation of an arylamine, a so-called fast colour base, or by dissolving a fast colour salt, which is a stabilised solid diazonium salt. Scheme 7.3 illustrates the diazotisation of a fast colour base, the zinc double salt of a stabilised fast colour salt and the insoluble azoic dye formed on coupling. As soon as the naphtholated substrate is introduced into the developing bath precipitation of the azoic dye begins, but more time is required before coupling is complete. The period of development depends in the first instance on the



Scheme 7.3

coupling energy and rate of coupling of the diazo component, and is less dependent on the chemical constitution of the naphthol.

Fast colour bases and salts can be classified into four groups according to their coupling energies. Table 7.2 illustrates typical examples from each of the four groups and also contains data on methods of stabilising the diazonium compounds in the form of fast colour salts. The production of zinc chloride double salts has already been mentioned and represents the most widely used method of stabilisation; cobalt chloride and tetrafluoroborate complexes are also marketed. Another method of stabilisation entails precipitating the insoluble complex formed when a solution of naphthalene-1,5-disulphonic acid is added to a solution of a diazonium compound.

Table 7.2 Examples of azoic diazo components

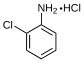
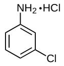
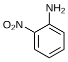
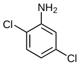
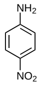
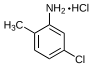
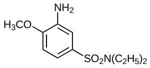
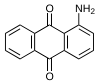
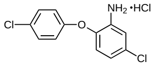
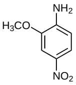
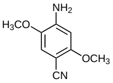
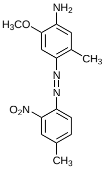
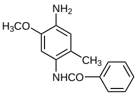
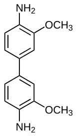
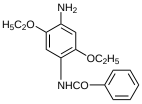
Fast colour bases	Structure	Stabilisation of corresponding fast colour salt	Coupling energy group[a]
CI Azoic Diazo Component 44		Tetrachlorozincate	I
CI Azoic Diazo Component 2		Tetrafluoroborate	I
CI Azoic Diazo Component 6		Tetrachlorozincate	I
CI Azoic Diazo Component 3		Tetrachlorozincate	I
C I Azoic Diazo Component 37		Tetrafluoroborate	I
CI Azoic Diazo Component 32		Napthalene-1,5-disulphonate	II
CI Azoic Diazo Component 42		Tetrachlorozincate	II
CI Azoic Diazo Component 36[b]		Tetrachlorozincate	I
CI Azoic Diazo Component 33		Tetrachlorocobaltate	II

Table 7.2 *Continued*

Fast colour bases	Structure	Stabilisation of corresponding fast colour salt	Coupling energy group[a]
C I Azoic Diazo Component 5		Napthalene-1,5-disulphonate	I
CI Azoic Diazo Component 40[b]		Tetrachlorozincate	I
CI Azoic Diazo Component 39[b]		Tetrachlorozincate	II
CI Azoic Diazo Component 41		Tetrachlorozincate	III
CI Azoic Diazo Component 48		Tetrachlorozincate	IV
CI Azoic Diazo Component 20		Tetrachlorozincate	III

a Optimum pH ranges for coupling:
I – pH 4–5.5
II – pH 5–6.5
III – pH 6–7
IV – continuous dyeing only

b Available as fast colour salt only

7.5.1 Diazotisation of fast colour bases

If the arylamine to be used is soluble in dilute hydrochloric acid, dissolved sodium nitrite is added slowly to this solution (direct diazotisation). If it is insoluble the amine is pasted with aqueous sodium nitrite and the mixture added in portions to dilute hydrochloric acid. Addition of ice is necessary to keep the

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diazotisation temperature below 5°C. Difficulties can arise if the indirect diazotisation does not reach completion, so that a portion of the fast colour base remains undiazotised. For this reason it is often advantageous to paste these arylamines with dilute hydrochloric acid and proceed by the direct route. The dye manufacturers provide precise data for diazotisation, the concentration and amount of hydrochloric acid used in diazotisation, depending on the chemical constitution of the fast colour base.

It is important to add a suitable dispersant in diazotisation; nonionic agents have proved ideal. An excess of free hydrochloric acid and sodium nitrite must also be maintained. Spotting onto starch-iodide paper is carried out to test for excess of nitrous acid. Completion of diazotisation of fast colour bases that are insoluble in dilute hydrochloric acid is evident when the solution becomes completely clear. Observation of the endpoint with fast colour bases that are soluble under these conditions is achieved indirectly as follows. Sodium acetate is added to a test solution until a neutral reaction to Congo Red (CI Direct Red 28) is obtained. If the test solution remains clear after neutralisation then diazotisation is complete. If the solution becomes cloudy, however, the diazonium solution must be allowed to stand for a time until the reaction is complete.

The diazonium solution contains excess mineral acid and is stable if protected from the action of light and heat. Just before development the strongly acidic solution must be neutralised, otherwise coupling will not take place. Sodium acetate for neutralisation can be added directly to the concentrated diazonium solution. As a rule, however, the required amount is added to the developing bath prior to addition of the diazonium solution.

7.5.2 Dissolving fast colour salts

Fast colour salts consist of diazotised and stabilised primary arylamines and are readily soluble in water. As a rule, solutions are prepared by pouring over the fast colour salt five times its weight of lukewarm water (25–30°C) containing a nonionic dispersant and stirring until dissolved. Products having a solubility below 200 g l^{-1} must be diluted further with cold water to effect complete solution. Some fast colour salts require an addition of acetic or formic acid. The clear concentrated diazonium solutions should not be allowed to stand too long and should be diluted with water to the required concentration. The majority of fast colour salts contain an alkali-binding agent, so that in most cases no further addition is necessary and the prepared developing baths have the correct pH.

7.5.3 Stability of development baths

Hydrochloric acid solutions of diazotised fast colour bases are more stable than those after neutralisation with acetate for development. Hence it is advisable to allow the prepared acidic solutions to stand and to neutralise them only shortly before use. It is advantageous to dissolve fast colour salts just prior to use. Addition of a nonionic dispersant to the developing bath is essential. With few exceptions development baths remain stable for several hours, but it is better to prepare only as much developing liquor as is required the same day. Stored developing liquors should be kept cool and protected from direct exposure to light.

7.5.4 Water quality and additions to dyebaths

In contrast to naphtholate solutions, which must always be prepared with soft water, hard water can be used for the preparation of developing liquors. Nonionic dispersants of the fatty alcohol polyoxyethylene type are suitable to use in dissolving fast colour salts and dispersing the insoluble azoic dye during development. Addition of these dispersants ensures that the azoic dye precipitated in the development bath will not be deposited on the fibre surface. Well-dispersed azoic dye is readily removed during washing-off. When the naphtholated material is entered into the developing bath coupling takes place immediately, but some naphtholate is desorbed from the material. The degree of desorption depends on the substantivity of the naphthol and the coupling properties of the diazo component. Except in padding processes, desorption of the naphthol can be counteracted by addition of salt, but this should be omitted with fast colour salts of poor solubility.

7.5.5 Alkali-binding agents in developing baths

Acetic acid is the most commonly used alkali-binding agent, produced after diazotisation by neutralising the excess of hydrochloric acid with sodium acetate. This is usually adequate to neutralise the alkali in the development bath, but if necessary more acetic acid can be added. Most fast colour salts contain alkali-binding agents in the form of aluminium, zinc or magnesium sulphate, or occasionally chromium acetate.

Acetic acid

Dilute solutions containing 0.01 mol l^{-1} (1.2 ml l^{-1} of 50%) acetic acid have a pH of 3.35 and those containing 0.04 mol l^{-1} (4.8 ml l^{-1} of 50%) have a pH of 3.0. Additions of increasing amounts of sodium acetate (up to 20 g l^{-1}) raise the pH in the first case to 5.8 and in the second to 5.1. Thereby acetic acid–acetate buffered systems can be produced over the pH range 3–6.

Aluminium sulphate

This product has a strong alkali-binding action and fast colour salts containing aluminium sulphate exhibit moderate to high coupling energy. With sufficient alkali aluminium sulphate forms soluble basic salts but if there is insufficient caustic soda insoluble basic salts are produced that cause clouding and finally flocculation of aluminium hydroxide.

Zinc sulphate

This is less acidic than aluminium sulphate and is present in some fast colour salts with low coupling energy. Zinc sulphate does not form basic salts with caustic soda but is precipitated immediately as zinc hydroxide, either partially or totally.

Chromium acetate

This is present in a few of the blue fast colour salts with a low coupling energy, which are speciality products for continuous dyeing. Replacement of the acetate ions in chromium acetate by hydroxide ions takes place slowly in the cold and more rapidly when the solutions are warm. This dependence of the alkali-binding power of chromium acetate on temperature necessitates treating the fabric in an open-width washer with hot water after it leaves the developing unit, so that even and rapid development takes place.

7.5.6 Strength of developing baths

Batchwise dyeing

The applied concentration (expressed in g l^{-1}) of a fast colour salt or base is related to the applied depth (in g kg^{-1}) of naphthol and the liquor ratio. In order to facilitate rapid and complete coupling, the development bath should be slightly acidic and contain excess diazo component.

Padding

The applied concentration (g l^{-1}) of fast colour salt or base is related to the applied depth (g kg^{-1}) of naphthol on the material, as in the case of batchwise dyeing. Data are available to calculate from the applied depth of naphthol the concentration of the developing solution required, depending on the diazo component used. In padding processes, liquor retention should be low to avoid a large excess of diazo solution. Development baths used in padding are highly concentrated, particularly if a high liquor retention is unavoidable, so that fast colour salts of high solubility must be used.

7.5.7 Coupling energy of diazo components

Diazo components are classified into four groups by dye manufacturers according to their fields of application and their energies of coupling. Table 7.2 contains examples from each group; groups I–III contain those fast colour bases and salts suitable for application by both batchwise and continuous techniques, whereas the fast colour salts in group IV are suitable only for padding.

Group I

These products have a high coupling energy and will couple fully even in the presence of a large excess of unbuffered acetic acid. The most suitable coupling range is pH 4–5.5.

Group II

These diazo components do not couple completely in the presence of excess acetic acid and an excess of sodium acetate is prescribed after diazotisation of these fast bases. The coupling range for these products is pH 5–6.5.

Group III

Products in this group have a low coupling energy. They do not couple well even in the presence of small amounts of unbuffered acetic acid, so that after diazotisation an excess of sodium acetate must be added. The optimum coupling range is pH 6–7.

Group IV

This heterogeneous group contains fast colour salts that couple with difficulty, complete coupling being possible only on a continuous range. Some fast colour salts in group IV have a high coupling energy and are substantive aminoazo compounds (giving navy blues and blacks on coupling), but are unsuitable for batchwise dyeing except by special methods.

7.5.8 Mixtures of fast colour bases and salts

With few exceptions, mixtures of fast colour bases and salts are not recommended since their use can lead to unlevel dyeings and poor reproducibility. Should a mixture be essential, in order to produce a particular hue, it is advisable to use a mixture of coupling components.

7.5.9 Neutral development

In exceptional cases, including the application of high-energy diazo components, it may be necessary to develop under near-neutral conditions. This is particularly advisable for the production of browns using CI Azoic Coupling Component 16 and a number of processes can be employed, outlined below.

Phosphate buffer method

Sodium dihydrogen phosphate is used to neutralise the caustic soda carried into the developing bath by the naphtholated substrate and the excess of hydrochloric acid used in diazotisation is neutralised with disodium hydrogen phosphate. The fast colour base is diazotised and filtered into the development bath without any addition of acetic acid or sodium acetate. The developing bath is prepared with the appropriate quantities of phosphates.

Sodium bicarbonate method

The fast colour base, diazotised without acetic/acetate addition, is filtered into the development bath containing twice as much sodium bicarbonate as the amount of sodium nitrite that was used to diazotise the fast colour base. Bases that are particularly sensitive to alkali cannot be applied by this method.

7.6 AFTERTREATMENT

Aftertreatment includes rinsing, acidification after development, and alkaline soaping followed by rinsing. Only when these processes have been carried out thoroughly do the resultant dyeings exhibit the desired final hue and fastness.

7.6.1 Alkaline soaping

Treatment in a boiling alkaline soaping liquor results in crystallisation of the major portion of the insoluble azoic dye within the fibre and only a small amount remains loosely adhering to the fibre surface [10]. There is a change in hue and the loosely held surface dye is easier to remove on subsequent rinsing. Olive oil soap and soda ash are suitable for alkaline soaping in soft water. With hard water it is necessary to add a sequestrant of the polyphosphate type. If necessary synthetic detergents that are stable to hard water can be used, but soft water is preferable.

7.6.2 Aftertreatment of batchwise dyeings

It is customary to rinse cold with the addition of 2–3 ml l^{-1} concentrated hydrochloric acid to the first rinsing bath. This addition is essential in the development of fast colour salts as it dissolves the basic metal hydroxides produced during development and facilitates their removal from the material. The addition of acid is particularly recommended if the development using fast colour bases or salts did not include an alkali-binding agent.

After acidification the material is given another cold rinse and then an alkaline soaping with 3 g l^{-1} soap or detergent, 1–2 g l^{-1} soda ash and 0.5–1.5 g l^{-1} polyphosphate for 10–20 min near the boil. This is followed by treatment in a second bath containing a nonionic dispersant for 10–15 min at 70–80°C. The overall procedure may be reversed, i.e. treatment first with a nonionic dispersant followed by hot alkaline soaping. Efficient rinsing that completely removes the surfactant solution containing the dispersed azoic dye is essential.

7.6.3 Aftertreatment of continuous dyeings

Development and aftertreatment are combined following padding and intermediate drying of the fabric, the first baths forming the development stage. At least three to four compartments of a continuous unit should be available for soaping in 3–5 g l^{-1} soap or detergent, 2–3 g l^{-1} soda ash and 1–2 g l^{-1} polyphosphate at the boil. This should be followed by treatment at 70–80°C with a nonionic dispersant, and a final cold rinse. Usually the rubbing fastness of dyeings produced on a continuous unit is very good, as naphthol application is followed by intermediate drying prior to development.

7.7 DYEING OF MERCERISED COTTON AND OTHER CELLULOSIC FIBRES

Although unmercerised cotton represents the main substrate for the application of azoic components, consideration must also be given to causticised and mercerised cotton, bast fibres (particularly linen) and regenerated cellulosic fibres.

7.7.1 Causticised cotton fabrics

Cotton fabrics can be causticised before dyeing to improve their dyeability and coverage of 'dead' cotton. The absorptive capacity of causticised cotton lies between those of unmercerised and mercerised cotton, but otherwise there is no difference in azoic dyeing techniques.

7.7.2 Mercerised cotton yarns and fabrics

Azoic coupling components have a much greater substantivity for mercerised cotton than for unmercerised cotton and the following modifications in dyeing technique are necessary.

Naphthol treatment

In view of the increased substantivity for mercerised cotton, the concentration of the naphtholate solution can be significantly reduced, particularly when naphthols of low substantivity are applied. These differences become less evident as the substantivity of the naphthol increases. As mercerised cotton absorbs more alkali, a small excess of caustic soda is necessary for naphthol treatment.

Aftertreatment

Although the naphtholated substrate is developed in the usual way, it must then be rinsed immediately in about 2–3 ml l^{-1} hydrochloric acid solution to avoid delustring of the material. This procedure is necessary with either fast colour salts or bases. The amount of soda ash added to the boiling soap solution can be reduced from about 2 g l^{-1} to 0.5–1 g l^{-1}. Treatment with 0.1–0.5 ml l^{-1} acetic acid (50%) after soaping and rinsing will often enhance the lustre.

7.7.3 Bast fibres

Bast fibres, such as flax, hemp, jute and ramie, and other vegetable fibres, such as sisal and coir, contain impurities that interfere with the absorption of both naphthol and diazo component. Thus a significant proportion of insoluble azoic dye remains on the fibre surface and, unless the impurities are removed by appropriate pretreatment, dyeings of inadequate penetration and fastness are obtained. Flax (linen) represents the most important fibre in this category.

Pretreatment

Bleaching of linen removes most of these impurities, so that bleached linen behaves similarly to cotton. Unbleached linen must be boiled out with soda ash and a suitable wetting and dispersing agent, but a prebleach is advisable in order to obtain dyeings of maximum rubbing fastness.

Naphthol treatment

In order to achieve satisfactory penetration, exhaustion should begin at 70°C or above, omitting the formaldehyde, and be completed in a cooling bath at 25–30°C. Addition of an alkali-resistant wetting agent to the naphtholate solution is recommended.

Aftertreatment

Although azoic dyeings are developed on linen in the same way as on cotton, a more intensive aftertreatment is required to remove the greater proportion of loosely held azoic dye from the fibre surface. In package dyeing it is necessary to prevent filtration of the dye particles by giving an initial treatment at 60–70°C, followed by soaping at the boil in a fresh liquor containing higher concentrations of soap and soda ash.

7.7.4 Regenerated cellulosic fibres

Viscose and polynosic fibres are available in filament or staple variants; absorption of naphthol varies amongst these fibre types.

Pretreatment

Regenerated cellulosic fibres contain only small amounts of water-soluble spinning assistants and softeners that can usually be removed by a weakly alkaline scour in soda ash with wetting and dispersing agents.

Naphthol treatment

As naphthols have higher substantivity for regenerated cellulose than for cotton, lower concentrations are required to attain the same depth. In batchwise processing it is advisable to pre-wet the material thoroughly in a solution of wetting agent before addition of naphthol, to avoid uneven uptake owing to inadequate wetting-out of the material. Regenerated cellulosic fibres swell to an appreciably greater extent than cotton in alkaline media and have increased alkali absorbency, so that the amount of alkali in the naphtholate solution can be reduced.

Aftertreatment

Dyeings on regenerated cellulosic fibres are usually soaped at 80–90°C with 2 $g\ l^{-1}$ soap and 0.5 $g\ l^{-1}$ soda ash. During soaping of certain azoic combinations 'blinding' (delustring) of the fibre may occur, but this undesirable effect can be avoided by soaping at 50–60°C.

7.8 EQUIPMENT FOR AZOIC DYEING

Cellulosic textiles can be azoic dyed in the form of loose stock, sliver, tow, yarn, fabric, terry towelling and knitted goods.

7.8.1 Dyeing of loose stock, sliver and tow in package machines

Viscose staple is commonly dyed in these forms in package-dyeing machines. Cotton sliver can be naphtholated and developed in package machines or wound on to perforated beams and dyed in beam machines. Loose stock must be tightly packed in a wet condition to prevent channelling and, as the tightly packed material has a strong resistance to flow, liquor circulation should be from inside to outside only. Depending on the type of material and machine used, it may be necessary to repack between naphthol application and development in order to obtain level dyeings.

Cotton can be yarn dyed in package-dyeing machines in the form of hanks or cheeses. Viscose can be dyed in cake form, but particular care must be taken to ensure that unsatisfactory packing does not cause unlevelness by channelling.

7.8.2 Hank-dyeing in becks

Yarn in hank form was traditionally suspended on sticks and turned by hand while dyeing in large-volume becks. This method gave azoic dyeings of particularly good fastness to rubbing because the naphtholated hanks were hydroextracted to about 50% before development. Intensive aftertreatment followed in the boiling soap liquor is becks. Dyeings of excellent rubbing fastness were obtained after warm and cold rinsing, hydroextraction and drying.

7.8.3 Hank-dyeing machines

Two types of machine are used, one in which the hanks are agitated in a stationary liquor and the other in which the liquor is circulated through the hanks. Spraying techniques are intermediate between these two methods.

In machines of the first type the hanks are suspended in the liquor from moving rods. This system can be used for naphthol exhaustion, development and aftertreatment, the dyeings produced being level and the yarns having a full handle. With the circulating-liquor type, both open and closed vessels are available, consisting of rectangular tanks fitted with holders for the hanks at the top or side of the vessel. Most machines have a stuffer box fitted outside the machine to fill the vessel with the dye liquor and to make additions of dyes and chemicals.

In the spray technique the yarn carriers are perforated and the dye liquor is pumped through onto the yarn hanks, which are suspended in the vessel without dipping into the dye liquor. The controlled addition of dye liquor is stopped at intervals during which the hanks are removed. This procedure can be used for both naphtholation and development and permits the use of short liquor ratios.

7.8.4 Cheese-dyeing machines

Conventional circulating-liquor machines are ideally suitable for azoic dyeing; closed machines with two-way liquor circulation are preferred. Machines with adequate suction are essential; suction treatment is desirable after each operation, particularly after naphtholation and intermediate rinsing. If soaping or rinsing liquors become highly coloured by the azoic dye removed from the material it is advisable to run off the liquor and refill.

7.8.5 Beam-dyeing machines

In this method cotton yarns are wound on perforated beams, uniform winding being essential to ensure the production of satisfactory dyeings. Beams are fitted into the vessel either vertically or horizontally, according to the type of machine used. In large beam machines there is considerable resistance to flow and the alternating cycle of flow direction should favour out-to-in rather than in-to-out.

7.8.6 Warp yarns in roller vats

Warp yarns can be dyed in the form of wound packages in roller vats. The warps run continuously over guide rollers and pass through squeeze rollers, whereby the expressed dye liquor returns to the dye vat. After naphtholation the yarn is squeezed and placed in a truck and then passes into the developing liquor in a roller vat.

7.8.7 Naphtholation during warp sizing

An alternative to indigo or sulphur dyes for the production of blue dyeings on cotton denim fabric is azoic dyeing during warp sizing [11]. The warp yarns are simultaneously sized and treated with naphthol, mainly CI Azoic Coupling Component 2 or 20; carboxymethylcellulose, alone or in admixture with potato starch, is used as size. Increase in the proportion of carboxymethylcellulose gives a less viscous size liquor and consequently better penetration of naphthol into the yarn. The warps can be dried in hot-air dryers or on heated cans, but rapid drying is not desirable if good penetration and rubbing fastness is required, since there is insufficient time for the naphthol to penetrate the yarn satisfactorily. Care must be taken to ensure that the prepared warps and woven fabric are not left exposed to direct sunlight and that no uneven friction occurs during weaving, as this can cause warp stripes. Both the beams and the undeveloped fabrics can be stored for a long period provided that they are protected from exposure to light, acid steam and high humidity.

Pad development of the woven fabric with fast colour salts or diazotised bases gives the best penetration. The concentration of the developing bath depends on the depth of naphthol applied. A normal aftertreatment is given, and in order to reserve the weft as much as possible, it may be necessary to include a boiling soap treatment, but this depends on the fabric construction. Bleached cotton must be used for weft if the maximum white effect is desired, but undyed grey cotton is frequently employed. Coloured weft yarns yield attractive two-coloured effects of interest in clothing for casual wear [12,13].

7.8.8 Winch dyeing of terry towelling and knitted fabrics

Certain hues and depths difficult or impossible to obtain with reactive dyes can be azoic dyed. Only highly substantive naphthols are applicable and preferably diazo components with high or moderate coupling energy should be selected. Diazotised fast colour bases and salts with low coupling energy are less suitable.

Excellent results are obtainable if the prepared tubular-knitted fabric is removed from the winch, hydroextracted and slit into open width for development on the winch. Alternatively, hydroextraction can be avoided by rinsing before development. Knitted fabrics naphtholated on the winch in tubular form may be developed continuously on equipment in which air is injected to inflate the tubular fabric into balloon form.

7.8.9 Jig-dyeing of woven fabrics

Piece goods are jig-dyed only when short lengths of fabric are to be dyed or where continuous units are not available. The dyeing is rinsed between preparation and development, but where rubbing fastness requirements are particularly high an intermediate drying stage is given. Intermediate drying of naphtholated fabric is also advisable before continuous development.

7.8.10 Pad–jig process

When a padder and drying unit are available, but a continuous range is not, an alternative process is the pad–jig technique. After padding with naphthol, with or without intermediate drying, the dyeing is developed and aftertreated on the jig.

7.8.11 Continuous dyeing with intermediate drying

This is the most important azoic dyeing method. Dye consumption is low and productivity high. Many hues can be dyed fully continuously; the naphtholated fabric is dried, developed and soaped on a continuous range. It is necessary, however, to cool the dried fabric before it passes into the developing bath.

The most common method is padding with naphtholate, hot flue drying and batching. The treated fabric is cooled and then developed, soaped and rinsed in a further padding and open-width washing range.

Naphthol treatment

Two- or multi-roller padders with shallow troughs are used. Tightly woven cotton fabrics that are difficult to penetrate are preferably impregnated on a three- or multi-roller padder and given a double dip and nip treatment for the best possible penetration.

Preference is given to naphthols with low to moderate substantivity. As naphtholation takes place at 85–90°C it is advisable to dissolve the naphthols by the hot method or to use the readily soluble naphthols that only require sprinkling to form the hot naphtholate solution.

Intermediate drying

Hot flue drying at 90–100°C is recommended. A regular air stream is necessary to avoid two-sidedness. If drying cylinders are used for intermediate drying, the first cylinder should be at a lower temperature. Pin stenters are preferable to clip stenters for drying and the temperature in the first heating zone should be at about 100°C to avoid premature drying. The residual moisture content should be within 8–12% in order to ensure rewettability and complete coupling. The fabric should be covered with a wrapper to protect it from the action of moisture, water spotting, acid vapour and light.

Development

In many cases a two-roller padder is suitable for lightweight fabrics. For heavyweight fabrics, particularly when dyed with blue and black salts produced specially for continuous dyeing, a three- or multi-roller padder is recommended. The diazonium salt is heat-sensitive, so the development liquor should be as cool as possible in order to prevent decomposition. A small trough should be used that can be quickly refilled with liquor. The fabric is padded, skyed for a short time and then passed into an open-width washer. With most azoic combinations a skying period of 30–60 s is followed by a cold rinse and, if necessary, neutralisation with 2 ml l^{-1} concentrated hydrochloric acid, and in the next compartment the fabric is rinsed cold, sometimes using an overflow.

With diazo components of low coupling energy, the development bath is prepared with an excess of 10–20 ml l^{-1} acetic acid (50%) and, after skying for 30–40 s, the fabric passes into the first compartment of an open-width washer containing 10 g l^{-1} soda ash at 30–40°C. In the second compartment the fabric is rinsed again, possibly with overflow. In the case of weakly coupling diazo components, which decompose in the soda bath and lose their ability to couple, a third method is recommended. After padding and skying for 30–60 s the fabric is treated in water at 80–90°C in an open-width washer. Finally, the fabric is soaped at the boil with a soda ash addition in several compartments, followed by warm and cold rinsing.

7.8.12 Continuous dyeing without intermediate drying [14,15]

Bulky fabrics such as tubular knitgoods, terry towelling, corduroy or velvet can be processed wet-on-wet by applying the coupling component in the first padding bath and the diazo component in a second padding. For the process to be successful it is vital that an additional pick-up of 50% or more is achieved in the second bath, otherwise the solubility limits of the diazo components can be a problem. The equipment required comprises:

(1) a pad mangle with an indirectly heated trough;
(2) a 30–60 s air passage, e.g. an unheated steamer with open hatches;
(3) a pad mangle for developing and cooling.

Aftertreatment is carried out on an open-width washer or, in the case of terry towelling or tubular knitgoods, on a rope washer.

7.9 FASTNESS OF AZOIC DYEINGS

Azoic dyeings exhibit exceptionally good wet fastness on cellulosic fibres. All naphthol combinations withstand washing at the boil and the light fastness properties are good to excellent. However, whereas most dyes show a gradual lowering of light fastness with decreasing depth, this drop is more evident with many azoic dyes and so they are not normally applied in pale depths. The light fastness of azoic dyeings is affected by the moisture content of the atmosphere in which they are exposed.

Most azoic combinations are fast to chlorine, so that they are suitable for materials to be bleached. With few exceptions, the fastness of azoic dyeings to mercerising and perspiration is excellent. Azoic dyes vary in fastness to hot pressing but there are many with excellent fastness. Inadequate fastness to hydrogen peroxide is frequently evident. Blue combinations are an exception, but they show lower fastness to chlorine. Most azoic dyeings are of good fastness to resin finishing [16–18]. The main weakness of azoic dyeings is their limited fastness to organic solvents used in dry cleaning and spotting [19].

Fastness to rubbing varies and is largely dependent on the dyeing process used. A recent study of the rubbing fastness of several Naphtol AS combinations on cotton revealed that the presence of granular dye particles consistently lowered the fastness ratings. This behaviour was aggravated with increase in size of the particles. On the other hand, needle-shaped dye particles showed scarcely any effect on the fastness. It was concluded that such particles are not substantially removed by rubbing because their surface area in contact with the fibres is relatively greater [20].

Azoic dyeings are readily discharged and are ideal for dyeing fabrics intended for white or coloured discharge prints. However, their use has greatly declined in favour of reactive dyes in this area, because of the brilliant colour gamut and easier application procedures of reactive dyeing.

7.10 STRIPPING OF AZOIC DYEINGS

7.10.1 Stripping naphtholated materials

Before development, naphtholated materials are relatively easy to strip using boiling alkaline liquors, particularly where weakly substantive naphthols have been used.

7.10.2 Stripping azoic dyeings

Azoic dyeings can be stripped with powerful reducing agents, although those based on highly substantive naphthols are more difficult to deal with. Certain yellow azoic dyeings are resistant to reduction and stripping is therefore incomplete. Azoic dyeings can be stripped from cellulosic fibres with 5–10 ml l^{-1} caustic soda (27% by weight), 3–5 g l^{-1} sodium hydrosulphite and 1–2 g l^{-1} dispersant. An addition of 0.5^{-1} g l^{-1} anthraquinone considerably enhances the effect. Anthraquinone causes the stripping liquor to turn red. If it should turn yellow or brown a further addition of caustic soda or sodium hydrosulphite must be made. Any staining should be removed by giving the stripped fabric hot and cold rinses.

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CHAPTER 8

Selection of dyes for dyeing cellulosic fibres

John Shore

8.1 INTRODUCTION

Cellulosic textiles are found at all price levels, from the pinnacle of *haute couture* to the humblest cotton duster. Military fabrics, produced to rigid specifications of colour reproducibility, fastness and durability, depend heavily on cotton and its blends. Indigo-dyed cotton denim meets the extraordinary requirement that the colour must readily bleed and fade to give the familiar washed-down, worn-out look early in the life of the garment. Cellulosic fibres in all forms from loose stock to finished garments can be dyed by numerous batchwise or continuous routes on all kinds of dyeing equipment designed for the substrate form to be processed.

In view of this remarkable versatility it is necessary to consider the selection of dyes for cellulose at several different levels. There are various important classes of dyes for cellulose, as described in the preceding chapters, and within each class there are often significant sub-classes differentiated from one another by differences in application characteristics. Such distinctions may be decisive in selecting the most suitable dyes for a given set of dyeing conditions. In certain circumstances, it may be necessary to consider the behaviour of individual dyes or groups of chemically related products, where these are sufficiently anomalous to be non-representative of the class or sub-class under discussion.

This chapter will be focused mainly on the differences between the major classes of cellulosic dyes that determine whether a class is selected for a given substrate. The choice between sub-classes has been dealt with already in some detail under the appropriate chapters. Limitations of space prevent a detailed and comprehensive discussion of individual products and, in any case, selection between these can be fully meaningful only in the context of a specific set of economic and technological criteria. Before taking into account the numerous factors that have a bearing on dye selection at these various levels, it is first necessary to explain why several major classes of dyes are used for the dyeing of cellulosic materials.

In the dyeing of non-cellulosic fibres one class of dyes invariably predominates on the substrate concerned, for example, anionic dyes on nylon or wool [1], basic dyes on acrylic fibres, disperse dyes on polyester or cellulose acetate [2]. This is not the case for cellulose, owing to the complementary nature of the classes of dyes used and the way in which the dyeing of cellulosic fibres has evolved.

Direct dyes represent the first of these classes to have become established, over a century ago. Before then, cotton almost always had to be mordanted before applying either natural mordant dyes or their synthetic replacements (basic dyes or anthraquinone mordant dyes). Most of the early fast colours were rather dull; there were no fast bright yellows, violets, blues or greens [3]. Mixtures were difficult to reproduce, especially if two or more mordants were present in the same recipe. Pale blues based on natural indigo were rather fugitive to light.

The brightness, varied colours and ease of application of direct dyes, with their substantivity for unmordanted cotton and good levelling properties, secured their ready acceptance in spite of the limited fastness to light and wet treatments of the early members of the range. By the turn of the century, however, more expensive reds with high substantivity and good fastness properties were being developed. Nevertheless, the light fastness of many of the blue, green and grey direct dyes marketed then was so inferior to the major yellows and reds that they gave unbalanced fading in mixtures [4].

The first sulphur dye appeared before the direct dyes, but it was not until the development of the sulphur blacks in the closing years of the last century that this class of dyes made a major impact on cotton dyeing [5]. Sulphur Black T (CI Sulphur Black 1) quickly became the best-selling individual dye for textile coloration, a position it has retained ever since [6]. The gamut of sulphur dyes was soon extended to dull yellow, orange, brown, blue and green, satisfying the need for full-depth dyeings at moderate cost, with better fastness than direct dyes in general.

Indigo, the natural forerunner of the vat dyes, was by now available in synthetic form, but there remained a lack of brighter blues with good all-round fastness. This gap was filled by the indanthrone blues, which appeared at the beginning of the present century, closely followed in the next few years by other anthraquinonoid vat dyes in the orange, brown, red, violet, blue, olive, grey and black regions of colour space. Collectively this range offered, at a price, standards of fastness to light, washing and weathering that had not been approached hitherto by natural or synthetic dyes.

The early success of direct dyes had been tarnished by their limited wet fastness, particularly now that sulphur and vat dyes had shown what could be achieved, but the azo dye chemists were fighting back. Primuline red, made by coupling β-naphthol with the first diazotisable direct dye (CI Direct Yellow 59), and Para red (*p*-nitroaniline→β-naphthol), the first successful azoic combination, had appeared in the same year (1887), but the orange, brown and blue dyes developed with β-naphthol were inferior to the reds from the viewpoint of cost, brightness and fastness. It was the discovery of the more substantive Naphtol AS (HOE, CI Azoic Coupling Component 2) in 1912 which provided the basis for a range of azoic dyes with improved colour gamut, brightness, build-up and fastness properties, although these developments were not brought to fruition until the 1920s.

The enhanced wet fastness of diazotisable direct dyes after development inspired a search for other techniques to improve the performance of direct dyes. Structures were designed to achieve better wash fastness by aftertreatment with formaldehyde, but high light fastness was difficult to attain in this way. The discovery of the first metal-complex dyes for wool (1912) led to interest in copper-complex direct dyes, initially applied by an after-coppering technique but later synthesised as premetallised dyes for conventional application.

Thus the stage was set in 1920s for a struggle for supremacy between azoic, direct, sulphur and vat dyes, by now all well established but still in a phase of active development. Demand for vat dyes began to grow, initially at the expense of azoic and direct dyes and later of sulphur dyes. This trend might well have been expected to continue, but several factors began to operate in the opposite direction in the 1930s [7].

The surge of interest in vat dyes was stimulated in 1922 by the discovery of Caledon Jade Green (ICI, CI Vat Green 1), the first homogeneous fast green for cotton. Green had been an unsatisfied research target for many years. Basic greens were fugitive and direct greens dull, with unattractive dyeing properties; no green azoic combination or sulphur dye had yet been found. Two years later the synthesis of the water-soluble Indigosol O (S, CI Solubilised Vat Blue 1), the leuco sulphuric ester of indigo, initiated development of a new range of solubilised vat dyes.

An important factor that strongly influenced the demand for direct dyes was the introduction of viscose, the first regenerated cellulosic fibre. The sensitivity of this fibre to caustic alkali (early forms of viscose were particularly low in wet strength) strongly favoured the use of direct dyes rather than Naphtol AS combinations, vat or sulphur dyes. The synthesis of highly substantive direct dyes by the judicious use of key intermediates such as J acid and cyanuric chloride, and of fast-to-light copper-complex types, brought the direct dyes closer to their rivals in terms of fastness performance (and cost). As a result vat dyes in particular showed a decline in demand relative to direct dyes in the 1930s [7].

In wartime conditions, however, the production of long runs in a limited range of colours was given priority. During World War II the United States, in particular, produced large quantities of military uniforms, tents and camouflage materials for the allied war effort. This urgent demand could be met only by the widespread introduction of continuous pad–steam dyeing of cotton fabrics with vat dyes. The increased use of durable resin finishes put more emphasis on fastness standards as an expression of quality. Labelling schemes were adopted and test methods for fastness against a wider range of agencies were developed.

As a result of these changes, by the early 1950s vat dyes had regained much of the predominance that they had attained 30 years earlier. On the verge of the discovery of reactive dyes, the main deficiencies of the anthraquinone vat range were identified as the absence of bright greenish yellows, bright scarlets or reds, and bright turquoise blues and greens [8]. These outer zones of colour space became notable targets for development in the first few years of the era of reactive dyeing. The growth in consumption of reactive dyes has been closely associated with the achievement of high wet fastness in bright, highly saturated colours. The demand for cheap, dull, homogeneous members of the direct, sulphur and vat dye ranges has been least affected by competition from reactive dyes, which are usually applied as trichromatic mixtures when used for the dyeing of subdued tones [9].

The various classes of dyes for cellulose have continued to contend with one another [10,11]. The surge in popularity of blue denim in the mid-1970s drove up the price of indigo until it approached that of alternative blues (e.g. azoic combination or sulphurised vat dye) suitable for this outlet. These competitive products were thus able to take advantage of the world shortage of indigo [12,13]. Alternatively, cheap sulphur blues have been used to ‘top’ indigo dyeings, to minimise the amount of the more costly indigo required to achieve the desired hue [14]. Efforts in recent years to minimise energy costs by operating at shorter liquor ratios have favoured the trends from winch to jet dyeing of knitgoods and from jet or jig to pad–batch processing; this has helped to further the continuing progress of reactive dyes. Azoic combinations and vat dyes have been the main casualties of this growth in demand for reactive dyes. Direct and sulphur dyes continue to dominate the dyeing of cellulose in heavy dull colours, mainly on economic grounds.

The introduction in the 1980s of the Indosol SF (S) range of selected premetallised direct dyes with special cationic aftertreating agents has brought higher standards of all-round fastness within reach of this class [15]. In recent years an exhaust method of applying organic pigments to cotton garments has aroused some interest, although there are recognised limitations of colour yield, levelness, penetration and fastness to rubbing. The process entails prewashing, pretreatment with a cationic polymer, exhaust coloration with the pigment dispersion, stone washing to minimise loose surface deposition, drying and finally thermofixation of the binder. Careful control of the application conditions, notably pH, time and temperature of pretreatment, is essential to achieve reproducible results [16].

8.2 PRINCIPLES OF EVALUATION AND TESTING OF DYES

It is impossible to arrive at a rational selection of dyes without having first examined the available data on them, supplemented where necessary by further screening tests to confirm their suitability for specific conditions of application. Most laboratories in the dyeing industry allocate substantial resources to dye evaluation. This aspect of product assessment is most important for efficient purchasing of materials and cost-effective operation of the dyehouse [17]. The methods employed in product development and standardising control by the dye manufacturer and in screening and quality checks carried out by the user have much in common. Research samples are screened until promising products emerge to justify commercial development. After exhaustive testing they are added to the manufacturing range, and subsequent batches are tested for quality against an initial standard. In a broadly similar way the dye user carries out extensive screening tests on commercial dyes to select those suitable for his or her process, machinery and in-service requirements on the substrate to be dyed. Having selected a small range of dyes to achieve these targets, the user maintains routine checks on deliveries and compares similar products which may be available from several suppliers.

The manufacturer, however, is screening speculative dyes at an incomplete stage of development, whereas the user is testing finished products from a variety of sources. In establishing and maintaining a quality standard the manufacturer must attempt to meet the needs of users operating in widely different sectors of the textile industry, his or her product having to perform satisfactorily within a wide range of exposure conditions. An individual dye user may need to satisfy a much narrower range of machine–substrate–process criteria, enabling closer definition of the preferred selection of dyes for his or her requirements. A laboratory representing a group of dyeing factories, perhaps situated in different countries, may have to make compromises based on local circumstances in evaluating the dyes available and selecting those most suitable for recommended use within the group.

8.2.1 Handling of dyes during manufacture and application

Numerous parameters have to be considered by both manufacturer and user of the product before it is eventually applied to an appropriate substrate for a specific end use. Properties of particular significance during safety testing, manufacture, standardising, transport and ultimate dissolving before use can be regarded broadly as the response of the dye itself, uncomplicated by the presence of the textile material, to its environmental conditions. Health and safety standards are increasingly significant and are particularly relevant to handling of the concentrated product during manufacture and application.

Commercial dyes are marketed at a strength convenient for consistent standardisation and contain diluents, such as electrolytes, solubilising agents or dispersing agents [18]. The presence of manufacturing impurities, by-products, isomers and shading dyes may give rise to slight differences in colour between dyes of the same Colour Index number. The nature and amount of such additives and impurities may have an influence on the dyeing behaviour, so that equivalence of colour content does not necessarily imply similarity of behaviour during application [19,20].

With any hygroscopic material, moisture content is an important commercial factor, since variations in ambient conditions can affect the price–strength relationship for the product. Wide variations in moisture content of disperse dye formulations have been recorded, depending on the prevailing conditions of storage [21,22]. If the moisture content of the dyes is changing during storage, poor reproducibility in batches dyed to the same recipe but at different times may result.

The solubility of ionic dyes in water is a property that is becoming increasingly important as equipment becomes more automated, dyeing cycles are rationalised or streamlined, batch processes are operated at shorter liquor ratios and economic trends favour semi-continuous and smaller-scale continuous methods [23]. Solubility data are often required over a range of temperatures, to take into account the cold-dyeing or warm-dyeing methods advocated in the interests of energy conservation.

Measurement of the aqueous solubility of nonionic dyes is less straightforward, but knowledge of this parameter, together with information on crystal form, particle size and response to dispersing agents [24] can be of a considerable value in interpreting the dyeing behaviour of disperse dyes or vat pigment dispersions. Apart from aqueous solubility, other related properties such as wetting characteristics of the solid dye, and the specific gravity, viscosity and surface tension of the dye solution or dispersion, are of practical significance, particularly when automated dye-dispensing facilities are being considered [25].

Work on physical form has been spurred on by environmental requirements, which favour the greater use of granular or liquid brands owing to their non-dusting properties [26]. Liquids are easy to handle and do not require special methods of dispensing, which can offer advantages in automated colour kitchens [27]. Particular attention has been devoted to the design of plastic containers for products that may suffer from sedimentation. These usually have a much wider opening than normal, so that the contents can be readily stirred.

Every supplier of dyes and chemicals must supply toxicological data on all products offered for sale, including information on techniques for safe handling and on any hazard that might be encountered in use. The need to meet health and safety requirements has had a significant effect on the cost of dyes. The impact of new product legislation is making it increasingly expensive to launch new chemicals on to the market. Hence new dyes are unlikely to be developed unless they make a significant advance on existing products [28].

In the dyeing industry, the main potential hazard is the effect of dye dust on lungs, skin and mucous membranes while dyes are being weighed and handled [29,30]. Much work has been done to eliminate this problem by developing improved physical forms such as non-dusting free-flowing granules, liquid brands and pourable pastes. A minimum test programme has been drawn up to assess safety in handling, and in many firms all dyes undergo the full programme.

8.2.2 Characteristics of dyes in dye–fibre systems

Many further tests must be considered when the decision is taken to use a specific product in a dyeing process and these are all evaluations of the characteristics of the dye–fibre system, rather than of the dye alone. Cost-effectiveness is obviously essential for the user to retain any interest in the manufacturer's product, and the user's customer invariably lays down certain requirements to which the dyed textile must conform. There often has to be a trade-off in properties [31]; a cheap dye may achieve only borderline fastness with difficulty, or it may only be possible to meet severe fastness requirements at the expense of level-dyeing properties.

The degree of levelness is a direct measure of the technical success of the dyeing operation and it is thus not surprising that great attention is paid to the properties of dyes that govern this factor. Interest in rapid-dyeing methods and automatic control systems has encouraged the study of more sophisticated methods of regulating the initial rate of sorption, to shorten the process by eliminating the need for any subsequent migration [32].

Tests to estimate the reactivity of the dye and substrate, and extraction techniques to determine the degree of fixation, are of great importance when attempting to optimise application methods for reactive dyes. The efficiency of cotton preparation can be a vital factor; the reactivity of the dye towards certain impurities may be decisive in limiting the colour yield obtainable on an imperfectly prepared fabric. Tests of the relative dyeability of different substrates, including measures of partition coefficient and saturation uptake, are of considerable practical importance for the design of rational dyeing processes.

Reproducibility problems in dyeing systems can sometimes be attributed to fluctuations in dyebath conditions, because certain dyes show undue sensitivity to such factors as dissolution temperature, pH or reduction potential. Screening tests to assess dye sensitivity are therefore a further aid to dye selection, especially when there is known to be a difficulty in controlling one or more of these variables. In reactive dyeing, control of pH is important for achieving the optimum balance between dye hydrolysis and reaction with cellulose.

8.2.3 Colorimetric techniques of dye selection

Increasing economic pressures have compelled dye users to select dyes with greater care in order to use the minimum number of dyes to obtain the maximum colour gamut, to reduce stocks and to gain from bulk purchasing price concessions. More stringent technical requirements have meant that for certain end uses only a few dyes will meet the defined specification. The adoption of automation and the need for cost-effective processes both favour the use of rationalised small ranges of dyes [33]. The choice of dyes, the determination of the recipe for a particular colour, and the definition of the application procedure and final treatment are the important steps in control of the dyeing process.

There are two commonly used empirical methods of selecting dyes to produce a given colour. One approach is to base most colours on a ternary combination of bright primary dyes and to supplement this by a small range of dyes compatible with the main combination, giving a wide gamut of attainable colours, particularly in depth and brightness. Approximately twelve dyes are required for this approach, which is adopted when cheaper and duller homogeneous dyes are not available for regions of the colour gamut fairly close to the lightness axis, e.g. with reactive dyes. In the second method a dye is chosen close to the colour required and small amounts of shading dyes are added to reach the desired target. This method gives a higher degree of reproducibility of colour from batch to batch, particularly if the concepts of internal primaries and colour mapping are employed. This approach is only possible for dye classes containing a sufficient number of well-spaced homogeneous dyes, such as direct and vat dyes. In an elegant application of this concept, reflectance data were used to construct colour maps, so that dyes in any given area of the gamut form a triangle of internal primaries [34,35].

8.2.4 Dye tests relevant to commercial acceptability of dyed textiles

Many aspects of testing for cost-effectiveness and dye application properties are linked indirectly with the end use of the material to be dyed. It is essential that quality standards for dyed textiles be considered, before any dye screening programme is undertaken to provide guidelines for operating ranges and pass/fail limits in such tests. There are certain in-service requirements, however, of direct relevance to specific dye screening tests: fastness properties are an obvious example, because here the results of generally recognised tests play an important part in determining the commercial acceptability of dyed textiles [36–38].

The degree of dye penetration into the fibre is another property of the dyed material which has a direct bearing on user acceptability, since the appearance and sometimes the fastness properties can vary with differences in penetration. Variations in the dyeability of different yarns within the same batch of material are outside the direct control of the dyer, but they can have a decisive influence on acceptance or rejection by the customer. It is essential to select dyes to give the best possible coverage of such irregularities.

Dyes which promote (or protect against) a loss in strength of the textile substrate during dyeing, or during washing and wearing of the finished garment, pose a further problem, especially if the finished material has marginally acceptable strength. The accelerating effect of certain vat and sulphur dyes on the photodegradation of cotton cellulose has long been known and preventive selection can be made.

8.3 INFLUENCE OF COLOUR AND DYEING PROPERTIES ON SELECTION BETWEEN DYE CLASSES

The advantages and limitations of colour gamut of the various classes have made a major contribution to trends in the development of new dyes, not least in securing a place in the sun for reactive dyes, latecomers to the cellulosic dyeing scene. By definition the azoic dyes are all unsulphonated monoazo or disazo

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pigments when fixed in the fibre. Almost all the direct dyes are disazo or polyazo compounds with two or more sulphonic acid groups. Sulphur and vat dyes, when oxidised to the pigment form in the fibre, are all unsulphonated polycyclic compounds with characteristic disulphide or keto groups respectively. These specific chemical categories impose restrictions on the colour gamut attainable within each dye class. Reactive dyes, however, are subject to no such limitation. The only common feature within this class is the presence of at least one fibre-reactive group. The chromophoric grouping may belong to one of several chemical classes (e.g. monoazo, disazo, metal-complex azo, anthraquinone, formazan, phthalocyanine, triphenodioxazine). This versatility provides scope for attaining the widest possible range of hues.

8.3.1 Colour gamut

Azoic dyes are severely limited in terms of their available range of hues, as are sulphur dyes with regard to attainable level of brightness. Direct dyes and vat dyes offer advantages in both respects, but do not compete with reactive dyes in brightness attainable, except for direct dyes in the bright yellowish red and bright turquoise sectors, where reactive dyes offer better wet fastness.

Azoic combinations cover only the range yellow–orange–red–violet–navy–black, and there are application limitations at both ends of this colour series. Only in the red sector is there real versatility, because practical problems arise when applying azoic components in mixtures. Bright blues and turquoises do not exist and the bright green naphthol is rather costly and lacks substantivity.

The direct range offers a complete circle of hues, but they are duller than reactive dyes in the yellow, bluish red, violet, reddish blue and green sectors. The direct dyes of higher fastness to light, particularly the copper-complex types, tend to be somewhat dull. Reactive dyeings in dull colours are often based on trichromatic combinations of three relatively bright primaries, whereas with direct, vat or sulphur dyes there is a wider choice of dull homogeneous members of these ranges, from which a trio of much duller primaries closer to the target hue can be selected. The risk of unacceptable variations in hue arising from weighing errors is significantly lower in the latter situation, but corrective steps may be easier to carry out with bright primaries. Shading additions made with dull primaries often result in a match for hue that is deeper than the target colour.

Sulphur dyes are restricted to drab colours and especially to cheap blacks. This limitation is attributable to their chemically complex and impure composition. Brighter red, violet and green members of the range are available but they are more costly than the conventional products. Dichromate oxidation gives the best brightness from sulphur dyeings, but also poses the most serious effluent problems [34].

Although they contain impurities, vat dyes are more homogeneous than typical sulphur dyes and encompass a broader gamut of brighter shades. Nevertheless, they lack the vivid brightness of azo chromophores in the greenish yellow, scarlet, red and violet sectors and of phthalocyanine greenish blues and turquoises. The vat dye range is well provided with duller homogeneous members in the central regions of colour space.

Yellow

In general, reactive yellows are more economical than vat yellows. Special naphthols are required for azoic yellows; they are more costly and have lower substantivity than Naphtol AS, so they are only of interest for continuous application. Some sulphur yellows have poor light fastness and some vat yellows (e.g. CI Vat Yellow 2) are only moderate in this respect. Flavanthrone (CI Vat Yellow 1) is phototropic but otherwise exhibits good fastness to light. Certain vat yellows catalyse the phototendering of cellulose during dyeing or on storage of the dyed material [39]. Some greenish yellows (e.g. CI Vat Yellow 2 or 33) promote the catalytic fading of green mixture recipes. Catalytic wet fading imposes restrictions on the selection of direct or reactive dyes in greens; in pale to medium depths certain yellow members of these ranges fade more quickly in the presence of phthalocyanine or triphenodioxazine blues [40].

Orange

Azoic combinations and reactive dyes offer equal brightness in the orange sector; both are more economical and build up better than vat oranges. Certain sulphur and vat oranges exhibit inferior fastness to light. Pyranthrone oranges level well but CI Vat Orange 2 gives a different hue by air oxidation than by chemical treatment, owing to over-oxidation [41]. These dyes (CI Vat Oranges 2 and 9) catalyse the photodegradation of cellulose.

Red and violet

Red is the strongest area for azo dyes. Azoic, direct and reactive dyes all achieve maximum brightness in the scarlet to mid-red sector, where azoics also offer maximum economy. The azoic range is, if anything, over-rich in cheap bright reds. Naphtol AS is the cheapest naphthol, but products are available at various levels of substantivity suitable for either batchwise or continuous methods. Azoic violets on Naphtol AS require special diazo components with low coupling energy.

Direct or reactive reds are more economical and build up better than vat reds; although not as cheap as azoic reds they are easier to apply. Cheap full reds dyed with unmetallised direct dyes have only limited light fastness; duller and bluer hues dyed with after-coppered directs show better fastness. Reactive reds offer better wet fastness and enhanced brightness in the bluish red to violet sector. Certain types of dye–fibre bond are sensitive to acid, alkali or perborate-containing detergents; these defects are often particularly troublesome with bluish reds derived from H acid.

Full-depth reds and violets tend to be difficult and costly with vat dyes (e.g. CI Vat Red 23 requires a special method of dyeing). The oxazole red CI Vat Red 10 has good levelling properties and very good fastness but it catalyses the photodegradation of cotton. Dyeings of isodibenzanthrone violets (CI Vat Violets 1 and 9) can give problems of rubbing and water spotting.

Blue and navy

In the blue sector vat dyes are able to compete with reactive dyes on cost grounds and provide better all-round fastness, although reactives have the edge with brightness in greenish blues and with ease of application. Dark blue azoic combinations are of interest only for continuous application, since the special low-energy components required on Naphtol AS couple particularly slowly. They are fast to peroxide bleaching but have lower fastness to chlorine. The dull reddish blue azo direct dyes build up well to navy depths and are of some interest on cheap outerwear fabrics, where the presence of a durable finish assists in providing adequate fastness. The unmetallised azo blue direct dyes have only borderline light fastness, especially if aftertreated with a cationic fixing agent or crease-resist resin, but the after-coppered types are economical and show generally good fastness [42]. The navy blue and bluish grey region is the most heavily represented in the range of Indosol SF (S) direct dyes, which are selected premetallised copper complexes requiring aftertreatment with a special cationic auxiliary or a mixture of this with a crosslinking resin [15].

Good economy is offered by indanthrone blues (e.g. CI Vat Blue 4, 6 or 14) in bright reddish blues and by violanthrone blues (e.g. CI Vat Blue 19, 20 or 22) in the navy region. They tend to exert a protective effect against photodegradation of cellulose when exposed to sunlight, but some blues show accelerated fading in the presence of the type of yellow (e.g. CI Vat Yellow 1) that promotes phototendering of the fibre. The indanthrone blues are sensitive to hard water, whilst indanthrones and violanthrones may give rub fastness problems in yarn dyeing. The violanthrone navies give only moderate coverage of dead cotton, and when exposed to soda boiling in the presence of cellulose they may suffer from over-reduction, leading to lower fastness ratings in subsequent tests. Nevertheless, vat navy blues are important on sewing thread for both economic and technical reasons; thread intended for swimwear needs the chlorine fastness that these dyes provide.

Finally, the importance of the sulphur blues and sulphurised vat blues at the cheaper end of the market should not be underestimated. Unlike the azoic dark blues they are highly substantive and build up well by exhaust methods [43]. The Hydron blues (sulphurised vats) are applicable with sodium dithionite as reducing agent, give good fastness to light and moderate bleach fastness, and are fast to washing at the boil if aftertreated with an *S*-alkylating agent.

Turquoise

In many ways the turquoise sector is a special case, because the ranges of azoic combinations and sulphur dyes are completely lacking in greenish blues, whilst mixtures of even the brightest vat blues and greens are hopelessly dull in comparison with the direct and reactive turquoises based on the phthalocyanine chromophore. Even here it is really no contest. As a chemical class the sulphonated phthalocyanines tend to aggregate badly, especially in salt solutions, and are prone to solubility problems. With direct dyes the balance between adequate solubility, satisfactory substantivity and build-up, and acceptable wet fastness is particularly critical. Under unfavourable circumstances they show excessive swealing, bleeding and adverse staining in wet treatments [44]. The further degree of freedom attainable by relying on the covalent dye–fibre bond to ensure good wet fastness allows more scope in designing reactive phthalocyanine turquoises with better application characteristics.

The inherent fastness to light of copper phthalocyanine is excellent but, when aftertreated with a cationic fixing agent or a crease-resist resin, direct or reactive dyeings of this type become sensitive to photoreduction, i.e. they tend to show a shift towards violet when exposed to light rich in u.v. radiation. Clearly this problem will be more prevalent with phthalocyanine blue direct dyes, since their moderate wet fastness makes some form of aftertreatment unavoidable. Certain direct and reactive azo yellows are prone to catalytic wet fading in mixtures with phthalocyanine blues, but here again the practical situation favours reactive dyes because of the wide choice of dyes from which satisfactory bright greens can be selected.

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Green

As noted above, really bright greens are possible only with direct or reactive dyes and, in practice, reactive dyes are mainly used because of their superior dyeing and fastness properties. A bright green naphthol is available but it is rather expensive and low in substantivity so it is of little interest except for printing. An olive green naphthol derived from anthracene can be used for exhaust dyeing but it is also somewhat costly. Cheap dull direct greens are important for olive dyeings on knitgoods, but unmetallised direct greens have only moderate fastness to light, especially if aftertreated.

Most green sulphur dyes are dull, but they exhibit good light fastness; some of them break down in the presence of alkaline dithionite [45]. Bright green sulphur dyes derived from phthalocyanine do exist, but they are not widely used because they do not show the economic attractiveness of typical sulphur dyes [6]. Where exceptional brightness is not demanded, vat greens and olives offer a desirable combination of good economy, level dyeing and excellent all-round fastness. Violanthrone greens (e.g. CI Vat Green 1) are necessary for the brighter hues and the acridone or carbazole types for olive greens. Light fastness of these green colours is extremely good, but combinations with phototendering yellows (e.g. CI Vat Yellow 1) should be avoided because of their catalytic effect on the fading rate of certain greens.

Brown

This colour is popular on corduroy, which is usually dyed with sulphur dyes by the one-bath pad–steam process [43]. Fastness to light and washing is satisfactory for civilian requirements, but a military workwear fabric dyed with sulphur brown gave acid tendering problems on storage owing to the prolonged storage times necessary before issue to servicemen. This was replaced by a more durable but more expensive azoic brown-dyed twill, but unfortunately this alternative caused allergy effects among sewing machinists [46]. Brown-shade naphthols have high substantivity for cellulose and are thus intended for batchwise application.

After-coppered direct dyes show economic build-up and good fastness in mode shades [42]. They are particularly useful in browns and greys since reactive dye recipes based on brighter primaries are often more sensitive to dyebath variables [44]. Solubility can be a problem with reddish brown premetallised reactive dyes, resulting in surface deposition in the package dyeing of cotton yarn [47]. Brown vat dyes of the carbazole type are reasonably economical and level well, although CI Vat Brown 3 is sensitive to immature or dead cotton. Their fastness ratings to light, chlorine bleaches and wet treatments are excellent.

Black

This is where sulphur dyes really come into their own. As noted earlier, Sulphur Black T has been manufactured in larger quantities than any other synthetic dye this century. Sulphur blacks are cheap and they have excellent fastness to light. Acid tendering of the dyed cotton on prolonged storage can be a problem, but aftertreatment with an *S*-alkylating agent converts the free thiol groups to the stable alkylthio derivative [43,45]. Conventional application methods are preferred; sulphur blacks give lower yields and poor reproducibility using alkaline dithionite [45]. Most blacks on knitgoods are produced with sulphur dyes. They are also important for black sewing threads; here the yarn is usually protected from strength loss on storage by aftertreatment with a pH buffer and an *S*-alkylating agent [34].

Reactive dyes are second in importance for blacks on cotton knitwear [45]. The largest-selling reactive dye is CI Reactive Black 5, a dark navy rather than a true black. It is a versatile product used as the basis for dull hues generally by most methods of application of reactive dyes; fixation efficiency is good owing to the presence of two vinylsulphone reactive groups, although this type of dye–fibre bond is somewhat sensitive to strong alkali at elevated temperatures. The use of azoic blacks on knitgoods has declined in favour of reactive dyes, which are easier to apply and more versatile. Cheap blacks of moderate fastness on Naphtol AS are dyed continuously with special black diazo components of low coupling energy. Higher fastness is obtained from conventional red diazo components on more expensive black naphthols of high substantivity, which are suitable only for exhaust dyeing.

Grey and black polyazo direct dyes are cheap and easy to apply, but the unmetallised types have only moderate light fastness in general, especially if aftertreated with cationic agents or resins to achieve wet fastness levels acceptable for relatively undemanding end uses. After-coppered direct blacks provide better fastness to light and wet treatments, but the presence of excess copper in the effluent can cause problems [42]. Vat black dyeings based on violanthrone derivatives exhibit excellent fastness to light and wet treatments but may be only moderate in fastness to rubbing and hot pressing. Vat greys and blacks of the acridone type have poor levelling properties but excellent fastness; they tend to exert a protective effect with regard to photodegradation of the dyed fibre.

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8.3.2 Dyeing properties

Exhaustion by cellulose using dyes of high substantivity in the presence of salt is one of the least complicated of all dyeing processes. Typical batchwise processes for reactive dyes go much of the way towards this ideal, but they generally require more salt than direct dyes, as well as alkali to promote fixation with the fibre. Direct dyes, however, although offering a simpler procedure, do not attain adequate wet fastness in full depths without aftertreatment. Even in pale depths there may be limitations with low light fastness or catalytic fading of unmetallised azo dyes, or lack of brightness of copper-complex types, for example.

The need for a more prolonged and complicated washing-off with reactive dyeings is a criticism often levelled against them when compared with direct dyeings [48], but some form of aftertreatment is essential for the latter if they are even to approach the levels of wet fastness attainable with reactive dyes. Cationic aftertreating agents and resin finishes often cause colour changes sufficiently marked to result in difficulties of matching, and light fastness ratings may be lowered by the aftertreatment. Even the carefully selected Indosol SF (S) copper-complex direct dyes require special aftertreatments to compete with reactive dyes in wet fastness performance.

The after-coppering stage is a critical process for those direct dyeings requiring this form of aftertreatment to achieve the desired hue, light fastness and wet fastness. Careful reoxidation and soaping treatments are required to meet similar objectives for batchwise dyeings of vat or sulphur dyes, which also demand careful preliminary reducing processes to convert the insoluble pigment to the alkali-soluble leuco form in which it is applied to the fibre.

In padding processes low-substantivity reactive dyes selected for continuous dyeing normally give no solubility problems even in full depths. They suffer much less from the tailing difficulties characteristic of direct dyes under these conditions. Solubilised derivatives of vat and sulphur dyes, i.e. the vat leuco esters and the *S*-arylthiosulphates (Bunte salts) respectively, show low substantivity for cellulose and perform well in padding applications. Immediately after padding, care must be taken to protect vat leuco ester dyeings from sunlight before they are given an oxidative development to regenerate the insoluble vat dye.

Probably the least attractive classes of dyes for cellulose from the viewpoint of ease of application are the azoic combinations and those direct dyes suitable for diazotisation and development. Diazotisation and coupling are inconvenient processes to carry out under dyehouse conditions; they require careful control for reproducible results. The relatively complicated recipe calculations for azoic dyeings, although made as simple as possible in the technical literature of the manufacturers, are often cited as a drawback [49]. A dyeing of an already diazotised direct dye before development with the coupling component, or a cotton fabric that has been prepared with a naphthol but has not yet been coupled with the selected fast base or salt, are both sensitive to sunlight and give unsatisfactory results if exposed to strong light before development takes place. Difficulty of application is probably the main reason for the marked loss of interest in diazotisable direct dyes nowadays.

Substantivity and build-up

Probably the most decisive feature of a dye for cellulose is its substantivity for the fibre under the preferred conditions of dyeing. This property determines whether the dye will be successful mainly in either batchwise or continuous methods. As the major determinant of build-up properties, substantivity in relation to price has a dominant influence on cost-effectiveness, particularly in batchwise dyeing. Azo dye chemists have developed an impressive degree of control over those aspects of molecular design governing substantivity, notably in the intensive search for more effective reactive dyes of this chemical class.

This approach really began many years ago, when azo chemists working on direct dyes found that by replacing, for example, γ acid by J acid, or phosgene by cyanuric chloride, analogous structures with intrinsically higher substantivity could be obtained. Many empirical rules of this kind were adopted before convincing explanations of the operation of substantivity forces were advanced. Almost by definition, direct dyes have to be high-substantivity products to achieve the desired economy and tolerable wet fastness in full depths, although some dyes introduced for special reasons, e.g. the bright turquoise blues of the sulphonated phthalocyanine type, have only moderate substantivity.

A wider range of substantivity levels is feasible for reactive dyes; these have been classified [50] as shown in Table 8.1.

Many reactive dyes of commercial interest have substantivity factors within the range 40–80%. It could be argued that values above about 80% are too high, since such dyes tend to strike rapidly, migrate with difficulty and wash off slowly. The most successful dyes for exhaust methods often belong to the 60–80% category. Dyes with substantivity values less than 40% are more suitable for padding methods; in exhaust dyeing, especially at long liquor ratios, they give poor yields and reproducibility problems.

Ideally the hydrolysed form of a reactive dye should have low substantivity and rapid diffusion to facilitate washing, but this is not always possible. There is

Table 8.1 Classification of reactive dyes by substantivity

Substantivity factor (%)	Category
>80	Very high substantivity
60–80	High substantivity
40–60	Medium substantivity
<40	Low substantivity

greater scope for this with high-reactivity dyes, since substantivity falls and diffusion coefficient rises as temperature increases. Such a dye will be much less substantive and more mobile during a soaping treatment at the boil than it was in a previous cold-dyeing process in the presence of a high concentration of electrolyte. In long-liquor dyeing processes, however, the best results in terms of yield, build-up and reproducibility are given by high-efficiency dyes of the low-reactivity type [51]. In jet dyeing the advantage of these dyes is less clear-cut. Additions of large amounts of salt to jet dyebaths may be troublesome and more of this is necessary for reactive dyes, especially low-reactivity types, than for direct dyes.

Direct dyes are inherently unsuitable for cold-padding processes owing to their generally high level of substantivity. Reactive dyes are much more versatile in this respect, since products of relatively low substantivity can be selected to minimise tailing problems. Conventional sulphur dyes reduced to the water-soluble leuco form suffer much more than reactive dyes from substantive tailing, but solubilised sulphur dyes of the Bunte salt type are low in substantivity for cellulose and thus of particular interest for continuous dyeing [45].

Vat dyes perform well in continuous processes, either by pigment padding, since the insoluble vat dye has practically no substantivity until reduced at the later chemical padding stage, or in the form of the low-substantivity vat leuco esters, which are particularly suitable for pale depths. Substantivity is much more of a problem for vat dyes in exhaust dyeing. When reduced to the alkaline leuco form, vat dyes are highly substantive and generally give higher exhaustion values than typical direct or reactive dyes. Migration of these polycyclic compounds at normal dyeing temperatures is poor and nonionic retarders are usually added to minimise the initial strike and promote level dyeing. Better migration is possible by dyeing at a higher temperature but there is a risk of over-reduction.

When dyeing with azoic combinations the dyeing process selected often depends primarily on the substantivity of the coupling component, since this is applied first. Only in the red sector do the available naphthols cover the whole range from low to high substantivity. Those naphthols with relatively high substantivity are obviously more suitable for batchwise application, whereas a continuous method is preferable for those with rather low substantivity, including Naphtol AS. Naphthols with an intermediate level of substantivity are less satisfactory for either approach. In batchwise application they require salt addition to promote exhaustion; this often results in inadequate penetration and poor fastness to rubbing. Conversely, in continuous treatment they must be padded at a higher speed and temperature than usual to minimise tailing, but reproducible results are more difficult to attain under these conditions.

It is always difficult and often invidious to try to compare different classes of dyes in terms of value or cost-effectiveness, which is strongly influenced by build-up properties. As already noted, this relationship varies according to the target colour, owing to the chemical types represented in each class and other factors. Furthermore, it is important to take into account differences between the dye classes in terms of process and chemical costs, as well as the cost of the dyes themselves. Nevertheless, it is possible to draw up an approximate order of decreasing cost:

vat leuco esters > vats > reactives > copper-complex directs > azoics and unmetallised directs > sulphurs

and to reiterate some of the differences between these classes that determine why there is a place for all of them. The more desirable characteristics, such as brightness, versatility and fastness, must normally be paid for and no single class has a monopoly of technical excellence.

For example, vat leuco esters offer water solubility, excellent reproducibility and superb fastness, but they do not build up well. Conventional vat dyes are less costly for moderate to full depths, but only in the blue and green sectors do they compete with reactive dyes of the non-azo types. Azo reactive dyes in the yellow to violet sectors are cheaper than vat recipes generally; the chemical costs for reactive dyeing are also lower. Thus in turn the azo reactive dyes in general compete economically with the copper-complex direct dyes, but the reactives usually have technical advantages in terms of brightness, wet fastness and versatility of application. Direct dyes requiring special development treatments are cheaper than these classes in terms of dye cost but they lack reproducibility and process simplicity. Unmetallised direct dyes are cheap to manufacture, easy to apply, but generally poor in fastness properties. Certain formerly important dyes of this kind derived from benzidine have been withdrawn for environmental reasons and replaced by more expensive alternatives. In their strongest suit of full bright reds, azoic combinations are cheaper than direct or reactive recipes, but in other sectors they are less competitive in terms of brightness, cost and ease of application. Sulphur dyes are the most economical of all within their restricted gamut of dull hues, notably for blacks. When dyed continuously they are cheap to apply, but batchwise methods are often troublesome and there are problems of reproducibility and light fastness in pale depths.

Diffusion, levelling and penetration

Since an azoic combination is applied by an ingrain method in which the diazo and coupling components react rapidly together within the fibre to form the azo pigment, problems of poor penetration attributable to slow diffusion are less likely than with a dye from another class, which generally has a relative molecular mass far higher than that of a typical azoic component. Normally, of course, maximum penetration is highly desirable to achieve optimum fastness, but in one process for dark blue colours the opposite effect is preferred. Azoic compositions of the Rapidogen (BAY) type represent an alternative to indigo for the coloration of denim jeans. They can be applied to warp yarns on a simple two-dip sizing machine rather than a much more extensive indigo dyeing range. By avoiding the use of a wetting agent, thus ensuring poor penetration of the azoic components into the yarn, the hue and rub-down characteristics of indigo jeans can be imitated fairly closely [12].

Dyeing problems associated with slow diffusion and poor migration are often encountered with direct dyes because all chromophores represented (e.g. disazo, polyazo, stilbene, metal-complex azo, phthalocyanine, triphenodioxazine) form large molecules that readily aggregate together in salt solution. The levelling properties vary from one sub-class to another, those of lower solubility and higher wet fastness generally requiring careful control by salt addition and sometimes temperature regulation for level results. More rapid diffusion and better levelling are possible in the package dyeing of cotton yarn by raising the dyeing temperature to 100–120°C, rather than the conventional 80–95°C, but the dyes must have adequate chemical stability under these conditions [52]. After-copperable direct dyes require careful control of pH, as well as temperature rise and salt additions, if unlevel results are to be avoided.

High substantivity and slow diffusion behaviour are the two main reasons for the often unsatisfactory performance of direct dyes in continuous dyeing. The former causes tailing problems at the padding stage, and rather long times of fixation are required to attain acceptable penetration and wet fastness, especially on viscose. In the design of reactive dye structures, on the other hand, there is much more freedom to achieve a satisfactory balance between reactivity, substantivity and dyeing method, favouring both level dyeing and very good wet fastness. Selected high-reactivity dyes with relatively low substantivity are especially suitable for low-energy processes such as pad–batch and pad–dry, combining rapid fixation with process reliability.

In the conventional two-stage batchwise dyeing process those reactive dyes that combine low initial substantivity with high fixation efficiency are often prone to unlevel dyeing, owing to the rapid and non-reversible strike taking place on addition of alkali. Certain sulphatoethylsulphone dyes suffer from this fault, since conversion to the active vinylsulphone form lowers the solubility and enhances the substantivity of the reactive dye. Similar difficulties of rapid strike are characteristic of high-substantivity, high-reactivity dyes, if insufficient migration is given before fixation takes place; slow-diffusing, low-reactivity dyes applied at higher temperatures are less troublesome because dye uptake is slower and more uniform.

Nevertheless, the degree of exhaustion of direct and reactive dyes is not too high to permit satisfactory migration and levelling when compared with the highly substantive leuco forms of many sulphur and vat dyes. These strike rapidly and migrate with difficulty at normal dyeing temperatures. A further risk of unlevelness with reduced leuco compounds is the possibility of premature reoxidation at the liquor surface, a major problem frequently encountered with vat or sulphur dyes in winches or partly filled jet and overflow machines.

Solubility and compatibility

Solubility in water is a feature that makes a major contribution to the ease of application of a dye for cellulose. As a rule an increase in relative molecular mass or a decrease in the degree of sulphonation of a direct dye tends to favour substantivity but may well have an adverse effect on solubility, increasing the risk of aggregation and possible precipitation in salt solution. Hard water is undesirable, particularly for the copperable direct dyes. Reactive dye structures offer greater scope for modification to improve the balance between substantivity and solubility. Special care is needed to minimise aggregation, however, when applying low-solubility, high-reactivity dyes in full depths.

Heavy depths of low-solubility direct or reactive dyes in padding processes present similar problems and solubilising agents may have to be used. Machine contamination is much more of a problem for vat or sulphur dyes, however, owing to the insoluble nature of the reoxidised dye that tends to be deposited on the vessel surface at the air–liquor interface. Thus it is difficult to follow dark colours dyed with these dyes on a pad–steam range by lighter or brighter colours [53]. Failure to keep the leuco solution of a vat or sulphur dye sufficiently alkaline, so that the less soluble acid leuco compound is formed, can be a further source of precipitation problems.

The satisfactory application of azoic components depends critically on thorough dissolution before the coupling stage is reached. Naphthols require sufficient alkali to convert them completely to the naphtholate; an alcoholic solvent is often required to ensure good solubility at the padding stage. Insoluble fast bases must be completely transformed into the soluble diazonium compound by the diazotisation reaction. Anionic surfactants must be excluded to avoid coprecipitation with the diazonium ions.

When claims are made for the versatility of azoic dyeing, attention may be drawn to the theoretical possibility of obtaining about 1700 possible combinations from about 50 diazo components and over 30 naphthols [49]. Only a selection from these are of interest with respect to hue and fastness properties. The potential scope for formulating mixtures of intermediate hue is even more restricted in practice. Naphthols vary in substantivity and diazo components differ widely in rate of coupling. It is possible with care to adjust a given Naphtol AS combination by adding another naphthol of good light fastness (e.g. CI Coupling Component 24 or 46), but if only traces are added the light fastness may drop severely [53].

The classifications of direct dyes and vat dyes into sub-classes according to the influence on dyeing behaviour of temperature and chemical additions are well established. These differences complicate the selection of specific combinations on grounds of desirable hue or fastness properties, owing to the difficulty of arriving at a compromise method for mixtures of incompatible dyes drawn from different classes. In the field of reactive dyes there is generally no more variation in dyeing properties between members of a range sharing a common type of reactive group than there is between members of a sub-class of direct or vat dyes. Certain sub-classes of reactive dyes do, however, contain representatives of more than one type of reactive system.

The conventional leuco forms of vat and sulphur dyes vary in substantivity on a scale from moderate to very high; thus incompatible combinations show poor reproducibility in pad dyeing. Not only are all component dyes in a recipe progressively depleted from the bath, so that higher concentrations must be used to replenish them, but these tailing effects are selective and each component must be adjusted individually, or both hue and strength may vary.

Choice of dyeing method

As noted already, the choice between batchwise and continuous application of azoic components is usually determined by the substantivity characteristics of the naphthol, which is normally applied first. Considerations of compatibility seldom arise since these components are usually applied singly. A possible alternative to the conventional two-stage process is to pad with a mixture of the naphtholate and a suitable stabilised diazo component, batch cold for 1–2 h and finally develop with acetic acid to release the diazonium compound and form the azoic dye [43].

Batchwise dyeing methods are much more important than padding processes for direct dyes because of the limitations imposed by solubility, substantivity and diffusion, as discussed above. Careful selection of compatible recipes is important to minimise ending and listing on the jig, but the pad–jig develop method eliminates such problems by ensuring a more uniform initial distribution. Compatible combinations with similar substantivity and diffusion properties at the fixation stage are particularly difficult to find for fully continuous processes.

Unlevel strike, excessive loss of reducing agent, premature reoxidation of the dye and contamination of the interior surfaces of the dyeing vessel are all reasons why winches and partly filled jet machines are far from ideal for the batchwise application of vat or sulphur dyes to knitgoods. With woven fabrics on open jigs listing is often a problem due to cooling and premature reoxidation at the selvedges. Fully enclosed jigs, beams or fully flooded jet machines provide more favourable conditions [52], but semi-continuous and continuous methods are more important for these classes of dyes. The one-bath pad–steam process is the main method of sulphur dyeing [45], e.g. in the dyeing of warp yarns for denim and the piece dyeing of corduroy fabrics.

Pad–steam application of vat dyes is the primary approach for high-quality woven goods, originally established for military fabrics [46]. This process permits a wider selection of compatible dyes than do the batchwise methods. For lengths greater than 2000 m to a colour, the pad–dry–chemical-pad–steam sequence is cheaper than jig dyeing for vat dyes on cotton. When vat leuco esters are chosen, the pad–batch–develop method is more economical than jig dyeing for runs of more than 1500 m, but equivalent cost is not attained by the quicker pad–develop process until batches of more than 5000 m are processed [54].

Reactive dyes are more versatile in application than any other class. All types of batchwise machines and many continuous sequences are available for accommodating numerous relatively simple dyeing methods. Pad–batch processing is more attractive from the viewpoint of energy conservation, capital investment, productivity and simplicity than batchwise or fully continuous methods. The unit cost of dyeing by the pad–batch route is only about 20% of that for conventional winch dyeing, excluding the considerable contribution of dye cost [23]. A comparison that included the cost of the dyes demonstrated that the cost of pad–batch dyeing was 76% of the cost of jet dyeing for a batch of 1000 kg, dyed to a 3% depth with reactive dyes [55].

Pad–batch processing, originally developed for woven fabrics, has made considerable inroads into the knitgoods sector. Taking into account the cost of the dyeing stage only for reactive dyes on wovens, the pad–batch method was more economical than the jig for lengths greater than 1600 m to a colour. If the costs of washing-off were included, the semi-continuous method was favoured and the breakeven point was reached at about 1000 m [54]. The pad–dry process is another alternative for high-reactivity dyes, requiring only simple equipment with low energy requirements, but low-reactivity dyes need a baking or steaming treatment for satisfactory fixation.

Vinylsulphone dyes are not usually recommended for the pad–dry–bake process, owing to their tendency to become deactivated in the presence of urea. Rather than a direct reaction between the dye and urea, this is believed to depend on the thermal decomposition of urea to biuret and ammonia, followed by conversion of the vinylsulphone dye to the inactive aminoethylsulphone [56] (Scheme 8.1). The decomposition of urea during baking can be responsible for another problem; certain reactive dyes that normally show satisfactory fastness to light may be adversely affected under these conditions.

$$2H_2NCONH_2 \rightleftharpoons H_2NCONHCONH_2 + NH_3$$

$$DSO_2CH{=}CH_2 + NH_3 \longrightarrow DSO_2CH_2CH_2NH_2$$

Scheme 8.1

Environmental problems

In recent years the choice of dyes and dyeing processes has been influenced increasingly by ecological and toxicological criteria. Many cheap disazo direct dyes based on benzidine were withdrawn from manufacture and sale by the major manufacturers in the 1970s. Dyes introduced since then as replacements for the benzidine-derived products are generally more costly. Sporadic instances of skin allergy are occasionally reported with certain intermediates or dyes [46] and these may necessitate changes in product formulation or method of application to avoid the risk of exposure.

The handling problems associated with inorganic chemicals used in traditional dyeing processes and the impact of these products on effluent treatment costs have come under increasing scrutiny in recent years. In the field of cellulosic dyeing the simple and relatively innocuous chemicals required for conventional application of direct and reactive dyes are particularly attractive in this respect. Reactive dyes generally require more salt than direct dyes, as well as alkali to promote fixation, but some type of cationic aftertreatment or resin finish is almost obligatory for direct dyeings, to confer adequate wet fastness in moderate and full depths. In general, however, these classes of dyes present few problems with regard to effluent disposal.

After-copperable direct dyes are more troublesome, since the exhaust dyebath contains salt, alkali and relatively unstable unmetallised dyes, whereas the coppering bath contains acid and the excess copper salt, together with some desorbed dye in the form of its copper complex. Azoic components, and the diazotised and developed direct dyes, are unpleasant in use because of the unavoidable evolution of nitrous acid fumes during diazotisation and the strongly alkaline nature of naphtholate solutions. Heavy-metal salts are used to stabilise some of the fast colour salts for azoic dyeing.

Probably the most difficult problems of effluent disposal from cellulosic dyeing processes are met in the batchwise dyeing of vat and sulphur dyes. In the conventional pigment form both classes require reduction with, for example, sodium dithionite or sodium sulphide respectively in strongly alkaline solution, as well as further dosing during the dyeing process to make good any losses of these relatively unstable reducing systems. After dyeing, both classes of leuco compounds must be reoxidised back with peroxy compounds or dichromate solution, followed by prolonged soaping to complete the process. Staining of the internal surfaces of the dyeing vessel by premature oxidation to insoluble dye necessitates regular cleaning with a further strongly alkaline reducing system. All the liquors needed for these various processes present some degree of environmental difficulty during preparation, application or effluent disposal.

8.4 SELECTION BETWEEN DYE CLASSES ACCORDING TO SUBSTRATE AND FASTNESS REQUIREMENTS

The exceptionally good all-round fastness of vat dyeings explains the consistent demand for these products on high-quality cotton materials, in spite of their relatively vulnerable position in terms of cost-effectiveness in a colouristic sense. The outstanding durability of vat-dyed cotton is well illustrated by reference to a showcase fabric of historical interest, which was dyed in 1910 using Indanthren

Blue RS (BASF). This was reported to have been on exhibition and in storage for 60 years without perceptible fading [57] and no doubt it has withstood the further intervening years better than most of us. Even fabrics that have to be subjected to the rough-and-tumble of heavy-duty wear and frequent vigorous laundering cycles, such as vat-dyed workwear, towelling and military clothing, are able to take a great deal of punishment without significant colour loss. Textile damage, such as abrasion and fraying, is much more likely to be the first sign that the material is unable to endure these conditions indefinitely.

None of the other classes of dyes for cellulose can claim this stainless reputation. All show some weaknesses when exposed to certain agencies, although these sensitive areas vary from one class to another. Thus azoic dyes, particularly in their optimum sector of full bright reds, show up reasonably well for fastness to hypochlorite bleaching, although not to kier boiling, where they are liable to bleed. They are often criticised for borderline fastness to rubbing and dry cleaning, and for poor fastness to light at high humidity or in pale depths. Reactive dyes offer satisfactory all-round fastness for many applications but their Achilles heel is their generally low fastness to chlorine bleaching treatments. Sulphur dyes generally rate badly towards this agency too; as a class they are not renowned for durability, particularly in view of the risk of fibre tendering under acidic conditions of storage, yet sulphur blacks and navy blues of the sulphurised vat type stand up well to light and wet treatments, especially if aftertreated.

Few direct dyes will meet all-round fastness requirements even for relatively modest quality standards without aftertreatment [42]. Even during the first decade after their discovery [5], when direct dyes displaced mordant dyes mainly on account of ease of application, dyers were finding that poor wet fastness was the penalty paid for this greater simplicity. Thus direct dyeings tended to gravitate towards the low-quality end of the market. Cheap cotton and later viscose fibres for a price-conscious mass market provided substantial demand, especially in the brighter hues not adequately satisfied by the dull sulphur colours. Viscose-containing furnishing fabrics, curtaining and carpets, where wet fastness demands were less critical than most apparel outlets, have been dyed successfully for many years with fast-to-light direct dyes. Resin finishing of woven fabrics helped to overcome the major fastness limitations of direct dyeings, but on knitgoods, where considerations of softness of handle restrict the usefulness of this approach, reactive dyes have eventually replaced directs except in the least demanding applications.

8.4.1 Light fastness

Outstanding fastness to light and weathering, even in pale depths, is one of the most characteristic features of the vat dye range. Yet this desirable state is not achieved effortlessly; thorough oxidation and soaping is necessary to promote the morphological changes associated with development of the final hue and light fastness of the insoluble vat dye on the fibre. The leuco sulphuric esters are sensitive if exposed to direct illumination on the fibre before acid development to regenerate the parent vat dye. A small minority of vat dyes (e.g. CI Vat Yellow 2, Orange 9 and Blue 1) exhibit only moderate fastness to light, certain yellows (e.g. CI Vat Yellow 2 and 33) catalyse the fading of some blues and greens, and the photodegradation of cellulose is accelerated by certain dyes (e.g. CI Vat Yellow 2, Oranges 2 and 9, and Red 10).

Most of the azoic combinations of practical interest show good to very good fastness to light, if exposed in full depths under dry conditions. Unfortunately this stability declines more sharply with increasing humidity or decreasing depth than for dyeings of any other class of cellulosic dyes. Cotton fabric that has been prepared with a naphtholate solution but not yet developed in a solution of the diazo component is fugitive to light, even though the dye formed on coupling may be fully satisfactory in this respect.

The light fastness of reactive dyes ranges from moderate to very good, depending on hue and chemical class, but these dyeings are much less sensitive than azoic dyeings to applied depth or humidity conditions during exposure. Not all members of this class are acceptable for all applications; the general standard is adequate for cotton dressgoods, but careful selection is needed for a wide gamut on cotton furnishings [58]. Although reactive dyes of the anthraquinone, formazan, phthalocyanine and metal-complex azo sub-classes are comparable with the premetallised direct dyes in this respect, some of the unmetallised azo directs and reactives show deficiencies, especially if aftertreated with certain cationic fixing agents.

Copper-complex directs and reactives usually hold their light fastness reasonably well in pale depths, but their duller hues tend to be less attractive for this purpose. After-coppered directs, and even more so the unmetallised directs, afford only moderate light fastness in many cases. Direct dyeings often require a cationic agent or resin treatment for adequate wet fastness and these products usually have an adverse influence on light fastness.

Sulphur blacks have excellent light fastness and most blues and olive greens are reasonably good; only in the yellow to orange sector do some sulphur dyes have poor light fastness. Dichromate oxidation is preferred for optimum brightness and fastness. Light fastness in pale depths is frequently inadequate but this is not a serious drawback in practice, because dullness and poor reproducibility make these depths unattractive for sulphur dyeing [59].

Summarising these comments on light fastness, the following approximate order of decreasing stability is arrived at:

vats and vat leuco esters > reactives and premetallised directs > after-coppered directs, azoics and sulphurs > unmetallised directs

Azoics and sulphurs fare reasonably well in practice relative to their position in this series since their major consumption is in heavy reds and blacks respectively, with virtually no interest in them for pale depths. On the other hand, directs, reactives and vats all have to meet the more demanding criteria of pastel dyeings as well as moderate to full depths.

8.4.2 Wet fastness

This is the most difficult area to generalise about the relative performance of different classes of cellulosic dyes. Not only are there considerable differences between individual members of a range and for the same dye on different cellulosic substrates in a given test, but the results depend considerably on the methods selected for dyeing, washing-off and subsequent aftertreatments, including durable finishing. Numerous wet fastness tests of various degrees of severity are available. In the field of washing fastness in particular, traditional 'soap and soda' tests are less meaningful than more recently developed tests that are representative of actual laundering practice [15]. Nevertheless it is possible to distinguish some qualitative trends and to arrive at an approximate ranking for purposes of discussion.

As with most fastness criteria, vat dyeings provide the quality standard against which other ranges are judged. They show very good to excellent fastness, even in severe washing tests at the boil; they are particularly resistant in blues, greens and heavy dull colours generally. Indigo has only moderate fastness to washing but it bleeds and fades on tone, a valuable characteristic for the special requirements of blue denim. Only in one respect can vat dyes be criticised relative to reactive dyes in severe wet tests: they do tend to stain adjacent synthetic-polymer fibres.

If properly soaped-off after dyeing to eliminate any loosely held pigment, azoic dyeings exhibit very good fastness to water, perspiration and washing at the boil. Like vat dyes, they are important for incorporation as coloured effect yarns in woven designs because they are fast to subsequent bleaching and mercerising of such fabrics, although they may bleed if kier boiled. As a class, reactive dyes cannot be considered for this purpose.

This limitation apart, reactive dyes achieve excellent wet fastness if given an effective washing-off to eliminate the unfixed dye. They are almost completely free from cross-staining problems. The dye–fibre bond formed by dyes that react by a substitution mechanism (e.g. halopyrimidines and halotriazines) is at its most stable in the pH range 6–7, so dyeings of more reactive ranges in this category may show sensitivity to certain tests carried out under mildly acidic conditions, if not protected by a suitable aftertreatment with an amine. Reactive dyes that react with cellulose by an addition mechanism (e.g. vinylsulphones) form cellulose ether-type bonds and these show maximum stability at about pH 4–5. Consequently the fastness of such dyes to severe alkaline washing treatments at elevated temperatures is moderate to poor, owing to alkaline hydrolysis of the dye–fibre bond [56]. Most dyes of the aminohaloheterocyclic category, on the other hand, rival vat dyes in their fastness to severe washing at the boil. Although reactive dyes are not fast to hypochlorite bleaching in general, products can be selected with satisfactory fastness to chlorinated water for swimwear. Many of the aminohaloheterocyclic dyes are sufficiently stable on the fibre for post-bleaching with hydrogen peroxide [50]. The high level of fastness to perspiration of reactive dyes has favoured their selection for the growth area of knitted leisurewear and sportswear garments [60].

Sulphur dyeings are moderately fast to washing and perspiration, but they fail to withstand repeated severe laundering at temperatures much above 60°C [43]. The sulphurised vat dyes provide navy blues with generally better wet fastness than the majority of conventional sulphur colours, especially after a stabilising aftertreatment.

Inferior wet fastness is undoubtedly the chief cause of the ‘sub-standard’ reputation of direct dyes. Their history has seen many attempts, none of them completely successful, to overcome this primary deficiency. The most radical approach was that of diazotisation and development, but this brought other drawbacks in its wake. Dyes in this sub-class often show better fastness to scouring and acid cross-dyeing than many conventional disazo types. Most copper-complex and after-coppered dyeings are reasonably fast to washing, by direct dye standards, but there is a risk of demetallisation causing hue changes in acid perspiration tests. Cationic aftertreatment provides some improvement in wet fastness, however, and the development of specialised agents and crosslinking reactants for use with selected copper-complex Indosol SF (S) dyes has enabled more effective competition with reactive dyes in meeting severe washing criteria [15,61].

The early disazo direct dyes made a disastrous start in terms of sensitivity to wet treatments. Self-levelling class A direct dyes bleed and stain even in cold wet tests. After resin finishing they show only a modest improvement. With borderline acceptability in moderate to full depths, such dyes can be considered only for the least demanding of applications.

In spite of the pitfalls implicit in drawing general conclusions about the relative wet fastness of dye classes on cellulose, the following order of decreasing fastness may be suggested:

vats and vat leuco esters > azoics > reactives and sulphurised vats > sulphurs and premetallised directs > unmetallised directs

These rankings are based on overall response to a multitude of tests (washing at various temperatures, acid and alkaline perspiration, water and so on), but the relative positions vary in regard to specific tests. This is particularly evident for washing in the presence of peroxy compounds, e.g. sodium perborate.

Vat dyes do not exhibit any significant problems with regard to detergent–perborate tests. Most reactive dyes are satisfactory in general, but the halotriazine sub-classes are superior to the chlorodifluoropyrimidines and dichloroquinoxalines. Certain of the vinylsulphone dyes also show sensitivity. As a class, azoic dyeings are inadequate to most tests of this kind. Sulphur dyes likewise show poor fastness, but thioalkyl stabilisation confers a marked improvement [43]. After-coppered direct dyeings are not fast to detergent-perborate washing and even premetallised copper complexes (direct and reactive) tend to be somewhat sensitive. To temper the ratings of azoic and direct dyes in the above series, therefore, the modified list below may be taken as representative of approximate fastness to detergents containing peroxy compounds:

vats and vat leuco esters > reactives and sulphurised vats > azoics and sulphurs > premetallised directs > unmetallised directs

8.4.3 Fastness to bleaching

Response to this criterion is more specific. It is simply the relative resistance of typical members of the various ranges to conventional cotton bleaching routines, essentially based on powerful oxidants: chlorite, hypochlorite or peroxide. Most azoic and vat dyes are highly rated. The azoic blues and the indanthrone vat blues (especially CI Vat Blues 4 and 14) will withstand peroxide but show inferior fastness to the chlorine bleaches. Indigo bleaches on tone with hypochlorite, another feature exploited to change the appearance of denim garments. Direct, reactive and sulphur dyes generally put up only token resistance to bleaching agents, although sulphurised vat navies have moderate fastness and selected reactive dyeings will withstand chlorinated swimming pools or laundering baths containing modest hypochlorite additions [62]. The differences noted above many be expressed in the following rankings:

vats and vat leuco esters > azoics > sulphurised vats > reactives > sulphurs > directs

8.4.4 Fastness to rubbing

This is another area in which hard and fast conclusions cannot be easily drawn. Fastness to wet and dry rubbing is tested by well-defined procedures and high ratings are not ambiguous. Unfortunately unless the complete dyeing process including washing-off and drying stages is carried out most carefully, reproducible and meaningful performance will be difficult to maintain. With the more vulnerable dye classes under unfavourable circumstances (e.g. package dyeing of yarn) these problems can be just as troublesome as for disperse dyeings on polyester.

Vat leuco esters are seldom if ever concerned in problems associated with this agency. For economic reasons their use is restricted essentially to pale depths, where adverse rub fastness results are rare. All fastness ratings vary with applied depth, but this dependence can be relatively acute for rubbing tests. It should also be borne in mind that chemically degraded cellulosic fibres may suffer abrasion and transfer of coloured fibrous debris. This can give the illusion of poor rubbing fastness even if the actual dye–substrate forces remain strong [63].

Self-levelling class A direct dyes tend to have good solubility in salt solution and to show highly satisfactory fastness to rubbing even in full depths. Virtually complete freedom of reactive dyeings from the rub fastness problems characteristic of many azoic colours has been a major factor in the displacement of azoic by reactive recipes [44]. Typical class C direct dyes and certain reactive dyes with only moderate solubility in electrolyte solutions, such as the phthalocyanine turquoises, may exhibit borderline performance, especially in wet rubbing tests, if not properly washed off and aftertreated where necessary in full depths. Copper-complex azo direct and reactive dyes are prone to rubbing [47], especially if hard water is present, and copperable direct dyeings suffer badly if not rinsed thoroughly before application of the copper salt.

The fastness to rubbing of typical sulphur dyeings leaves much to be desired [42]; it is often much inferior to reactive dyeings of comparable depth. A thorough wash of a sulphur dyeing before reoxidation may help (although more wasteful in dye usage and process time) but wet abrasion arising from dye-catalysed acid tendering of the cellulose may, in due course, aggravate a wet rub fastness problem. Except on blue jeans, where poor penetration of indigo is a virtue rather than a vice, vat dyes are always capable of yielding unacceptably poor fastness to rubbing in full depths, especially with batchwise-dyed fabrics. Failure to reduce fully while vatting, excessive loss of reducing agent causing premature reoxidation, lowering of the pH with formation of the less soluble acid leuco compound, or insufficient attention to the effectiveness of reoxidation and soaping stages are all potential sources of surface deposition and inadequate rub fastness [64].

Azoic dyeings, almost entirely confined nowadays to heavy depths, are often problematical, usually in respect of wet rubbing and difficulties of mark-off onto adjacent materials. The level of fastness achieved depends on the process and substrate; careful control of the diazotisation, coupling and washing-off stages is essential. Naphthols of intermediate substantivity need special attention since they require more salt for exhaustion than do the high-substantivity products, whereas in continuous dyeing they must be padded under relatively adverse conditions to minimise tailing. It is difficult to remove deposits of unfixed azoic pigment from package-dyed yarn at the soaping stage [34,47]. Slow and gentle drying is crucial or poor rub fastness may develop, even at this late stage, by thermal migration [53].

An approximate series in terms of fastness to rubbing may be represented as follows:

vat leuco esters > unmetallised directs and reactives > premetallised directs and reactives > sulphurs and vats > after-coppered directs > azoics

This series should be interpreted, like the results of rub fastness tests, with great care. It is intended to represent the increasing likelihood of encountering a rub fastness problem in the series from vat leuco esters to azoics. The fact should be borne in mind that azoic dyeings are often criticised on these grounds, but they are almost always met with in heavy depths. Vat and sulphur dyeings at comparable depths tend to rub badly too. Conversely, vat leuco esters are prohibitively expensive at depths where they might be expected to show this defect. Heavy depths of direct and reactive dyes, if processed and washed-off carelessly or inadequately, may well fail for poor wet rubbing [43].

8.4.5 Response to dry cleaning and resin finishing

Direct, reactive and sulphur dyes [43] all exhibit very good fastness to dry cleaning, significantly better than some vat dyes. Azoic dyeings have only moderate fastness to this agency [44]; as in the case of rubbing tests, the level of performance achieved depends considerably on the conditions of application, rinsing, soaping and drying of the dyed material. Many vat dyes are sensitive to the selective stain removal agents often applied by spotting techniques before dry cleaning; more or less pronounced changes in hue may occur where the cleaning agent has been applied [65].

Sensitivity to resin finishing is much more a problem for direct and reactive dyeings than for azoics and vats, which are scarcely affected at all in hue or light fastness. The acidic conditions of resin fixation have a favourable influence on the subsequent wet fastness of sulphur dyeings; melamine–formaldehyde finishes in particular tend to enhance their fastness to bleaching. Most reactive dyes show perceptible changes in hue and sometimes lower light fastness after resin finishing. The effect on wet fastness is generally good, especially for dyeings on viscose. Few reactive dyeings bleed significantly in resin pad liquors, providing they have been washed off effectively after dyeing.

Direct dyeings are more sensitive to resin finishing than any other class. Fluctuations in hue and decreases in light fastness are of a similar order to reactive dyeings. The beneficial influence on wet fastness is much more striking, however, because of the markedly lower level shown by the untreated direct dyeing.

8.4.6 Response to different types of cellulosic substrate

The relative importance of the various classes of dyes for cellulose differs according to the type of fibre to be dyed. Special dyeing procedures are necessary for applying vat dyes to flax yarns and to tightly twisted mercerised cotton yarns in order to ensure satisfactory penetration. Caustic alkali is essential for dissolving naphthols and in the reduction of vat and sulphur dyes to their leuco compounds; viscose and linen fibres are more readily attacked by hot alkali than is cotton, so the use of direct and reactive dyes for these fibres is favoured. Nevertheless, to meet the highest standards of fastness, substantial quantities of vat dyes have been used successfully on viscose.

Reactive dyes are sufficiently versatile to adapt to the special requirements of such substrates without difficulty. Improved penetration of high-twist yarns is achieved using low-reactivity dyes at 80°C or above. Certain mercerised fabrics benefit from the slower rate of fixation in the long-batch (bicarbonate) variant of the pad–batch process for high-reactivity dyes, which is also a satisfactory technique for viscose. Reactive dyes diffuse readily in the pad–batch dyeing of woven linen, but the impurities present may cause off-tone or speckled effects in some instances. Transfer of recipes between these various substrates requires calibration; for a given visual depth, more dye is required on unmercerised than on mercerised cotton, whereas viscose usually needs less than mercerised cotton.

Viscose is the cellulosic fibre most suited to direct dyeing. Many textile fabrics made from short-staple cotton or viscose are cheap to manufacture and need to meet only moderate wet fastness criteria. Care in dye selection and choice of a suitable dyeing procedure is especially important for optimum results on viscose. It may be necessary to buffer the dyebath with ammonium sulphate to avoid alkaline reduction of unmetallised disazo direct dyes during the dyeing of viscose. The premetallised copper-complex types are more stable in this respect and have higher light fastness.

8.4.7 Dye selection for yarn dyeing

Typical data for dye consumption on cotton yarn and loose fibre [66] showed the following distribution: vats 42%, reactives 22%, directs 20%, sulphurs 11%, azoics 5%. Virtually all of this consumption was for batchwise dyeing. Colour fastness is particularly important for yarn as the ultimate requirements are more difficult to define than for piece-dyed goods. The vat dyeing process is easier to control in yarn package dyeing than in many fabric-dyeing machines [66]. The cost-effectiveness of vat dyes is often more favourable than reactive dyes in the dark blue and green sector, and the fastness of vat dyes to severe washing and bleaching is valuable for sewing thread dyeing [34,47]. Reactive dyes are important for bright colours on yarn, including greenish yellow, orange, turquoise and bright green. Azoic combinations are virtually limited to bright reds based on high-substantivity naphthols and rapid-coupling diazo components [43], whereas sulphur dyes are mainly for aftertreated blacks [34]. Direct dye use is mostly confined to viscose and short-staple cotton yarns.

In sharp contrast to the conventional yarn dyeing sector, relatively low fastness to light, washing, rubbing and bleaching is regarded as acceptable in the dyeing of warp yarns for blue denim manufacture. This derives from the traditional selection for this purpose of indigo, which fades on tone to all these agencies. Since the application requires multiple dips and oxidation steps to attain the desired hue, indigo warp sizing ranges are costly to install and viable only for large-volume production [12]. The main alternative to this approach is the one-bath pad–steam process with sulphurised vat dyes [43,45]. Most denim warps not dyed with indigo or sulphurised vats are dyed with azoics at the sizing stage. Stabilised azoic compositions are suitable for the one-bath combined dyeing and sizing process if an acid-stable size is used; they require only a simple two-trough sizing machine and are thus more appropriate for small-volume producers [12], since the capital expenditure required is low. An alternative approach is to apply a naphthol from an alkaline size bath, dry, weave and then develop in fast salt solution after weaving. Problems associated with this technique, however, are dusting of naphtholate during weaving, water-spotting of the naphthol-prepared warp yarns and cross-staining of the white weft during development.

8.4.8 Dye selection for knitted fabrics

Typical data for dye consumption on knitted fabrics [66] are: reactives 71%, vats 13%, directs 12%, sulphurs 3%, azoics 1%. Exhaust dyeing on winches and jets is the most important technique for knitgoods; these conditions are especially favourable for reactive dyeing. These dyes offer a wide range of bright colours at fastness levels that are satisfactory for high-quality dressgoods and leisurewear. The dyeing temperature appropriate for low-reactivity dyes ensures good running properties and level dyeing in jet and winches. The harshness of handle associated with after-coppered direct dyeings on knitwear is avoided. Reactive dyes in most cases have sufficient fastness to chlorinated water for use in swimwear [58] and sewing thread [47] for these garments. Careful selection for green mixtures on swimwear and towelling is essential owing to the risk of catalytic wet fading of certain azo yellows by phthalocyanine or triphenodioxazine blues.

Before the advent of reactive dyes, direct dyes were well established on knitgoods and even in the early 1970s they were still widely used in winch dyeing. Premetallised copper-complex types provided satisfactory light fastness for pale-depth fashion colours and cheaper copperable or diazotisable direct dyes gave moderate wet fastness in fuller depths, but these recipes became increasingly vulnerable to competition from reactive dyes. Two trends that favoured reactive dyes were the adoption of more realistic wet fastness criteria [15], and the replacement of some winch dyeing capacity by jet machines and pad–batch units in the interests of energy conservation [60]. Resin finishing is not usually favoured on knitgoods owing to the unattractive handle obtained; this limits the scope of aftertreatment to enhance the wet fastness of direct dyes. Nevertheless there will always be a residual demand for cheap fabrics coloured with direct dyes, mainly for reasons of economy, e.g. viscose linings, cheap underwear and dressing gowns, toy covers and dusters [44].

There used to be significantly more activity in winch dyeing of knitted fabrics with vat dyes [44], but premature oxidation problems limited their usefulness under these conditions [43]. Recommendations for the jet dyeing of tubular knitgoods with vat dyes have been given [67]. Sulphur dyes are also of interest here, mainly for cheap blacks and other sombre hues [68]. High-substantivity red naphthols retain a marginal share of the knitgoods market, notably on terry towelling, since they will withstand severe washing in the presence of hypochlorite.

8.4.9 Dye selection for woven fabrics

The dyeing of woven cellulosic materials is dominated by the cheaper ranges of dyes, although certain high-quality articles demand the better fastness properties attainable with reactive and vat dyes. Thus typical data for dye consumption on woven fabrics [66] showed the following breakdown: directs 30%, sulphurs 29%, reactives 21%, vats 17%, azoics 3%. Continuous dyeing methods (vat leuco esters in pale depths and conventional vat dyes in medium to full colours) are especially important for high-quality cotton poplin shirtings. The pad–steam route has remained the standard process for the almost exclusive selection of vat dyes for military uniforms, which require exceptional durability to light, weathering and severe laundering, as well as colour constancy over prolonged periods of storage and use. Equally demanding in terms of practical exposure to light and weathering are awnings and tents. Furnishing fabrics occupy another major area of interest for vat dyeing, although many curtain fabrics are dyed with selected reactive or premetallised direct dyes.

Workwear too demands good fastness to light and exceptional resistance to repeated severe laundering since the vigorous removal of obstinate stains and soiling is an occupational hazard for such fabrics. Vat and sulphurised vat dyes are widely established in this field. Not quite so demanding are corduroys and velveteens, the traditional fabrics dominated by sulphur dyes (approximately 70% of the available market), applied by the one-bath pad–steam method [45,53]. There were attempts to promote corduroy, dyed pad–batch with reactive dyes or continuously with vat leuco esters in pale depths, as a fashion fabric [53]. Cheaper qualities have been jig dyed with azoic combinations but it is easy to run into problems of poor fastness to rubbing and wet treatments on pile fabrics of this kind [69].

Outerwear, rainwear and fabrics for subsequent coating or laminating present suitable opportunities for the selection of premetallised directs and reactives with above-average fastness to light. Direct dyes have been used traditionally in those domestic textiles where wash fastness is not critical, including bedspreads, curtains and tufted floor coverings, as well as sleepwear and low-cost leisure clothing. The application of a crease-resist resin or water-repellent finish after dyeing has a markedly favourable influence on the degree of wet fastness attainable with direct dyes in full depths. To some extent the bond between a reactive dye and the fibre is also protected from hydrolytic attack by the presence of a hydrophobic finish. Nevertheless, producers of high-quality outerwear may choose the more expensive vats or vat leuco esters, so that they do not have to rely too much on the stability of the polymeric finish to provide durability of the coloured effect.

One field of application in which sulphur and vat dyes are definitely undesirable is the dyeing of woven fabrics for discharge printing. Until the discovery of reactive dyes, azoic components were popular with printers for their versatility in printing styles. As they are readily dischargeable they came to be widely used as dyed grounds for discharge styles as well. The economy and simplicity of the pad–batch process of reactive dyeing, however, as well as the sensitivity of vinylsulphone dyeings to the print (alkaline discharge)–steam treatment [56], have captured a great deal of this business. Reactive dyes have also replaced direct-dyed grounds for colours not obtainable with azoic components. Readily dischargeable unmetallised direct dyes tend to have low wet fastness, and reactive dyes are usually brighter and more readily dischargeable than the copper-complex types.

8.5 FACTORS GOVERNING CHOICE BETWEEN SUB-CLASSES WITHIN THE MAJOR DYE CLASSES

All classes of dyes for cellulosic dyeing may be further subdivided, the differentiation being based mainly on dyeing properties (Table 8.2). An alternative approach would be to subdivide each dyeing class according to the chemical classification of dye structures, as used in the Colour Index. However, as noted already in relation to the limitations of colour gamut, each of these dyeing classes except reactive dyes is dominated by one main chemical class, so this approach would be much less useful in practice.

Table 8.2 Basis of sub-division of dye classes

Dye class	Basis of sub-classification
Reactive	Reactivity and dyeing temperature
Direct	Substantivity and dyeing rate
Vat	Substantivity and dyeing temperature
Sulphur	Substantivity and solubility
Azoic	Substantivity and coupling rate

8.5.1 Reactive dyes

The obvious basis for sub-classification of monofunctional reactive dyes is in terms of the relative reactivities of their characteristic reactive systems. Comments have already been made in the above discussion on the behaviour of specific ranges, where this is markedly non-typical of reactive dyes in general. The relative reactivities of the major systems in descending order, together with typical values of fixation temperature under moderately alkaline conditions in batchwise dyeing are as follows:

dichlorotriazine (30°C) > chlorodifluoropyrimidine (40°C) > dichloroquinoxaline and aminofluorotriazine (50°C) > vinylsulphone and vinylsulphonamide (60°C) > aminonicotinotriazine (70°C) > aminochlorotriazine (80°C) > dichloro- and trichloro-pyrimidine (95°C)

This series corresponds reasonably well with the relative reactivities of the various commercial ranges, but it should be noted that more than one type of reactive system is represented in some ranges.

A general classification of these reactive dye types has been formulated recently [70], in an attempt to simplify the relationship between them. Three groups related to the most important control parameters have been defined:

Group 1 Alkali-controllable reactive dyes – these have low inherent substantivity, fixation temperatures of 40–60°C and high reactivity that necessitates care in addition of alkali.

Group 2 Salt-controllable reactive dyes – these are more substantive, require care with salt addition, react more slowly and are fixed at 80–100°C.

Group 3 Temperature-controllable reactive dyes – these have self-levelling characteristics, do not require alkali for fixation, are intermediate in reactivity and respond to control by temperature rise.

On the other hand, it may be necessary to take account of differences in dyeing characteristics by even more subdivision. Thus the Remazol (HOE) vinylsulphone dyes may be placed in four categories based on differences in substantivity, and hence various conditions of fixation pH and temperature are possible to optimise yield and levelling properties. Complicated recommendations are necessary for the Levafix E, E-A and E-N (BAY) moderate-reactivity dyes, in which four different reactive systems are represented. These dyes have been classified into nine groups depending on their substantivity (low–medium–high) and reactivity (low–medium–high) ratings. An appropriate dyeing procedure is chosen, either a conventional two-stage sequence at 40, 50 or 60°C, or an addition of alkali (0.5–2 g l^{-1} sodium carbonate) to pre-sharpen the dyebath before dyeing at 40 or 50°C. The pre-sharpening technique is adopted for dyes with low–medium substantivity and medium–high reactivity in order to minimise the risk of unlevel dyeing.

The fixation temperatures quoted in the above series for moderately alkaline conditions are thus only approximate and intended for purposes of overall comparison. It may be desirable to exhaust at a lower temperature to enhance substantivity or a higher temperature to promote migration before adding alkali at the optimum temperature of fixation. Applying a high-reactivity dye at a temperature above the optimum, however, results in loss of yield owing to premature hydrolysis of the dye before exhaustion is complete. For easy washing-off, low substantivity and rapid diffusion at the washing stage are desirable. Since substantivity falls as temperature increases, the high-reactivity dyes exhaust well at 30–40°C but are usually relatively low in substantivity during washing-off at the boil, especially after the electrolytes have been removed. Listing problems in jig dyeing are less likely for high-reactivity dyes because cooling of the selvedges is less serious at 30–40°C than at 80–90°C. Short batching times in pad–batch dyeing are an attractive feature of high-reactivity dyes, but pad liquor stability is correspondingly more critical.

Low-reactivity dyes, on the other hand, benefit from the rapid diffusion and effective migration that are possible at relatively high dyeing temperatures; knitted fabrics dyed in this way show good running properties in winches and jets. Most fabrics can be dyed level with good penetration of high-twist yarns and densely woven fabric constructions. Low-reactivity dyes often show outstanding reproducibility and to a considerable extent they are able to cover minor differences in pretreatment history [51]. Dyes of this type have been criticised on grounds of higher energy consumption, but this is misleading. When dyeing knitted cotton at 40°C on a jet machine the cost of steam consumed in the dyeing stage is only about 4% of the total steam cost for the full process, and even at 80°C the steam cost is only 12%. If considered as a proportion of the total process costs, steam for dyeing amounts to only 0.3–4%, depending mainly on temperature, so that differences between the methods in this respect can be neglected for all practical purposes [71].

It is true that the difference in substantivity between that at the optimum dyeing temperature and that during soaping at the boil is less marked for low- than for high-reactivity dyes, but washing-off behaviour is not impaired if the liquor interchange is adequate for efficient dilution of the residual electrolyte in the system. Low-reactivity dyes are more prone to listing on the jig as a result of inadequate fixation close to the cooler selvedges of the fabric. The need for longer batching times in the pad–batch process, however, is offset by the much superior stability of low-reactivity dyes in alkaline pad baths at ambient temperature.

Symmetrical reactive dye structures with two identical reactive groups, such as the Procion H-E (Zeneca) dyes containing two aminochlorotriazine groups per molecule, provide scope for designing products with better compatibility, more reproducible exhaustion and high fixation efficiency [50]. One of the earliest, but still the most important, of the vinylsulphone dyes, CI Reactive Black 5, contains two sulphatoethylsulphone precursor groups per molecule. More recently, bifunctional reactive dyes with two dissimilar reactive groups have been introduced. These are capable of reacting with cellulose by two different mechanisms, nucleophilic substitution and nucleophilic addition. In both systems the ring imino substituent in an iminohalotriazine dye carries a 2-sulphatoethylsulphone grouping. The halo substituent can be either chlorine, as in the Sumifix Supra (NSK) range, or the more reactive fluorine, as in the Cibacron C (CGY) range.

In general, the rate of fading of reactive dyeings is directly related to the strength of the dye–substrate bond [72]. The stability of the bonds formed by the reaction of aminohalotriazine dyes with cellulose is exceptionally good. The level of fastness to alkaline washing at the boil achieved by these dyes is difficult to reach with other ranges of reactive dyes [50,51]. Vinylsulphone dyes, on the other hand, exhibit poor fastness to severe alkaline washing [56] because the dye–fibre bond in this case is labile to alkaline hydrolysis at temperatures above about 70°C. A thorough rinsing in dilute acid is essential before soaping of dyeings of vinylsulphone dyes, but this is neither necessary not desirable for dyes of the haloheterocyclic types.

In contrast to vinylsulphone dyes, high-reactivity dyes of the dichlorotriazine or dichloroquinoxaline types form dye–fibre bonds that are somewhat sensitive to hydrolysis under mildly acidic conditions. If such dyeings are delayed for a prolonged period in the wet state before drying, or if damp fabric containing these dyes is exposed to an industrial atmosphere during storage, there is a risk that lower wet fastness will be observed, e.g. in subsequent perspiration tests [56]. This phenomenon is believed to arise by protonation of the oxygen atom linking the heterocyclic ring to cellulose, followed by hydrolysis [73]; the degree of sensitivity to acid hydrolysis varies from dye to dye, depending on the degree of activation of the oxygen atom by other substituents in the vicinity of the heterocyclic ring, which may favour or hinder protonation. Highly reactive red dyes derived from H acid often show this fault; the problem can be minimised by aftertreatment with a suitable primary amine, or preferably an oligomeric compound containing several amino groups. These agents are able to react with any residual activated chloro substituents on the heterocyclic ring of the fixed dye molecule, thereby decreasing the sensitivity of the dye–fibre bond to possible protonation and hydrolysis [44].

Unusual fastness problems were observed with dyes of the chlorodifluoropyrimidine type shortly after their introduction. Dyeings that had been fast to washing deteriorated badly in performance when laundered with a detergent containing perborate (or given a cold steeping treatment in such a solution) and then exposed to sunlight. No immediate effect was observed at this stage, but if subsequently laundered again or simply rinsed in warm water, the dye–fibre bonds in areas exposed to light were found to be no longer effective, since considerable bleeding occurred immediately. Certain dyes of the dichloroquinoxaline and vinylsulphone types were also found to be somewhat sensitive, but dyes of the halotriazine sub-classes were generally satisfactory for resistance to these combined agencies. The mechanism of this sensitivity of 5-chloro-2,4-difluoropyrimidine dyes has now been elucidated [74]. The perborate anion acts as a donor of the perhydroxide anion, which is capable of displacing the 5-chloro substituent, even if both fluorine atoms have been already lost by hydrolysis and reaction with cellulose. The heating effect associated with exposure to light is sufficient to catalyse the subsequent oxidative breakdown of the dye–fibre bond. This explanation also accounts for the fact that dyes of the *s*-triazine type do not suffer decomposition of the dye–fibre bond under these conditions, since all three positions *ortho* or *para* to the dye–fibre linkage are occupied by ring nitrogen atoms.

The presence of two types of dye–fibre bond has certain consequences for fastness properties. Mixed bifunctional dyes show superior fastness to acid storage, compared with dichlorotriazine or dichloroquinoxaline systems, and better fastness to peroxide washing than difluoropyrimidine or dichloroquinoxaline dyes [75]. Conversely, mixed bifunctional dyes do show some of the weakness to alkaline treatments characteristic of vinylsulphone dyes, although less so than monofunctional dyes relying solely on these groups for fixation [76].

8.5.2 Direct dyes

The ABC classification of direct dyes based on dyeing properties was established many years ago and this retains considerable practical significance. Self-levelling dyes of the class A type are generally monoazo or disazo dyes with at least two solubilising groups. They show relatively high solubility and thus a fairly low degree of aggregation in salt solution, which accounts for their good migration properties. In view of these characteristics they tend to build up well in padding methods and are suitable for the package dyeing of yarn in pale depths, owing to their good levelling and penetration. Class B dyes of the salt-controllable category are usually disazo or trisazo dyes with three or four sulpho groups. They are more sensitive to salt concentration in terms of their exhaustion behaviour. Thus dyeing rate and levelling properties can be controlled by careful additions of salt during the dyeing process. The third category is represented by the temperature-controllable class C dyes; these are mostly disazo or trisazo dyes with only one or two sulpho groups. They tend to be highly aggregated in salt solution. Owing to their high substantivity they build up well by exhaust dyeing. Levelling tends to be difficult, however, so careful control of both dyeing temperature and salt addition is necessary. Dyes of class C and especially class B generally show better wet fastness than those of class A. Unmetallised dyes from classes A and B are preferred for satisfactory levelling in the combined peroxide bleaching and dyeing process. Copper-complex types are sensitive to peroxide oxidation.

Apart from this classification on the basis of dyeing properties, which is mainly of significance in selecting compatible combinations at the dyeing stage, direct dyeings may be categorised according to whether or not they have been given an aftertreatment (e.g. with a cationic agent, formaldehyde or a resin finish) and whether or not the dyeing is a copper-complex (either dyed in the premetallised form or dyed as the unmetallised azo compound and aftertreated with a copper salt). These differences are important in terms of fastness performance as well as dyeing procedure.

If direct dyes with class B or C dyeing properties are selected for the package dyeing of yarn, they may be applicable at 120°C for optimum levelling and penetration. Care in control of pH is necessary to ensure stability, particularly for unmetallised dyes under these conditions. Especially in the presence of viscose fibres there may be a risk of alkaline reduction; ammonium sulphate as an acid donor and a mild oxidant as reduction inhibitor are added to counteract this problem.

When dyeing with metal-complex dyes in the presence of hard water, hexametaphosphate rather than an organic sequestrant should be used, because the latter can cause demetallisation of some copper-complex dyes. For optimum stability and reproducibility with copperable dyes on scoured cotton these should be dyed at a mildly alkaline pH but after-coppered in a weakly acidic bath. On viscose fibres or unscoured cotton, however, it is usually preferable to dye and aftertreat at a slightly acidic pH. Acid perspiration can cause demetallisation of some copper-complex dyes, and certain of these products are sensitive to alkaline washing in the presence of perborate.

8.5.3 Vat dyes

Migration and strike levelling tests to characterise vat dyes were published many years ago. A classification of vat dyes based on substantivity data, with particular significance for rapid-dyeing techniques, was established later [77]. Cold-dyeing or IK types have relatively low substantivity. They are somewhat obsolescent and are mainly of interest in specific hues not readily attainable with dyes from other sub-classes. The most important sub-class for batchwise dyeing contains the moderately substantive warm-dyeing IW brands applied with less salt at 45–50°C. Most IK and IW dyes can be applied without retarder in full depths, but the best levelling and penetration is achieved in pale-medium depths if a nonionic retarder is present. The high-substantivity IN dyes require an exhaust dyeing temperature of 55–60°C and a retarder but no salt; they are predominantly used in medium to heavy depths for reasons of economy and to avoid the levelling problems associated with pale dyeings. In continuous dyeing, however, the IN brands are generally preferred, both for performance and economy.

8.5.4 Sulphur dyes

The most important subdivision of the class of sulphur dyes is in terms of formulation or presentation of the commercial brand for dyeing. The traditional CI Sulphur dye is insoluble in its oxidised form as a dry powder or aqueous dispersion. Although the cheapest and most stable variant, this has become increasingly obsolescent for many purposes because of the necessity for boiling with sodium sulphide solution to form the soluble leuco form [6]. This is especially inconvenient for padding methods of application [45]. Sulphurised vat dyes are also available as insoluble powders or finely dispersed in paste form.

Pre-reduced solutions of CI Leuco Sulphur dyes have been available in the USA since the 1930s and this is by far the most popular type of formulation for continuous dyeing, since the reducing agent is already included [6]. European manufacturers of pre-reduced sulphur dyes have favoured solid mixtures of the leuco form with a stable reducing compound because they are more readily transported to export markets. For batchwise or continuous dyeing there is the further possibility of using the highly soluble but virtually non-substantive CI Solubilised Sulphur dyes. These are Bunte salts that are converted to the substantive leuco form during dyeing in the presence of an alkaline reducing agent.

8.5.5 Azoic components

There is no formal classification of azoic coupling components but they vary in substantivity from low to high and this does impose some limitations of colour gamut attainable by batchwise or continuous methods. Thus the high-substantivity naphthols for exhaust application cover the rather dull series red–bordeaux–brown–olive–black, whereas the low-substantivity naphthols more suited to continuous padding provide the generally brighter but sometimes more costly range of bright green–yellow–orange–red–violet–navy–black, although this does include the economical Naphtol AS colours. The diazo components with high coupling energy (class I, coupling at pH 4–5) provide the broadest sector: yellow–orange–scarlet–red–bordeaux. The other classes of these components are much more restricted: red–bordeaux (II, pH 5–6), violet–navy (III, pH 6–7) and navy–black (IV, continuous application).

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