Basic Principles of Textile Coloration

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2001

Society of Dyers and Colourists
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Preface

Around 1993–94 I became interested in writing a textbook on textile dyeing and related topics along the lines of E R Trotman's *Dyeing and chemical technology of textile fibres*, the sixth edition of which was published in 1984. This led to a sabbatical leave in the Department of Colour Chemistry at the University of Leeds during 1994–95 that allowed completion of the planning and some initial writing of this work. My original idea was to produce a book dealing with the basic principles of textile dyeing and related subjects. In teaching these subjects, I had found that the available multi-author books, published mainly by the Society of Dyers and Colourists, were often too advanced for students, and I thought that a single book serving as an introduction to these works might be useful.

I remember reading around that time that such an undertaking is partly ego driven. Over the past six years, any ideas of fame or fortune rapidly dissipated. The constant effort required of a single author to produce a 25 chapter book, in addition to full-time professional work, was only sustained because of my love for the subject and of my fascination with how dyeing takes place. The latter was reinforced on reading once again Tom Vickerstaff’s classic book *Physical chemistry of dyeing*. I began to realise that, despite all the wonderful technology available for textile dyeing, we really understand so very little of the fundamentals. I firmly believe that the optimum choice, use, control and adaptation of modern dyeing technology can only be achieved through a sound understanding of basic principles. This book is the fruit of my efforts to provide that understanding. It is designed for readers who have completed studies in chemistry and mathematics up to pre-university level. Because of the wide range of topics included, some subjects only receive superficial coverage. Those that are presented in more detail obviously reflect my personal bias. I am solely responsible for any limitations of content or detail, as well as the invariable errors required by Murphy’s law.

At the end of each chapter are a limited number of references. Some of these are cited in the chapter text, the latter ones are usually general reading references. The interested reader will find more detailed information and references in the books published by the Society of Dyers and Colourists and in technical periodicals. In addition, several of the colorant structures shown in the book are identified by their Colour Index Generic Name. It is worth noting that in the Colour Index itself many of these structures appear as sodium salts and not in the free acid forms shown in these pages.
My thanks to Prof. David Lewis and the staff of the Department of Colour Chemistry at Leeds for their kind hospitality during my 1994–95 leave. The photographs of fibre cross-sections were kindly provided by Tom Micka of DuPont Fibers (Figure 4.2) and by Doug Tierce of Acordis Fibers (Figure 6.2). The American Association of Textile Chemists and Colorists (AATCC) kindly allowed reproduction of Figure 4.6. I would also like to acknowledge Greentex Inc. (Montréal), Regent Ltd. (Montréal), C A Kennedy Inc. (Montréal), Then GmbH (Germany), Macart Textiles Ltd. (UK) and MCS SpA (Italy) for dyeing machine illustrations.

The completion of this book is the result of the dedicated work of the editorial staff of the SDC, in particular Paul Dinsdale and Carol Davies, who all have my sincere gratitude.

ARTHUR D BROADBENT
CHAPTER 1

An introduction to textiles, dyes and dyeing

The manufacture of textiles is a major global industry. It provides vast quantities of materials for clothing and furnishings, and for a variety of other end-uses. This book deals specifically with textile coloration. It begins by introducing this subject along with some technical terms and concepts related to dyes, fibres and dyeing. At this stage, mastery of all the new ideas is not necessary. They will be encountered again throughout the book.

Several examples of the molecular structures of dyes will be presented in this chapter so that the reader gains some familiarity with the variations in molecular size, shape and ionic character. Do not be intimidated by these. In due course, the relationship between the key features of the molecular structure of a dye and its dyeing properties will be more evident.

1.1 HISTORICAL BACKGROUND

1.1.1 Natural dyes and fibres

The production of fabrics and their coloration precedes recorded history. Several cultures had established dyeing technologies before 3000 BC. These ancient artisans transformed the available natural fibres – linen, cotton, wool and silk – into fabrics, at first by hand, and later using simple mechanical devices. Short fibres were first carded or combed, to lay them parallel to one another. Drawing out of a band of combed fibres by pulling, with gradual twisting, produced yarn. Finally, yarns were interlaced to form a woven fabric. The techniques used hardly changed until the Industrial Revolution, when they became fully mechanised.

Although finely ground, coloured minerals, dispersed in water, were used in paints over 30,000 years ago, they easily washed off any material coloured with them. Natural dyes were extracted from plant and animal sources with water, sometimes under conditions involving fermentation. Fabric was dyed by soaking it in the aqueous extract and drying. These dyes had only a limited range of dull colours and the dyeings invariably had poor fastness to washing and sunlight. The fastness of a dyeing is a measure of its resistance to fading, or colour change, on
exposure to a given agency or treatment. Most natural dyes also lacked substantivity for fibres such as wool and cotton. Substantivity implies some attraction of the dye for the fibre, so that the dye in the solution gradually becomes depleted as it is absorbed by the fibres.

The poor substantivity and fastness properties of natural dyes often improved if the fabric was first treated with a solution containing a salt of, for example, iron, copper or tin. The conditions used favoured combination of the metal ions with the particular fibre, or their precipitation inside it. These metal salts were called mordants. When the pre-mordanted fabric was soaked in a bath of a suitable natural dye, the dye penetrated into the fibres and reacted with the metal ions present. This reaction decreased the water solubility of the dye so the colour was less likely to bleed out on washing. The word 'mordant' originated from the French verb *mordre* meaning 'to bite'. In Chapter 13, we shall see that the idea of the dye biting the mordant, to form a stable dye–metal complex, is a useful description. In modern dyeing procedures, the dye reacts with the mordant in the fibre in a separate process after dyeing, or the metal is incorporated into the dyestuff during its manufacture.

A few natural dyes gave better quality dyeings of cotton or wool, but involved long and difficult processes. For example, the colorant extracted from madder root, from the plant *Rubia tinctorium*, dyed cotton pre-mordanted with aluminium and calcium salts to give the famous Turkey Red. Using an iron mordant, the same colorant gave a purplish-black.

Indigo, extracted from leaves of the plant *Indigofera tinctoria*, and Tyrian Purple from Mediterranean sea snails of the genera *Murex* and *Purpura*, are water-insoluble pigments called vat dyes. These do not require mordants. During the time of the Roman Empire, wool cloth dyed with Tyrian Purple was so highly prized that only the ruling class wore garments made with it. For dyeing with Indigo, a water-soluble, reduced form of the dye was first obtained by extraction and fermentation. The process became known as vatting, from the name of the vessels used – hence the term 'vat dye'. The soluble, reduced form of the dye is called a leuco derivative. Leuco Indigo has substantivity for wool and cotton fibres. After dyeing, air oxidation of the pale yellow leuco dye, absorbed in the fibres, regenerates the dark blue, insoluble pigment trapped inside them. Because of this, the fastness to washing is very good in comparison to most natural dyes. Scheme 1.1 outlines the essential steps in vat dyeing.
1.1.2 The development of synthetic dyes and fibres

In 1856, William H Perkin reacted aniline with acidic potassium dichromate solution in an attempt to prepare the anti-malarial drug quinine. From the dark, tarry reaction mixture, he isolated a purple, water-soluble compound that dyed both wool and silk directly when immersed in its solution. No mordant was required. Perkin established a factory for the large-scale production of aniline and for the manufacture of this dye, later called Mauveine. He not only discovered the first major synthetic dye, but founded the modern chemical industry.

Mauveine (proposed structure 1, Figure 1.1) is a cationic dye since each of its molecules has a positive ionic charge. The methyl groups in the structure of Mauveine arose from the use of aniline contaminated with toluidenes (aminotoluenes). Such cationic dyes are often called basic dyes since many, like Mauveine, have free amino groups capable of salt formation with acids.

Mauveine has some substantivity for wool and silk. Such protein fibres contain both amino and carboxylic acid groups. In a neutral dyebath, the amino groups (NH₂) in the wool are neutral but the carboxylic acid groups (CO₂H) dissociate giving negatively charged carboxylate anions (CO₂⁻), associated with positively charged sodium cations (Na⁺). Under these conditions, dyeing with a cationic dye
(Dye\textsuperscript{+}) involves a process of cation exchange in which the more substantive dye cation replaces the sodium ion associated with the carboxylate group in the wool or silk (Scheme 1.2).

\[
\text{H}_2\text{N-Wool-CO}_2\text{Na}^+ + \text{Dye}^+(\text{aq}) \rightarrow \text{H}_2\text{N-Wool-CO}_2\text{Dye}^+ + \text{Na}^+(\text{aq})
\]

Scheme 1.2

Perkin even developed a method for dyeing cotton with Mauveine using tannic acid as a mordant. This polycarboxylic acid was precipitated inside the cotton fibres as a tin salt. The mordanted cotton, immersed in a solution of Mauveine, absorbed the cationic dye (positively charged), which combined with the anionic carboxylate groups of the tannic acid (negatively charged) inside the fibres. Perkin's achievements are all the more impressive when we consider the limited scientific information available in 1856. This was a period of heated debate over Dalton's atomic theory; the formation of organic compounds was still believed to require a living organism, and Kekulé had not yet proposed the hexagonal structure of benzene (1865).

Two years after the isolation of Mauveine, Peter Greiss discovered the diazotisation reaction of primary aromatic amines, which produces diazonium ions, and later, in 1864, their coupling reaction with phenols or aromatic amines to give azo compounds. Primary aromatic amines such as aniline (\(\text{C}_6\text{H}_5\text{NH}_2\)) are often diazotised by treatment with sodium nitrite (\(\text{NaNO}_2\)) in acidic aqueous solution at temperatures around 0–5 °C (Scheme 1.3). The diazonium cation produced (\(\text{C}_6\text{H}_5\text{N}_2\text{H}^+\)) will couple with a phenol in alkaline solution (in a similar way to the reaction shown in Figure 1.2), or with an aromatic amine in weakly acidic solution, to form an azo compound. This coupling reaction is an electrophilic aromatic substitution, like nitration or chlorination, with the diazonium ion as the electrophile. Today, over half of all commercial dyes contain the azo group (\(-\text{N}═\text{N}−\)) and many thousands of azo compounds are known. Diazotisation and coupling are therefore two very significant reactions.

\[
\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \rightarrow \text{C}_6\text{H}_5\text{N}^2\text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}
\]

Scheme 1.3

Each molecule of the azo dye Orange II (Figure 1.2) has an anionic sulphonate group and will dye wool in the presence of an acid. It is therefore classified as an
acid dye. In acidic solution, both the amino and carboxylate groups in wool bond with protons, becoming cationic (\(\text{NH}_3^+\)) and neutral (\(\text{CO}_2\text{H}\)), respectively. Under these conditions, the wool absorbs anionic dyes (\(\text{Dye}^-\)), such as Orange II, by a process of anion exchange (Scheme 1.4).

Figure 1.2 Formation of the azo dye Orange II by diazotisation and coupling

\[
\text{Na}^+\text{O}_2\text{C} - \text{Wool} - \text{NH}_3 + 2\text{HCl} \rightarrow \text{HO}_2\text{C} - \text{Wool} - \text{NH}_3^+\text{Cl}^- + \text{NaCl}
\]

\[
\text{HO}_2\text{C} - \text{Wool} - \text{NH}_3^+\text{Cl}^- + \text{Dye}^-\text{(aq)} \rightarrow \text{HO}_2\text{C} - \text{Wool} - \text{NH}_3^+\text{Dye}^- + \text{Cl}^-\text{(aq)}
\]

Scheme 1.4

Many of the first synthetic dyes were cationic dyes like Mauveine (1). These had brilliant colours, but poor fastness to washing, and particularly to light. Their use on cotton still required pre-mordanting with tannic acid. Congo Red (2, Figure 1.3), first prepared in 1884, was one of the first synthetic dyes that would dye cotton directly, without a mordant. This is also an anionic azo dye, but, unlike Orange II, its more extended molecular structure imparts substantivity for cotton. Dyeings on cotton with Congo Red only had poor fastness to washing, but the so-called direct cotton dyes that followed were better in this respect.

Figure 1.3 Congo Red
Synthetic Indigo was first prepared in 1880 and produced commercially in 1897.
Indigo is a vat dye applied to both wool and cotton according to Scheme 1.1. The
water-insoluble, blue pigment gives a pale yellow, water-soluble leuco form on
reduction (Figure 1.4). Indigo, one of the oldest colorants, is widely used for
dyeing cotton yarn for blue jeans. It was not until the discovery of Indanthrone in
1901, however, that other synthetic vat dyes of outstanding fastness to washing
and light became available. Precipitation of a water-insoluble pigment inside a
fibre is still one of the important ways of producing a dyeing with good fastness to
washing.

![Figure 1.4 Reversible reduction and oxidation for Indigo](image)

The first fibre-reactive dyes did not appear until 1956. Under alkaline
conditions, these dyes react with the ionised hydroxyl groups in cotton cellulose
forming a covalent bond with the fibre (Figure 1.5). Cellulose is the name of the
chemical constituting cotton. It is a polymer of glucose and therefore a

![Figure 1.5 The molecular structure of a simple reactive dye (Dye-Cl) and its reaction with the hydroxyl group in cotton (Cell-OH)](image)
polyalcohol. It is conveniently represented by the short formula Cell–OH. The strong bond between the reactive dye and the cellulose ensures good fastness to washing and the simple chemical structures of the dyes often result in bright colours. Dyes with simple molecular structures can often be prepared with a minimum of contaminating isomers and by-products that tend to dull the colour. Inducing a chemical reaction between a fibre and an absorbed dye molecule is another significant way of producing dyeings of good washing fastness. Reactive dyes have become one of the most important types of dye for dyeing cotton and some types are valuable for wool dyeing.

Synthetic dyes, obtained from coal tar and petroleum chemicals, have totally replaced natural dyes. It would be quite impossible to meet even a small fraction of today’s market requirements for colour using only naturally occurring dyes, although a few are still used to colour foods and cosmetics. Since the earliest days of the synthetic dyestuff industry, there has been a constant demand for dyes with brighter colours, and with better fastness properties, for an increasing range of fibre types. Of the many thousands of known synthetic dyes, only a few thousand are manufactured today. They represent the market-driven selection of those with the required performance.

Before the twentieth century, textiles were made exclusively from natural fibres such as cotton or wool. The first artificially made fibre of regenerated cellulose was Chardonnet’s artificial silk, first produced in 1884. This was manufactured from cellulose nitrate (Cell–O–NO₂), obtained by esterification of cellulose with nitric acid (Scheme 1.5). Forcing an ethanol-diethyl ether solution of cellulose nitrate through tiny holes in a metal plate, and then rapidly evaporating the volatile solvents in warm air, produced very fine, solid filaments of this material. This is the extrusion process. It is a key step in the production of all artificially made fibres. Because cellulose nitrate is highly flammable, the filaments were then treated to hydrolyse it back into cellulose. Later, better processes were found for the preparation of cellulose solutions, their extrusion, and the solidification of the cellulose. Modern fibres of regenerated cellulose are called viscoses. They have some properties similar to those of cotton and can be dyed with the same types of dye.

As for most alcohols, the hydroxyl groups of cellulose can also be esterified with

\[
\text{Cell–OH} + \text{HONO}_2 \rightarrow \text{Cell–O–NO}_2 + \text{H}_2\text{O}
\]

Scheme 1.5
acetic anhydride to produce cellulose acetates (Scheme 1.6). In 1921, a cellulose acetate fibre was produced with about 80% of the cellulose hydroxyl groups acetylated. This cellulose acetate gave silky, lustrous filaments on extrusion of its acetone solution followed by immediate evaporation of the solvent. These filaments were quite different from cotton or viscose. In particular, they were relatively hydrophobic (water-repelling), whereas cotton and viscose are hydrophilic (water-attracting). Initially, cellulose acetate proved difficult to dye satisfactorily with existing ionic dyes. Effective dyeing occurred, however, using a fine aqueous dispersion of non-ionic, relatively insoluble, hydrophobic dyes. This type of dye is called a disperse dye, of which (3) is an example (Figure 1.6). We now know that such dyes are soluble in the hydrophobic cellulose acetate and dyeing occurs by the fibres continually extracting the small amount of dye dissolved in the water. Dye dissolving from the surface of the fine particles in suspension constantly replenishes the dye in solution. As we shall see later, disperse dyes are suitable for dyeing almost all types of artificially made fibre by the same mechanism (Figure 1.7).

\[
\text{Cell} \text{OH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{Cell} \text{O} \text{COCH}_3 + \text{CH}_3\text{CO}_2\text{H}
\]

Scheme 1.6

Figure 1.6 Disperse Blue 14

Figure 1.7 The mechanism of dyeing a synthetic fibre with a disperse dye
We often forget that the development of fibres of regenerated or modified cellulose, and much of dyeing technology, occurred with little understanding of the molecular nature of fibres. The idea of a polymer molecule was not accepted before 1925. The work of Staudinger, Mark, Carothers and others, eventually confirmed that fibres consist of bundles of long, linear molecules of very high molecular weight. Without this scientific advance, the production of the fully artificially made fibres such as nylon (1938) and polyester (1945) might have been impeded. Today, thanks to advances in polymer chemistry and engineering, there are a variety of artificially made fibre types to meet the demand of a growing world population. They account for almost half of total fibre consumption.

During most of the twentieth century, almost all the major developments in the dyestuff and coloration industries originated in Western Europe, predominantly in Germany, Switzerland and Britain. Then, over the last two decades of the twentieth century, a massive global reorganisation took place and the European suppliers of dyestuffs and of dyed or printed materials were seriously threatened as manufacturers in developing countries became much more competitive. A number of factors contributed to this continuing trend:

1. The rapid industrial development of many developing countries and the global availability of technology and machinery for textile manufacture and coloration; countries such as Japan, India, China and Korea have become major players on the textile stage.

2. Much more restrictive legislation in Europe and North America for dyestuff manufacture and use with minimum impact on health and the environment; this has become a key issue in the future of the colorant and textile industries in the developed nations of the Western block.

3. The majority of chemicals and processes presently in use were introduced prior to 1975 and their originators have no further patent protection; the perceived low probability of developing new types of textile fibres and dyes has considerably limited fundamental research in these areas.

One effect of these influences has been a drastic rationalisation of the dyestuff industry in Western Europe. Some dyestuff divisions separated from their parent company (Zeneca from ICI in Britain, and Clariant from Sandoz in Switzerland). In other cases, dyestuff producers have merged: Ciba merged with Geigy in Switzerland and may yet absorb Clariant; Hoechst and Bayer joined forces as DyStar in Germany; and BASF bought Zeneca. More recently, Yorkshire Chemicals has bought Crompton and Knowles, the major American dye
manufacturer, and the merger of DyStar and BASF is imminent. The more recent
history of the dyestuff industry is described in a series of four articles by Park and
Shore [1].

1.2 MODERN TEXTILES

1.2.1 The classification of fibres

There are seven major fibre types. Table 1.1 shows these in bold face along with
their estimated global consumption for the year 2000. The four main groups of
textile fibres are:
(1) animal or protein fibres;
(2) vegetable or cellulosic fibres;
(3) regenerated fibres based on cellulose or its derivatives;
(4) fully synthetic fibres.

There are, of course, other natural and artificially made fibres besides those listed
in Table 1.1, but these are of lesser importance. All these fibres are dyed in a wide
range of colours, with various fastness properties, for a multitude of different
textile products. Each type of fibre requires specific types of dyes and dyeing
methods. Fortunately, the dyeing of many minor fibres is often very similar to that
of a chemically related major fibre. For example, the dyeing of mohair is very
similar to wool dyeing. The $5 \times 10^9$ kg of fibres consumed annually require about

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<th>Natural fibres</th>
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<td>Protein</td>
<td>Cellulose</td>
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<td>Wool</td>
<td>Cotton</td>
</tr>
<tr>
<td>$3.1 \times 10^9$</td>
<td>$23.7 \times 10^9$</td>
</tr>
<tr>
<td>Silk</td>
<td>Linen</td>
</tr>
<tr>
<td>Mohair</td>
<td>Ramie</td>
</tr>
<tr>
<td>Cashmere</td>
<td></td>
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<td></td>
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</tbody>
</table>
1.2.2 Textile manufacture

Textile consumption is closely related to growing world population and consumer affluence. To satisfy market demand for fabric, fully automated, high-speed production, with a minimum of defects, is essential. The following outline of textile manufacture identifies the major processes, the division of operations, and situates coloration in the overall scheme. Chapter 2 provides more details on fibres and textile manufacturing.

Cotton and wool are only available as short staple fibres of pre-determined length, but artificially made fibres are available either as continuous filaments or short fibres cut to any required length. Textile manufacturing using natural fibres starts with the opening, separation and mixing of short fibres. The carding process draws them out into a band of parallel fibres (sliver), and drawing out and twisting of this yields spun yarn. Opening, carding or drawing may also serve to blend two or more staple fibres; for example, cotton and staple polyester. Continuous filaments do not require such preliminary operations.

The major methods of fabric assembly from yarns of staple fibres, or from continuous filaments, are weaving and knitting, both of which, being fully automated, have significant production rates.

The production of a textile material from fibres involves a defined sequence of operations to produce yarns and assemble them into fabric. Each process is a necessary prerequisite for the next. The situation of dyeing in the production scheme, however, is not necessarily rigidly defined. Dyeing may occur at any stage during textile manufacture: on loose fibre, or on the intermediate forms such as sliver or yarn, or on fabric, towards the end of the manufacturing cycle. Even garments and finished articles can be dyed. This means that a variety of dyeing machines is required for the different types of textiles. Dyeing usually involves contact between an aqueous solution or dispersion of the dyes and the textile material, under conditions that promote substantivity and produce uniform coloration throughout. Printing, on the other hand, is the localised application of different dyes to different specific areas on one face of a fabric, according to some predetermined colour design. This book primarily discusses textile dyeing but Chapter 23 deals with printing.

Before textile fibres are dyed, they are washed or scoured to remove natural
impurities, lubricating oils (added to aid carding, spinning or knitting) and size (used to reinforce the warp yarns in weaving). Bleaching eliminates any coloured impurities and is often necessary for white goods containing natural fibres, and before dyeing pale, bright shades. This stage of production is called preparation. Its objective is to clean the material before dyeing and finishing so that it wets easily and uniformly absorbs solutions of chemicals and dyes. Poor quality preparation, particularly when it is uneven, is a major cause of faulty dyeings.

The final stage in the manufacture of a textile is finishing. This involves treatments to improve the appearance or performance of the material. It might consist of a simple mechanical process such as calendering (to give the fabric a flat, compact surface) or napping (to break fibres and raise the ends forming a pile). Modification of the functional characteristics of a fabric often involves chemical finishing. The processes range from the simple application of a softening agent to improve the material’s handle and reduce static electricity, to those that render cotton fabric flame resistant or crease resistant. Most chemical finishing is for fabrics of natural fibres, particularly for those containing cotton. This satisfies consumer demand for cotton materials having the easy-care characteristics associated with fabrics made from synthetic fibres. Many finishing processes, particularly those involving chemicals, can modify both the colour and the fastness properties of a dyed fabric, and these effects must therefore be known in advance.

Table 1.2 illustrates the sequence of some of the processes used for production of a knitted cotton fabric that will be dyed before assembly into the final article. Piece dyeing usually refers to dyeing of fabric as distinct from dyeing of a completed article such as a garment. Textile manufacture is highly specialised.

<table>
<thead>
<tr>
<th>Type of process</th>
<th>Specific process</th>
<th>Industrial unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yarn Production</td>
<td>(1) Opening</td>
<td>Spinning mill</td>
</tr>
<tr>
<td></td>
<td>(2) Carding</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3) Spinning</td>
<td></td>
</tr>
<tr>
<td>Fabric construction</td>
<td>(4) Knitting</td>
<td>Knitting mill</td>
</tr>
<tr>
<td>Preparation</td>
<td>(5) Scouring</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(6) Bleaching</td>
<td></td>
</tr>
<tr>
<td>Coloration</td>
<td>(7) Dyeing</td>
<td>Dyehouse or finishing mill</td>
</tr>
<tr>
<td>Finishing</td>
<td>(8) Mechanical or chemical finishing</td>
<td></td>
</tr>
</tbody>
</table>
Consequently, yarn production, fabric construction, and dyeing and finishing often take place in different locations with clear divisions between mechanical manufacturing operations and the wet processing associated with preparation, dyeing or printing, and finishing.

The seven major fibre types have quite different properties. The materials produced from these have a wide variety of end-uses, and each fabric has its particular aesthetic, colour fastness and technical requirements. There are therefore different types of dyes and processing methods for dyeing and printing. The manufacture of any fabric will always involve a compromise between the desired quality and performance, and the overall production cost. Today, fully automated and environmentally friendly processes are the norm: automation is essential to remain competitive, and national and local governments now demand lower levels of air and water pollution. The environmental impact of textile production and coloration is the most significant challenge facing the industry in Europe and North America today. Eventually, more environmentally sound methods of production and disposal will also be forced upon producers in the developing world as they expand further.

1.3 COLOUR, DYES AND DYEING

1.3.1 Light and colour

Colour sensation is a characteristic of human experience. Nature provides a particularly vivid display of colour. We use colours in many varied ways; for example, for clothes, paints, foods, lighting, cosmetics, paper, furnishings, and for identification and security. Despite our familiarity with it, there is no simple answer to the question 'What is colour, and how do we see it?': we understand so very little of the complex processes involved in colour vision. There are three main stages in the perception of colour, but each one consists of numerous complicated processes:

1. absorption of coloured light entering the eye by the sensitive cells in the retina lining the back of the eyeball;
2. transmission of nerve impulses from the retina to the brain via the optic nerve;
3. interpretation of these signals when they reach the visual cortex in the brain.

To understand colour, some knowledge of the nature of light is essential. Light is a form of energy usually considered as being propagated at high speed in the form of
Electromagnetic waves. All types of electromagnetic radiation are characterised by their wavelength (\(\lambda\)) (the distance between the wave crests), or by the frequency (\(f\)) (the number of waves that pass a point in a given time). Figure 1.8 illustrates the variations of the electric and magnetic fields associated with an electromagnetic wave.

\[\text{Electric field} \quad \text{Distance at a given time} \quad \text{Wavelength} \quad \text{Magnetic field} \quad \text{Time at a given distance}\]

**Figure 1.8** Variations of the electric and magnetic fields associated with an electromagnetic wave

The wavelength multiplied by the frequency (\(\lambda \times f\)) gives the speed of wave propagation. This is always constant in a given medium (speed of light in a vacuum, \(c = 3.0 \times 10^8 \text{ m s}^{-1}\)). The human eye can detect electromagnetic waves with wavelengths in a narrow range between about 400 and 700 nm (1 nm = 1 \(\times\) 10\(^{-9}\) m), comprising what we call visible light. We are also familiar with X-rays (\(\lambda = 0.3\) nm), ultraviolet light (\(\lambda = 300\) nm), infrared rays (\(\lambda = 3000\) nm) and micro- and radio waves (\(\lambda > 3 \times 10^9\) nm = 3 mm), whose wavelengths vary by many orders of magnitude. Spectral analysis of daylight, or white light – using a prism, for example – separates it into various coloured lights, as seen in the rainbow. The red, orange, yellow, green, blue and violet spectral colours of the rainbow correspond to lights with wavelengths of about 650, 600, 575, 525, 460 and 420 nm, respectively.

An object viewed in white light, which consists of all wavelengths in the visible region (400–700 nm) in about equal proportions, will appear coloured if there is selective absorption of some wavelengths and reflection or transmission of the others. Objects with high reflectance of all wavelengths of white light will appear white, whereas strong absorption of all wavelengths produces black. Table 1.3 lists the colours that an observer sees when the colorant in a material absorbs a single
Table 1.3 Colours of typical spectral bands, and colours perceived after their absorption by a material viewed in white light

<table>
<thead>
<tr>
<th>Wavelength band (nm)</th>
<th>Colour of the light absorbed</th>
<th>Perceived colour of the reflected light</th>
</tr>
</thead>
<tbody>
<tr>
<td>400–440</td>
<td>Violet</td>
<td>Greenish-yellow</td>
</tr>
<tr>
<td>440–480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480–510</td>
<td>Blue-green</td>
<td>Orange</td>
</tr>
<tr>
<td>510–540</td>
<td>Green</td>
<td>Red</td>
</tr>
<tr>
<td>540–570</td>
<td>Yellowish-green</td>
<td>Magenta</td>
</tr>
<tr>
<td>570–580</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>580–610</td>
<td>Orange</td>
<td>Greenish-blue (cyan)</td>
</tr>
<tr>
<td>610–700</td>
<td>Red</td>
<td>Blue-green</td>
</tr>
</tbody>
</table>

A colorant is a substance capable of imparting its colour to a given substrate, such as paint, paper or cotton, in which it is present. Not all colorants are dyes. A dye must be soluble in the application medium, usually water, at some point during the coloration process. It will also usually exhibit some substantivity for the material being dyed and be absorbed from the aqueous solution. On the other hand, pigments are colorants composed of particles that are insoluble in the application medium. They have no substantivity for the material. Since the particles are too large to penetrate into the substrate, they are usually present on the substrate surface. The pigment is therefore easily removed unless fixed with an adhesive.

Most textile dyeing processes initially involve transfer of the coloured chemical, or its precursor, from the aqueous solution onto the fibre surface; a process called adsorption. From there, the dye may slowly diffuse into the fibre. This occurs down
pores, or between fibre polymer molecules, depending on the internal structure of the fibre. The overall process of adsorption and penetration of the dye into the fibre is called absorption. Absorption is a reversible process. The dye can therefore return to the aqueous medium from the dyed material during washing, a process called desorption. Besides direct absorption, coloration of a fibre may also involve precipitation of a dye inside the fibre, or its chemical reaction with the fibre. We have already seen that these two types of process result in better fastness to washing, because they are essentially irreversible processes.

For diffusion into a fibre, dyes must be present in the water in the form of individual molecules. These are often coloured anions; for example, sodium salts of sulphonic acids such as Congo Red \((2, \text{Figure 1.3})\). They may also be cations such as Mauveine \((1, \text{Figure 1.1})\), or neutral molecules with slight solubility in water, such as disperse dyes \((3, \text{Figure 1.6})\). The dye must have some attraction for the fibre under the dyeing conditions so that the solution gradually becomes depleted. In dyeing terminology, we say that the dye has substantivity for the fibre and the dyebath becomes exhausted.

The four major characteristics of dyes are:

1. intense colour;
2. solubility in water at some point during the dyeing cycle;
3. some substantivity for the fibre being dyed;
4. reasonable fastness properties of the dyeing produced.

### 1.3.3 Dye classification and nomenclature

The Colour Index was first published in 1924 by the Society of Dyers and Colourists (SDC) and is the major catalogue of dyes and pigments. The third revised edition is published jointly by the SDC and the American Association of Textile Chemists and Colorists (AATCC). In it, dyes are classified according to chemical constitution (30 subgroups) and usage (19 subgroups) \([2]\). Table 1.4 gives partial classifications of dyes as presented in the Colour Index.

The first three volumes of the third edition of the Colour Index (CI) give extensive information on the 19 subgroups of dyes classified according to usage. In each subgroup, dyes have a Colour Index Generic Name based on the particular application and hue. For example, CI Acid Red 1 is a red acid dye, with similar dyeing properties to Orange II in Figure 1.2 (CI Acid Orange 7). CI Reactive Blue 4 is a blue reactive dye. Dyes in any one application subgroup will be used for specific fibres using similar dyeing methods. For each dye listed, useful data on
Table 1.4 Classification of dyes according to chemical constitution and usage

<table>
<thead>
<tr>
<th>Classification according to chemical constitution</th>
<th>Classification according to textile usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo dyes</td>
<td>Acid dyes</td>
</tr>
<tr>
<td>Anthraquinone dyes</td>
<td>Azoic dyes</td>
</tr>
<tr>
<td>Heterocyclic dyes*</td>
<td>Basic dyes</td>
</tr>
<tr>
<td>Indigoid dyes</td>
<td>Direct dyes</td>
</tr>
<tr>
<td>Nitro dyes</td>
<td>Disperse dyes</td>
</tr>
<tr>
<td>Phthalocyanine dyes</td>
<td>Mordant dyes</td>
</tr>
<tr>
<td>Polymethine dyes</td>
<td>Pigments</td>
</tr>
<tr>
<td>Stilbene dyes</td>
<td>Reactive dyes</td>
</tr>
<tr>
<td>Sulphur dyes</td>
<td>Sulphur dyes</td>
</tr>
<tr>
<td>Triphenylmethane dyes</td>
<td>Vat dyes</td>
</tr>
</tbody>
</table>

* Includes a number of different subgroups containing heterocyclic systems (only the most important subgroups in each classification are given).

Dyeing methods and fastness properties are tabulated where the information is available. Dyes of known molecular structure are given a CI Constitution Number (5 digits). The direct dye Congo Red (2) is CI Direct Red 28 and has CI Constitution Number 22120. Information for other dyes illustrated in this chapter is given below:

1. Figure 1.4, Indigo, CI Vat Blue 1, Constitution 73000;
2. Figure 1.5, CI Reactive Red 1, Constitution 18158;
3. Figure 1.6 (3), CI Disperse Blue 14, Constitution 61500.

Volume 4 of the Colour Index gives the chemical constitutions, along with tables of intermediates used in dye manufacture. Volume 5 is particularly useful because of the documentation on the commercial names used by the dye manufacturers. In addition, later volumes and supplements of the Colour Index provide regular updates of the information in the first five volumes. The Colour Index is also available in digitised form on a compact disc (CD-ROM). The 4th edition of the Colour Index, which appeared in 2000, is available on-line with particularly favourable registration fees for multiple users.

The variety of commercial names of dyes from different suppliers is a problem for the uninitiated. Most dyes with the same manufacturer’s brand name belong to the same dyeing class. They are usually applied to a particular type of fibre by the same or similar dyeing methods. For example, the Remazol dyes, marketed by
DyStar are all reactive dyes with vinyl sulphone reactive groups, used mainly for dyeing cotton.

A reference to the colour of the dye usually follows the brand name. The name may also include other descriptive references to particular characteristics of the dye, such as particularly good fastness properties, ability to form metal complexes, or its physical form. The commercial name usually ends with an alphanumeric code. These codes range from quite simple to quite obscure. They may relate to the particular hue of the dye, the relative amount of actual colorant in the formulation, or the application properties.

For example, Indanthren Golden Yellow RK is a vat dye manufactured by BASF (Badische Anilin und Soda Fabrik). 'Indanthren' is the brand name used for their range of vat dyes. 'Golden Yellow' indicates the colour and the code 'RK' shows that this dye is a reddish yellow and applied using a cold-dyeing method. The letter 'R' stands for the German word rot = red (the dye is listed as CI Vat Orange 1) and the 'K' comes from the German kalt = cold. On the other hand, BASF manufacture Procion Red H-E3B. 'Procion' is their brand name for reactive dyes for cotton. All the Procion dyes with 'H-E' in the code are dyes with two identical reactive groups. Reaction of the dye with the cotton occurs under hot ('H') conditions. The '3B' in the code shows that this is a bluish red (B = blue); bluer than similar red dyes with a code B, but redder in hue than dyes with a 6B in the code. In other cases, the alphanumeric code following the name of the dye may be of little or no value to the dye user. An old paper on dyestuff nomenclature by C.L. Bird [3] is still useful reading on this subject.

One major problem with the Colour Index classification is that dyes from different suppliers, which have the same registered CI Generic Name and Constitution Number, may have quite different dyeing properties. The Colour Index information is simply an indication that dyes of the same Generic Name contain the same base colorant. The different commercial products will usually contain different amounts of the predominant dye, of other minor dye components, and of auxiliary chemicals. They may, therefore, have different dyeing properties. Some manufacturers erroneously use the Colour Index nomenclature without official registration and their products may not be equivalent, or even close, to those with registered names.

Figure 1.9 illustrates the approximate relative annual consumption of the major types of fibres and dyes estimated for the year 2000. The inner pie chart gives the data for fibres and the lengths of the outer arrows indicate the relative proportions of the various kinds of dyes used. There is a close relationship between the relative
amounts of fibres produced and the quantities of dyes used to colour each type. The arrows showing dye consumption are situated around the types of fibres that they are used for. Thus, direct, reactive, vat and sulphur dyes are used to colour the cellulosic fibres cotton and viscose, whereas acid and mordant dyes are used for wool and nylon.

This chapter has introduced some simple concepts related to fibres, textile production, dyes, colour and dyeing processes. Before discussing the use of specific kinds of dyes in textile dyeing, and the basic principles involved, the following chapters first deal with the materials to be dyed: the textile fibres, their polymeric nature, manufacture and properties.

REFERENCES

CHAPTER 2

Fibres and textiles: properties and processing

This chapter on textile production complements the brief introduction in Section 1.2.2. It reviews some properties of fibres, their conversion into yarns and fabrics, and the objectives of wet processing in manufacturing textiles. The emphasis is on the relationship between dyeing and textile properties and processes. Table 1.1 in the previous chapter identified the seven major fibre types: cotton, wool, viscose, cellulose acetates, nylons, polyesters and acrylics. Later chapters will consider the production, characteristics and dyeing of all these fibres.

2.1 PROPERTIES OF FIBRES

A fibre is characterised by its high ratio of length to thickness, and by its strength and flexibility. Fibres may be of natural origin, or artificially made from natural or synthetic polymers. They are available in a variety of forms. Staple fibres are short, with length-to-thickness ratios around $10^3$ to $10^4$, whereas this ratio for continuous filaments is at least several millions. The form and properties of a natural fibre such as cotton are fixed, but for artificially made fibres a wide choice of properties is available by design. The many variations include staple fibres of any length, single continuous filaments (monofilaments), or yarns constituted of many filaments (multi-filaments). The fibres or filaments may be lustrous, dull or semi-dull, coarse, fine or ultra-fine, circular or of any other cross-section, straight or crimped, regular or chemically modified, or solid or hollow. The lustre and handle depend on the shape of the cross-section and on the degree of crimping developed in a process called texturising (Section 3.4).

Natural fibres have a number of inherent disadvantages. They exhibit large variations in staple length, fineness, shape, crimp, and other physical properties, depending upon the location and conditions of growth. Animal and vegetable fibres also contain considerable and variable amounts of impurities whose removal before dyeing is essential, and entails much processing. Artificially made fibres are much more uniform in their physical characteristics. Their only contaminants are small amounts of slightly soluble low molecular weight polymer (oligomers) and
some surface lubricants and other chemicals added to facilitate processing. These are relatively easy to remove compared to the difficulty of purifying natural fibres.

Water absorption is one of the key properties of a textile fibre. Protein or cellulosic fibres are hydrophilic and absorb large amounts of water, which causes radial swelling. Hydrophobic synthetic fibres, such as polyester, however, absorb almost no water and do not swell. The hydrophilic or hydrophobic character of a fibre influences the types of dyes that it will absorb. Dyeing in a wide range of hues and depths is a key requirement for almost all textile materials.

The regain of a fibre is the weight of water absorbed per unit weight of completely dry fibre, when it is in equilibrium with the surrounding air at a given temperature and relative humidity. Table 2.1 shows some typical values. The regain increases with increase in the relative humidity but diminishes with increase in the air temperature. Le Châtelier’s principle states that a system at equilibrium will respond so as to counteract the effects of any applied constraint. Water absorption by a fibre liberates heat (exothermic) and will therefore be less favourable at higher temperatures (more heat). The heat released is often a consequence of the formation of hydrogen bonds (Section 3.3) between water molecules and appropriate groups in the fibre. When the final regain is approached by drying wet swollen fibres, rather than by water absorption by dry fibres, the
regain is higher. The swollen wet fibres are more accessible to water so they retain more of it at equilibrium (Figure 2.1).

For hydrophilic fibres such as wool, cotton and viscose, the relatively high regain values significantly influence the gross weight of a given amount of fibre. This has consequences in buying and selling, and is also significant in dyeing. Amounts of dyes used are usually expressed as a percentage of the weight of material to be coloured. Thus, a 1.00% dyeing corresponds to 1.00 g of dye for every 100 g of fibre, usually weighed under ambient conditions. For hydrophilic fibres, the variation of fibre weight with varying atmospheric conditions is therefore an important factor influencing colour reproducibility in repeat dyeings. For example, the weight of 100 g of dry cotton varies from about 103 g to 108 g as the relative humidity of the air changes from 20% to 80% at room temperature.

The mechanical properties of fibres, such as tensile strength, flexibility and elasticity, are important in determining the behaviour of a fabric. Some fibres have quite remarkable physical and chemical properties, such as high heat or chemical resistance, or high elasticity with good recovery. Although a detailed discussion of these is beyond the scope of this book, the important physical and chemical properties of the major fibres are discussed in subsequent chapters, particularly in relation to dyeing [2,3].

### 2.2 PRODUCTION AND PROPERTIES OF YARNS

Natural staple fibres arrive at the spinning mill in large bales. A number of

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Regain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wool</td>
<td>13.0-15.0</td>
</tr>
<tr>
<td>Viscose</td>
<td>13.0</td>
</tr>
<tr>
<td>Cotton</td>
<td>7.0-8.0</td>
</tr>
<tr>
<td>Cellulose diacetate</td>
<td>6.0-6.5</td>
</tr>
<tr>
<td>Nylons</td>
<td>4.0-4.5</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>2.5-3.0</td>
</tr>
<tr>
<td>Acrylics</td>
<td>1.0-2.5</td>
</tr>
<tr>
<td>Polyester</td>
<td>0.4</td>
</tr>
</tbody>
</table>
preliminary, mechanical operations open up the compressed fibrous mass, eliminate non-fibrous debris, and blend the fibres in preparation for carding. All natural fibres have inherent variations in their properties because of growth differences, and blending of the fibres is vital to ensure constant quality of the yarns produced. Good opening and separation of clumps of fibres is essential for level dyeing of loose fibre in a dyeing machine with circulating liquor.

The objective of carding is to make a continuous band of parallel fibres called card sliver. This process also removes any residual debris and those fibres that are too short for spinning. During carding, the wide band of fibres passes around a large, rotating roller, with metal pins projecting from its surface. Other small rotating rollers on its periphery have similar pins, and comb and align the fibres held on the pins of the larger roller. The natural wax in raw cotton provides sufficient lubrication for carding. In the case of scoured or degreased raw or recycled wool, additional lubricating oil is necessary to avoid excessive fibre breakage and to control the development of static electricity during carding. Scouring removes this oil before dyeing.

Combing is a process similar to carding. It removes more short fibres from card sliver, leaving the longer staple fibres even more parallel to each other. Longer staple length allows greater drawing out of the combed fibres and thus the production of finer yarn. Spinning of carded wool gives the coarse, low-twist yarns for woollen articles, whereas drawing and spinning of combed wool produces the much finer and stronger high-twist yarns for worsted materials.

After carding, the sliver passes to the drawing or drafting process. Several bands of sliver are combined and gradually drawn out by passing them between pairs of friction rollers of increasing speed. The fibres slide over each other increasing their alignment. This produces a finer band of fibres. It is quite weak and a slight twist helps to hold it together. Further drawing and twisting produce a coarse yarn called roving.

Spinning involves drawing out the band of fibres even more, gradually reducing its thickness, but simultaneously twisting the fibres around each other. Twisting increases the number of contact points between fibres so that their natural adhesion provides sufficient strength to avoid breaking the yarn. The yarn will be stronger the longer the staple length of the fibres, the greater the degree of twist inserted, and the higher the fibre adhesion. The latter is greater if the fibres have a natural or artificially-made crimp.

The various spinning technologies give yarns with quite different characteristics. Classical ring spinning requires a pre-formed roving, which is
drawn even more and twisted. This produces quite fine yarns. The open-end and friction spinning techniques give much faster rates of production since the yarn is produced directly from card sliver without intermediate drawing. The bobbins of yarn can also be much larger since the twist is not inserted by rotation of the take-up bobbin, as in ring spinning. Open-end and friction spun yarns are coarser and cannot be mixed with ring-spun yarns because of their different structures and twist characteristics.

The final step in yarn production is winding. The yarn is wound into hanks, or bobbins of various types, whose size depends on its subsequent use. Winding also allows an opportunity to detect overly thick or thin sections of the yarn and to eliminate them, and ensures that all the yarn on the bobbin has the same tension. Ply yarns are produced at this stage by twisting two or more yarns together, in the opposite sense to their own twist.

During dyeing, it is imperative that all the yarn in hanks or bobbins has equal access to the circulating dye liquor. Yarn uniformly wound onto perforated supports gives packages with either parallel sides (cheeses) or slanting sides (cones). Their permeability must be uniform throughout. Permeability depends on the type and twist of the yarn, the type and density of winding, and the degree of swelling that occurs when the yarns are wet. If packages are too dense, the pressure required to force dye liquor through them is excessive. Obviously, the package must not deform during dyeing, and the yarn must be easy to unwind. Low density or poorly wound packages may become unstable during liquor circulation, or when the direction of circulation changes, and yarn becomes detached from the body. For these reasons, the preparation of yarn hanks and bobbins for dyeing merits particular attention.

The two major characteristics of a yarn are its degree of twist and its thickness or count. The thickness of a yarn, or of continuous filaments, is expressed as the length of a given weight of yarn, or vice versa. For example, the denier of a continuous filament is the weight in grams of 9000 m. A considerable number of older measures gave the yarn count as the number of hanks, containing a defined length of yarn, obtained from a given weight of fibre. Different standard lengths were used for different fibres. For example, a cotton count of 40 corresponds to 40 hanks, each containing 840 yd of yarn produced from 1 lb of cotton fibre. The standard lengths for wool vary from 100 to 560 yd hank⁻¹ depending on the region and the spinning system used. This type of count increases as the yarn becomes finer. Since 1960, the tex system has become increasingly popular. In this, the count of a yarn or filament is the weight in grams of 1 km of yarn. The tex
number increases as the yarn thickness increases. Since the tex is a metric unit, decimal multiples and fractions are used for coarser and finer yarns. The kilotex (1 ktex = 1000 tex = 1000 g km\(^{-1}\)) is used for sliver, and the decitex (1 dtex = 0.1 tex = 0.1 g km\(^{-1}\)) for fine yarns and filaments. Note that 1.0 dtex (0.1 g km\(^{-1}\)) is equal to 0.9 denier (0.9 g (9 km)\(^{-1}\)).

Much of the technology used today for yarn production originally developed from wool and cotton processing. Modern yarn production from natural staple fibres involves considerable resources because of the large number of operations involved. Continuous filament yarns have the advantage of being ready for direct assembly into fabrics. They are also much cleaner than yarns from natural fibres.

### 2.3 FABRIC MANUFACTURE

There are four major types of textile fabric:

1. woven fabrics have yarns interlaced at right angles in a repeated pattern (A, in Figure 2.2);
2. knitted materials consist of interlocking loops of yarn with a regular pattern (B, in Figure 2.2);
3. non-woven or felt materials have fibres compressed together in random orientations, held by their natural cohesiveness, or by adhesives;
4. laces are open materials in which yarns are twisted, looped and knotted together.

![Figure 2.2 Photographs of woven fabric (a) and knitted fabric (b)](image-url)
The characteristics of a woven fabric depend on the type of fibres present, the fineness and twist of the yarns, the number of yarns per centimetre, and the pattern or weave of the interlaced yarns. The warp yarns, wound side by side on a beam, are threaded through the loom under tension. They run along the length of the fabric. During weaving, raising some warp yarns and lowering others creates a gap for inserting the weft or filling yarn from the side. The positions of the warp yarns then change ready for the next insertion of filling yarn. The two types of yarn are thus woven according to a specific pattern. Winding the warp yarns onto the beam and weft insertion, in the correct colour sequences, is vital when weaving coloured patterns with dyed yarns.

The newer weaving technologies use small projectiles, rapiers, or water or air jets to insert the filling between the warp yarns rather than the older, classical shuttles. They generate much less noise and vibration and increase production speeds.

A woven fabric exhibits maximum resistance to extension in the warp and weft directions. The selvages, running along the edges of the fabric, usually have a more robust and compact woven structure. They stabilise the shape, prevent unravelling and form an area where the fabric can be gripped during manufacturing operations.

During weaving, there is considerable abrasion of the warp yarns from their guided movement through the loom, and from the repeated rapid lifting and lowering required to separate them for insertion of the filling. To avoid excessive abrasion and yarn breakage, the warp yarns usually have a greater twist and a smooth film of size coating their entire length to reinforce them. Sizing chemicals of various types are used depending upon the kinds of fibres present. Good size adhesion on cotton, which has a polar hydrophilic surface, requires use of a polar hydrophilic polymer such as starch. For the hydrophobic surfaces of synthetic fibres, less polar synthetic polymer sizes are preferred. Sizing mixtures include one or more film-forming polymers such as starch, carboxymethyl cellulose (cellulose with some of its hydroxyl groups converted into $\text{Cell-O-CH}_2\text{-CO}_2\text{Na}$) or polyvinyl alcohol (1, in Figure 2.3), as well as wax lubricants, anti-static agents, preservatives, emulsifying agents, and anti-foaming agents. The yarns are usually

\[
\text{CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-}\]

\[
\text{OH}\text{-OH}\text{-OH}\text{-OH}_{\text{1}}
\]

Figure 2.3 Polyvinyl alcohol, used as a film-forming agent in size mixtures.
treated with an aqueous solution or emulsion of the size, and dried. The amounts of size applied vary from 10–15% solids for cotton (based on the weight of yarn), to 3–5% for synthetic fibres. Optimised recipes give minimum yarn rupture during weaving and are often closely guarded secrets. The size must be removed during preparation for dyeing (Section 2.4), since it interferes with wetting and penetration of dyes and chemicals into the yarns [4].

The perpendicular warp and weft yarns characterise a woven fabric. Knitted materials, however, are constructed of interlocking loops of a single yarn, or a series of parallel yarns. In simple knitted styles such as jersey, each loop, in a series of loops from a single yarn, passes through a loop of the preceding row. Each loop is produced by the action of its own needle carrying the yarn. To minimise friction with the needles and guides, the yarns used in knitting contain a considerable amount of lubricating oil that must be removed before dyeing. The fabric is constructed row after row across the width of the material, or around in a circle, to form what is called a weft knit. When laid flat, circular knitted fabrics have two layers. The higher the number of loops (wales) and rows (courses) per unit distance, the greater the weight and rigidity of the material, the better its recovery after stretching, and the less it is likely to shrink.

Knitting produces fabric much faster than weaving. Knitted materials are flexible, elastic and relatively crease resistant so that clothing made from them fits well. Simple weft-knitted fabrics, however, deform easily in all directions and their dimensional stability is often poor since the yarn is inserted under considerable tension. The shrinkage observed after wetting can be significant. They often have a pronounced tendency to curl at the edges. A yarn breakage can cause the disappearance of a whole series of loops and the formation of a ‘run’. Their handling during wet processing therefore requires more care than for a woven fabric.

In warp knitting, a series of parallel yarns is fed into the machine from a beam, similar to a warp beam in weaving. Each yarn passes through its own needle. Warp knits have vertical columns of loops, but each yarn loops into columns to the left and right in a zigzag pattern. This gives greater resistance to deformation than for a simple knit and a material that is more snag resistant. Interlock knits have a construction intermediate between weft and warp knits.

Besides simple woven and knitted fabrics, there are a large number of other types that have a pile of surface loops or cut loops. These are manufactured by knitting or weaving, or by techniques that combine the features of these two methods. Other types have complex woven or knitted patterns, or may have more than one warp or filling.
The vast majority of carpets are made by simultaneously needle-punching a row of thousands of nylon multi-filaments into a polypropylene backing material in a process called tufting. The backing then advances slightly and another row of tufts is inserted. Application of a latex adhesive to the rear of the backing anchors the tufts in place. Carpet manufacture also consumes lesser amounts of polyester, wool, polypropylene and acrylic fibres. Like fabrics, carpets can be assembled from coloured yarns, dyed using both continuous and batch processes, or even printed.

Non-woven fabrics are formed of a mass of disoriented fibres pressed together and held by their natural adhesion, by tangling them using a needle-punch, with the help of an adhesive, or by heat welding of synthetic fibres, which soften when hot. They often have poor strength but are equally resistant in all directions. Their major applications are for industrial and engineering textiles, and for disposable materials such as sanitary products. Non-woven fabrics are less likely to be dyed than woven or knitted materials but manufacture from pre-dyed fibres is simple if colour is required.

A multitude of different textile fabrics are manufactured, each type with its own characteristic structure and uses. The machinery used for handling these materials, particularly during wet processing, is dictated by the strength and weight of the fabric and its ease of deformation. In addition to weight and strength, the other major attributes of a fabric are flexibility, elasticity, handle, water absorbency, resistance to the conditions met during use, and good dyeability. Many fabrics have a different appearance on the two sides, which becomes even more evident on dying. The face of the fabric is usually the one presented during use. Carpets and pile fabrics are extreme examples of this.

Fabrics come in a wide range of widths, superficial weights (g m\(^{-2}\)), and air permeabilities, the latter two properties depending on the thread or loop spacing and the degree of twist of the yarns. Heavier fabrics provide better draping characteristics. The properties of a fabric depend on its construction and upon those of the component fibres. For example, fabrics made from viscose filaments are often weak and very absorbent whereas those made from polyester filament are strong and do not absorb water. Fabric properties can thus be modified by using combinations of fibres. Fibres are blended for aesthetic and special effects, for economy and to give fabrics of superior performance in use. For the production of yarns containing different fibres, blending takes place during the opening, carding or drafting operations. Alternatively, yarns of different fibres can be combined during fabric production. Of all fibre blends, those of cotton and polyester staple in particular have become the most important in the modern market. The polyester
component gives tensile strength, abrasion resistance and dimensional stability to the fabric, while the cotton provides water absorbency, comfort and reduced pilling (Section 4.3.2).

2.4 PREPARATION FOR DYEING

Newly constructed textile materials are called grey or greige goods. At this stage, the overall manufacturing sequence is far from complete. Natural or synthetic chemicals in fabrics can interfere with wetting and dyeing. Preparation is the series of processes used to remove them in readiness for dyeing and finishing. The objective of preparation is to remove as much of the unwanted impurities as possible from the fibres to produce a fabric that will uniformly absorb solutions of dyes and chemicals. Uniform water absorbency is more critical than complete removal of contaminants. Penetration of solutions into very compact fabrics, made from fine, high-twist yarns packed tightly together, is not necessarily rapid and is even more difficult for poorly prepared goods. Good preparation is vital for successful dyeing and printing since non-uniform absorption of dyes is immediately visible.

The unwanted chemicals are of a very diverse nature. They are often processing aids such as lubricants or warp size. Fabrics containing wool and cotton, however, may contain substantial amounts of natural impurities that impede uniform wetting. These include hydrophobic waxes that are difficult to emulsify. The preparation of wool or cotton fabrics can involve much of a textile finishing mill's resources. Some of the processes that are used in the preparation of materials made from natural fibres are discussed below.

Raw wool fibres may contain 30–50% of impurities including wool wax (often called grease), and inorganic salts (suint), as well as varying amounts of dirt, straw, excrement, and burrs. Before textile manufacturing begins, gentle scouring at 40–50 °C with a weakly alkaline detergent solution removes the bulk of these (Section 7.2.3). Mild alkaline scouring of wool fabric before dyeing eliminates lubricating oil that was added to facilitate carding and spinning. Residues of vegetable material are often apparent in grey wool fabrics. This cellulosic material does not absorb the dyes used for colouring the wool and shows up as pale patches after dyeing. Impregnating the wool with sulphuric acid solution and drying has no effect on the wool but causes hydrolysis of all cellulosic materials. Beating the dried fabric pulverises and removes the brittle cellulose hydrolysis products. The process is called carbonising (Section 7.3.3). The acid remaining in the wool serves for subsequent dyeing operations.
Table 1.2 shows a typical production sequence for manufacture of a cotton jersey. A typical preparation sequence for a woven cotton fabric might include singeing, desizing, kier boiling (alkali-boiling), bleaching and possibly mercerisation (Section 5.4.6). All these processes remove unwanted material from the cotton and improve its quality. In singeing, the fabric rapidly passes through a gas flame. This burns off any short fibres projecting from the fabric surface that abrasion has lifted from the yarns during weaving. The result is a much smoother fabric surface. The next step for most woven fabrics is desizing. Various types of starch are used for sizing cotton warps to reinforce them. Washing alone does not effectively dissolve starch sizes but digestion with appropriate enzymes will eliminate them.

The sizing washed out of a woven fabric is often discarded, so it must be cheap and have minimal environmental impact. Washing liquors from desizing contain substantial quantities of organic chemicals that cause an important pollution problem. They are mostly biodegradable, but this consumes considerable amounts of dissolved oxygen from the water, which adversely affects the local ecosystem. Increasing government requirements for effluent treatment, to prevent high values of this "biological oxygen demand" (Section 8.5.1), have spurred developments in water treatment, and in the use of sizes that can be recovered from the washing liquors and re-used. For cotton/polyester warps, it is now common to use polyvinyl alcohol (PVA) for sizing. This is a water-soluble polymer removed by simple washing in hot water and then possibly recovered by hyperfiltration membrane techniques [5]. Newer no- or low-wetting processes include solvent desizing, sizing with molten, water-soluble polymers, and the application of size in foams.

In kier boiling (alkali-boiling) of cotton materials, the cotton is heated with dilute NaOH solution under pressure for several hours, in the absence of oxygen (Section 5.4.3). Small quantities of detergents and solvents are frequently added. The objective is to eliminate the waxy cotton cuticle, the natural oils, waxes and proteins, as well as various salts and soluble cellulose and carbohydrate derivatives. It also helps to remove any size residues. The removal of the hydrophobic constituents of the cotton fibres renders them much more absorbent. In many modern plants, much faster, continuous processes of this type use higher concentrations of NaOH. They are, however, less efficient than the classical kier process because of the short treatment times.

The aim of bleaching is to remove any unwanted colour from the fibres. This may be the grey or yellow tinge of a natural fibre, or it may be a consequence of discoloration from the manufacturing processes. Bleaching is essential if high
quality white goods are being produced, or if the goods will be dyed with pale bright colours. The bleaching process also eliminates any traces of other impurities remaining from the previous preparation steps and improves the absorbency of the material for dyeing and printing. Bleaching agents are usually oxidising agents. Today, the most common bleaching agent is a stabilised alkaline solution of hydrogen peroxide (H$_2$O$_2$). This is a powerful oxidising agent that destroys the natural colouring matters present in cotton without undue oxidative damage to the fibres. Any residue of starch in the cotton is rapidly oxidised by the hydrogen peroxide used in bleaching so that the peroxide is less effective in destroying undesirable coloured impurities. In addition, residual starch can also reduce some dyes during dyeing, particularly under alkaline conditions, resulting in decreased colour depth.

Hydrogen peroxide has largely replaced solutions of sodium hypochlorite (NaOCl) as a bleaching agent, since the latter chemical requires careful pH and temperature control during bleaching to avoid oxidising the cotton. Hydrogen peroxide also offers other advantages: alkali-boiling and bleaching can be combined into one process; continuous operation is relatively easy; and thorough washing of the bleached fabric is less critical since traces of residual peroxide are less damaging than those of chlorine from sodium hypochlorite. Again, both alkali-boiling and bleaching remove unwanted contaminants from cotton material, which results in waste liquors and large volumes of washing water producing a dilute effluent with an appreciable biological oxygen demand.

Bleaching, in the sense described above, must be distinguished from the destruction of the colour of a dyed fabric, which may be necessary if it must be re-dyed. Such colour stripping usually involves solutions of reducing agents such as sodium hydrosulphite (Na$_2$S$_2$O$_4$).

Materials manufactured from artificially made fibres are much easier to prepare than those from natural fibres. Artificially made fibres are relatively clean and any spin-finish or other chemicals such as size are, by design, removable by simple washing with a detergent solution. Bleaching of artificially made fibres is not usually necessary. It is most common when a fabric made of synthetic fibres has a yellow cast from over-heating, or has picked up dirt during manufacture. The process is much milder than for natural fibres.

Since many fabrics requiring bleaching tend to be somewhat yellow, they have a stronger absorption of blue and violet light in the 400–500 nm wavelength range (Table 1.3). Certain colourless compounds absorb non-visible, near ultraviolet light at wavelengths between 300 and 400 nm and transform some of the
absorbed energy into a visible blue-violet fluorescence in the 400–500 nm region. This emission of light offsets the absorption of the fibres in this wavelength region, even producing an effect where the reflected light plus the fluorescence causes more visible light to leave the fabric surface than is apparently incident upon it. This gives the impression of a brilliant white. Such compounds are called fluorescent whitening agents or optical brighteners (Section 5.4.5). They are widely used for textiles, paper and in domestic detergents.

Cellulosic and protein fibres are particularly vulnerable to growth by microorganisms under warm humid conditions. Even though the synthetic fibres are fairly resistant to bacterial degradation, a variety of residual chemicals on the fibre surfaces can serve as nutrients for air-born micro-organisms. Rapid growth of colonies of bacteria produces coloured spots and often a distinct odour. The odour of mildew is from the growth of fungi. Once formed, the coloured pigments from bacterial metabolism are often resistant to vigorous bleaching. This problem can be minimised by ensuring that stored fabric is completely dry and relatively clean. Use of an anti-bacterial agent such as a chlorophenol or a quaternary ammonium compound will prevent this problem.

Effective preparation before dyeing is essential, no matter what the physical form of the textile material, but particularly for fabrics. Uneven preparation invariably results in unlevel dyeing. For loose dyed fibre, and to a lesser extent for dyed yarn, uneven colour is blended by the mixing that occurs in subsequent manufacturing processes. This is impossible for dyed fabric and unlevel colour usually leads to rejection of the goods. In later chapters, we will discuss the preparation of various different types of fibres and see more of the impact of preparation on dyeing processes.

2.5 DYEING AND FINISHING

Textile finishing consists of a variety of mechanical, thermal and chemical processes that improve the appearance, texture or performance of a textile material. Dyeing is usually the first finishing process. Textile materials come in a wide variety of forms and coloration occurs at almost any stage from loose fibres right through to fully formed fabrics, or even made-up articles. Coloration involves dyeing or printing in either batch or continuous processes, depending upon the quantity of material to be processed. The objective of dyeing is to colour the entire material so that the dye has completely penetrated into the fibres and the visible surface has a completely uniform colour. Good penetration of the dyes ensures
optimum fastness properties. The diversity of fibres and materials necessitates different types of dyeing machine (Chapter 12).

Mechanical finishing produces a variety of different effects (Section 25.2). In calendering, compressing the fabric between rollers under pressure produces a flat, smooth fabric surface. Raising or napping involves abrading the fabric surface using sharp steel points to break and lift fibre ends, giving a surface pile. Compressive shrinking of cotton fabrics avoids shrinkage when a fabric is wetted. Heat setting of materials made from thermoplastic synthetic fibres stabilises their shape and dimensions (Section 3.4).

The majority of chemical finishing processes are for fabrics containing cellulosic fibres (Section 25.4). The chemicals used often form polymers on heating and are also capable of reacting with the cellulose to generate crosslinks between the polymer molecules. The result of this is a fabric with improved dimensional stability to washing, and crease resistance. In addition, there are a large number of chemical treatments for fabrics that impart specific properties such as water repellence, softness of handle, flame resistance, easy soil release or resistance to bacteria.

The effects of the actual finishing processes on the colour characteristics of the material must be carefully evaluated in advance since finishing can change the shade of a dyed fabric and modify the fastness properties.

REFERENCES

CHAPTER 3

Fibrous polymers

This chapter introduces some principles of polymer chemistry and discusses the structural characteristics of the major fibrous polymers and their important properties, particularly those related to dyeing. Later chapters will provide more details on specific fibres.

3.1 POLYMER STRUCTURE

Polymers consist of molecules with very high molecular weights. The word ‘polymer’ comes from the Greek words poly meaning ‘many’, and meros meaning ‘part’. It therefore refers to the many simple structural units, linked in a continuous chain, that constitute a polymer molecule. These units are often identical. This repetitive structural pattern in polymers was not clearly recognised before about 1925, after the development of much of the technology for dyeing natural and regenerated fibres.

A monomer is a simple chemical species whose molecules link to produce a polymer. The structures of the monomer acrylonitrile (cyanoethene, 1) and the polymer that it forms (polyacrylonitrile, 2) are shown in Figure 3.1. Because the same structural motif often occurs repeatedly in a polymer molecule, the empirical formula can be deceptively simple, despite the very high molecular weight. For example, the empirical formula for polyacrylonitrile is C₃H₃N, the same as for the monomer. The molecular weight of the polymer depends upon the number of repeated monomer units, or degree of polymerisation (DP). To a good approximation, the polymer molecular weight equals the DP times the molecular weight of the monomer.

![Figure 3.1 Structures of the monomer cyanoethene (1) and the polymer that it forms, polyacrylonitrile (2)](image-url)
weight of the repeating unit. This is because the number and mass of the groups at
the ends of the long polymer molecules (–OSO$_3^-$ in the case of 2) are negligible in
collection with the total number and mass of the repeating units. The end groups
in a polymer come from the monomer itself, or from the initiators used in the
polymerisation process. Polycrylonitrile often has sulphate (–OSO$_3^-$) and
sulphonate (–SO$_3^-$) end groups derived from the sodium persulphate (Na$_2$S$_2$O$_8$)
and bisulphite (NaHSO$_3$) that initiate the polymerisation of acrylonitrile. Ionic
end groups in a polymer have an important role in ion exchange dyeing processes
(Section 1.1.2).

The repeating units and end groups define the molecular structure of a polymer.
The next structural level involves the distribution of the values of the molecular
weight or DP. Unlike most chemicals, in which all the molecules are identical, the
molecules in a polymer have varying numbers of repeating units resulting in a
distribution of molecular weights. At an even more refined level, the arrangement
of the polymer molecules in three dimensions, and the possibility that their
alignment and interaction can lead to the formation of ordered crystalline regions,
becomes relevant.

Because polymers consist of molecules with high molecular weights, they are
involatile and often insoluble in common solvents. They have poorly defined
melting points, or decompose before melting. Not all polymers form fibres. Those
polymers that do, have a high molecular weight and long, unbranched, linear
molecules with regular structures. Alignment of the long polymer molecules along
the fibre axis results in intermolecular attractive forces and the formation of
crystalline regions. This promotes fibre strength. Although intermolecular bonding
is weak, these attractive forces, between aligned neighbouring molecules along a
significant portion of their length, provide resistance to deformation and chain
slippage.

Fibrous polymers, with a minimum of chain branching, are made from
bifunctional monomers. Vinyl compounds, such as acrylonitrile, are bifunctional
since two new bonds form to each monomer unit during polymerisation. The
polymerisation of vinyl compounds can be initiated by free radicals, cations or
anions. A free radical is a reactive chemical species possessing an unpaired
electron. Radical polymerisation is a chain reaction. The initially generated free
radical rapidly adds a monomer molecule but each addition regenerates the free
radical reactive site at the end of the growing polymer molecule. Termination of
the growing chain occurs when two radicals couple together or react by transfer of
a hydrogen atom. Cationic and anionic vinyl polymerisation are similar, except the
reactive sites are now ionic and the polymerisation is terminated by addition of appropriate chemicals.

Such chain reactions are usually very fast and the product isolated from an interrupted process consists of only residual monomer and fully formed polymer of high DP. Figure 3.2 illustrates the radical polymerisation of acrylonitrile. Polymers made by polyaddition invariably have a skeletal chain composed only of carbon atoms and the repeating unit in the polymer has the same types and numbers of atoms as the monomer.

\[
\begin{align*}
O_3S&O^+ + CH\equiv CH \rightarrow O_3S-CH=CH_2^+ + CH\equiv CH \\
O_3S-CH=CH_2^+ + CH\equiv CH &\rightarrow O_3S-CH=CH=CH_2 + \text{polymer}
\end{align*}
\]

Figure 3.2 Radical polymerisation of acrylonitrile

The formation of esters and amides from carboxylic acids and their derivatives involves the elimination of a simple product of low molecular weight, such as water. These are called condensation reactions (Scheme 3.1). Nylon and polyesters are made by polycondensation. These polymers have long chains containing atoms other than carbon derived from the functional groups of the monomers. Unlike the polyaddition chain reaction, polycondensation involves the stepwise formation of species of gradually increasing molecular weight. Figure 3.3 shows the formation of a nylon polyamide by such a process starting from adipic acid (1,6-hexanedicarboxylic acid) and hexamethylenediamine (1,6-hexamethylenediamine). Because the monomers are both bifunctional, the polymer chain has no lateral groups.

\[
\begin{align*}
RCO_2H + CH_3OH &\rightarrow RCO_2CH_2 + H_2O \\
RCO_2H + CH_3NH_2 &\rightarrow RCONHCH_2 + H_2O
\end{align*}
\]

Scheme 3.1
The number of reactive functional groups of the monomer or monomers determines the degree of branching along the molecular chain of the polymer they produce. For example, a polyester forms on heating a mixture of a dicarboxylic acid such as terephthalic acid (1,4-benzenedicarboxylic acid) and a diol such as ethylene glycol (1,2-ethanediol). These monomers are both bifunctional and an unbranched linear polymer molecule results, suitable for fibre formation (Figure 3.4). This polymer is thermoplastic. This means that the solid polymer will soften and deform easily when heated to a temperature below its melting point, but it will re-harden on cooling.

If an anhydride, such as phthalic anhydride (cyclic anhydride from 1,2-benzenedicarboxylic acid), is reacted with a triol, such as glycerol (1,2,3-propanetriol), the trifunctional alcohol allows extensive chain branching during the polymerisation reaction. By using a 3-to-2 anhydride-to-triol mole ratio, which gives the same initial numbers of hydroxyl and carbonyl groups, the product is a highly branched network polymer (Figure 3.4). When a partially formed polymer of this type is heated, it will initially soften, like a thermoplastic polymer, but the chain-linking process then continues as uncombined hydroxyl and carboxyl groups react. The polymer becomes even more crosslinked and more rigid. Such materials are called thermohardening or thermosetting. Ultimately, the entire sample of solid polymer may consist of a single giant molecule. Thermosetting polymers are very useful for heat moulding of hard plastic articles. Although such polymers are not crystalline, the molecules are so effectively linked that a mechanically strong material results. They are not used as fibres.

\[
\begin{align*}
HO_2C(CH_2)_4CO_2H & + H_2N(CH_2)_6NH_2 \\
& \rightarrow HO_2C(CH_2)_4CONH(CH_2)_6NH_2 + H_2O \\
HO_2C(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CO_2H & + H_2O \\
& \rightarrow HO_2C(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CONH(CH_2)_6NH_2 + (2n-1) H_2O
\end{align*}
\]

Figure 3.3 Formation of a nylon by stepwise polycondensation
Some fibrous polymers have a single type of repeating unit and are called homopolymers. Cellulose (in Figure 3.5), for which the repeating unit consists of two linked glucose units (cellobiose), is an example. Others, obtained from a mixture of two or more monomers, are called copolymers. The properties of a copolymer depend upon the relative amounts and the sequence of the different monomer units present in the polymer chains. In many synthetic copolymers, two monomers are present. These may have a regular alternating or random sequence along the polymer chain. In other types, the monomer units may be present in
alternating long sections either along the main chain (block copolymer), or as branches of one type grafted to the main chain of another (graft copolymer) (Scheme 3.2). The three latter types all have textile applications. Proteins are complex copolymers formed by polycondensation of mixtures of α-amino acids. These are carboxylic acids with an amino group attached to the carbon atom next to the carboxyl group. Each protein has a specific sequence of different amino acid units in the polymer chain (Scheme 3.3). There will usually be one amino and one carboxylate end group derived from the appropriate terminal amino acids.

\[
\begin{align*}
\text{Regular alternating copolymer} & \\
\text{Random copolymer} & \\
\text{Block copolymer} & \\
\text{Graft copolymer} & 
\end{align*}
\]

\[
\begin{align*}
(n + 2)H_2N-\text{CH-CO}_2H \\
H_2N-\text{CH-CO}(\text{NH-CH-CO}_2H)_{n-1}-\text{CH-CO}_2H + (n + 1)H_2O
\end{align*}
\]

Scheme 3.3

Whatever the chemical structure of a fibrous polymer, the nature of the groups along the molecular chain and the end groups determine its chemical and dyeing behaviour. As outlined above, an apparently homogeneous sample of a polymer consists of a variety of molecules of varying length and mass. The molecular weight is not a constant, as for most compounds, but varies depending upon the distribution of polymer molecule sizes. This is known as polymolecularity.
The molecular weight of a polymer may be defined in various ways. The usual molecular weight is the number average molecular weight (Eqn 1). This is the mass of an Avogadro’s number of molecules \( (6.023 \times 10^{23}) \). Molecular weight determinations based on end group analysis or the colligative properties of polymers give this type of molecular weight, from which the average value of the DP is obtained. Polymer molecular weights may also be defined by a weight average (Eqn 2). This type of molecular weight is obtained from measurements of light scattering. The definitions of these two types are

\[
\text{Number average MW} = \frac{\sum (n_i \times m_i)}{\sum n_i} \quad (1)
\]

\[
\text{Weight average MW} = \frac{\sum (w_i \times m_i)}{\sum w_i} \quad (2)
\]

where \( n_i \) and \( w_i \) are, respectively, the number of moles and weight of each type of polymer molecule of molecular weight \( m_i \). Of the two, the weight average molecular weight is usually higher.

### 3.2 MOLECULAR ORGANISATION IN FIBRES

Many properties of fibrous polymers reveal that the molecular chains run along the main fibre axis with a considerable degree of alignment. When the polymer molecules are parallel and closely spaced, intermolecular attractive forces operate and the regular ordering of the chains leads to crystalline behaviour. A crystal is a solid in which there is a regular repetition of the atomic arrangements in three dimensions. When a beam of X-rays is directed at a crystal, and the diffracted beams detected on a photographic film, a pattern of dots is found, characteristic of the crystalline substance. The regular repetition of atomic positions produces sharp diffraction patterns. Less crystalline and non-crystalline materials give diffuse diffraction patterns, or no pattern at all. Analysis of the positions of the dots allows calculation of the distances between repeated planes of atoms in the crystal. The intensities of the diffracted beams producing the dots provides information about the relative electron densities around atoms in the crystal. X-ray
Diffraction thus identifies the atoms and their relative positions. It is a powerful method for determining the structures of molecules.

Diffraction of an X-ray beam impinging on an extended fibre at right angles to its axis often gives a pattern of dots characteristic of a crystal, but accompanied by the more diffuse pattern characteristic of amorphous materials. Many fibres are partly crystalline in regions where chain orientation is high and the closely spaced chains interact. Fibres also have zones where the arrangement of the molecular chains is completely random. There will be varying degrees of order between these two extremes. The overall conclusion is that the polymer chains may pass through several different crystalline regions and also through zones with increasing degrees of disorder. In the crystalline regions, the polymer chains are aligned in close contact with either neighbouring chains, or with another part of the same chain that is folded back on itself. Some models are shown in Figure 3.6.

Fibre crystallinity has a considerable influence on its mechanical and chemical properties. Usually, the more crystalline the fibre, the harder it is to extend (higher elastic modulus) and to break (higher tensile strength). It is difficult for chemicals to penetrate into the crystalline regions of a fibre since this would require breaking the intermolecular bonds responsible for crystallite formation. Even the small molecules of water may be excluded from the crystalline regions. It is the more amorphous regions of the polymer structure that are readily accessible to

---

Figure 3.6 Some models of molecular organisation in fibres: (a) fringed micelles; (b) fringed fibrils; (c) folded chains
chemicals and it is here that dye molecules can penetrate. The amorphous regions are those zones where the fibre is weaker but that provide flexibility and accessibility to chemicals. The most crystalline fibres will be those with regularly repeating structural units along the chains, aligned in proximity so that intermolecular bonds stabilise the three-dimensional structure. Copolymers will generally be more amorphous than homopolymers, and polymers with large irregular branching groups will have difficulty crystallising. Fibrous polymers are often insoluble in common solvents, or only dissolve very slowly after considerable swelling. Their solubility depends upon the degree of crystallinity and the molecular weight.

The extent of chain orientation along the filament axis influences the degree of crystallinity. Orientation increases on extending the filaments under tension. The process is called drawing. It causes the molecular chains to slide by one another as the plastic filament extends and increases in length. This promotes chain orientation and therefore crystallisation. Drawing is an important operation for improving the mechanical properties of artificially made filaments.

All fibres exhibit their own characteristic morphology. They may have crystalline and amorphous zones. They may be non-porous, or have porous structures in which the fibres themselves are constituted of bundles of much smaller fibre-like units called fibrils. They may have pronounced differences between the fibre skin and core. Molecular organisation in fibres has many different forms and fibres cannot be considered to be homogeneous materials. The following chapters review the morphology and properties of different types of individual fibres.

3.3 INTERMOLECULAR FORCES

In the preceding section, we saw that polymer molecules will form crystalline structures if they arrange themselves so that the position of each type of atom has an exact repeated pattern in three dimensions. The proximity of the molecules allows intermolecular attractive forces to operate that stabilise the crystalline arrangement. What is the nature of this kind of force? It is a kind of bonding. Like covalent and ionic bonding, these forces originate from the mutual attraction of negatively charged electrons in an atom in one molecule for positively charged nuclei of atoms in a neighbouring molecule. These attractive forces, however, only operate over short distances and are generally quite weak. They therefore lack the relative stability of ionic and covalent bonds. These weak intermolecular bonding
forces are responsible for many phenomena in textile chemistry, including the coherence of the crystalline regions in fibres, and even the dyeing process itself.

Ionic bonds are the simplest to understand since they involve the attraction of oppositely charged ions that have atoms with more or less than the required number of electrons for electrical neutrality. In wool, ionic bonds between adjacent protein chains arise from interaction between carboxylate anions attached to one chain and ammonium cations to another (Figure 3.7). As we saw in Section 3.1, covalent bonds between polymer chains lead to the formation of network structures that are not conducive to fibre formation. The only fibrous polymer with significant covalent inter-chain bonds is wool. These crosslinks come from the incorporation of the double amino acid cystine into two separate protein chains (Figure 3.7). Such inter-chain bonding is deliberate during crease-resist finishing of cotton materials. The crosslinked cellulose chains are less easily displaced when the material is folded (Section 25.4.1).

Another type of much weaker intermolecular bond is that occurring between permanent dipoles. Such dipoles arise from the unequal sharing of electrons in covalent bonds between atoms of different electronegativity. The result is a bond with one end somewhat electron deficient and therefore more positive than the other electron rich and relatively negative end. The separated partial charges represented by $\delta^+$ and $\delta^-$ constitute a dipole, and attraction between the opposite ends of the dipoles in molecules results in weak bonds. Figure 3.8 illustrates

![Figure 3.7 Some inter-chain bonds between protein chains in wool](image-url)
dipole–dipole attraction between the cyano groups in polyacrylonitrile. In some cases, molecules with permanent dipoles can exert attractive forces on neighbouring non-polar molecules by polarising their electrons. The electropositive end of a dipole attracts and polarises the electrons in a bond between two atoms in a neighbouring molecule while the electronegative end of the dipole becomes attracted to the neighbouring atom’s more exposed nucleus. Dipole–dipole and dipole-induced dipole bonds are weak and only significant when molecules are in close contact. They are therefore continually being broken and reformed as molecules collide.

A special kind of dipole–dipole interaction occurs between the pronounced dipoles of covalent bonds between electronegative atoms such as oxygen or nitrogen and a hydrogen atom. This type of bond is called a hydrogen bond because the interaction or bond energy is about 10 times stronger than that of a typical dipole–dipole bond (See Table 3.1). Even at its boiling point, water is a highly associated liquid in which clusters of water molecules associate together by hydrogen bonding (Figure 3.8). Cellulose is a polyalcohol. It is insoluble in water because water molecules are unable to penetrate into the crystalline regions and break the hydrogen bonds between the hydroxyl groups of the ordered cellulose molecular chains. Hydrogen bonds between amide groups are important in proteins and nylon (Figure 3.8).

The weakest intermolecular forces are those that exist between all types of molecules, even those without particular ionic or dipolar sites. These forces involve the attraction of the electrons of an atom in a given molecule for the partially exposed nucleus of an atom in a neighbouring molecule. They are a
Table 3.1 Approximate energies of various types of chemical and intermolecular bonds

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Typical bond energy (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>700</td>
</tr>
<tr>
<td>Covalent</td>
<td>400</td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>40</td>
</tr>
<tr>
<td>Dipole–dipole</td>
<td>5</td>
</tr>
<tr>
<td>Dispersion forces</td>
<td>5</td>
</tr>
</tbody>
</table>

consequence of the unequal distribution of electrons around atoms at any given instant. The attraction will only exist for a short time since the electron arrangement is continuously in flux, the atoms are in constant motion, and the energy of interaction decreases dramatically with increasing molecular separation. These instantaneous attractions are called dispersion or London forces. They have a significant influence on molecular properties. Even the completely non-polar polyethylene has a fairly high melting point because of the cumulative effect of dispersion forces at many locations along the polymer molecules. The weak dipole and dispersion intermolecular forces discussed above, often collectively referred to as van der Waals forces, are responsible for the non-ideal behaviour of all gases and are intimately involved in the interaction between dye and polymer molecules during dyeing.

3.4 THERMAL PROPERTIES OF POLYMERS

The different polymers used as fibres have varied responses to heat. Natural polymers, such as cellulose and proteins, have high average molecular weights but invariably decompose before they reach their melting temperature. During drying or curing, temperatures as low as 150 °C can cause fabrics from natural fibres to become yellow and more brittle. The thermal damage is greater the longer the exposure to the high temperature. The consequences of this are quite obvious on dry pressing wool or cotton fabrics with an over-heated iron.

Synthetic fibrous polymers consist of unbranched molecules. They are usually thermoplastic. This means that materials made from them tend to soften and deform on heating, but become rigid again on cooling. Cellulose diacetate and acrylic fabrics require careful treatment during dyeing to avoid deforming the fabric structure. They become quite plastic at temperatures below 100 °C. A hot
iron can melt cellulose diacetate and produce a hole in a fabric made from it. To avoid creasing and over-extension of the fabric, cellulose diacetate materials must be dyed at no higher than 85–90 °C, in open width, and with a minimum of tension. High-bulk texturised acrylic fibres usually give fabrics with good crease resistance. Such materials are, however, quite plastic when hot and excessive tension must be avoided during dyeing. Rapid cooling of the goods by flooding a hot dyebath with cold water causes a sudden change from plastic to rigid behaviour and will set creases in the fabric. Slow cooling of the bath and gentle motion of the material are essential.

For thermoplastic materials, the glass transition temperature (T_g) is that at which molecules in the solid, glassy state, characteristic of the amorphous zones of the polymer, have sufficient energy for entire segments of the polymer chains to become mobile. At temperatures below T_g, the molecules are frozen in position and the polymer is rigid. Above this temperature, the available thermal energy is sufficient to cause bond rotations allowing segments of the polymer chain to move into new positions. This results in significant changes in the physical properties of the polymer. For example, above the T_g, the specific volume of a thermoplastic polymer increases more rapidly with increasing temperature and the stress required to deform a sample of polymer will be less than at lower temperatures. The changes in such properties can be used to measure T_g, although the values obtained tend to be dependent on the actual experimental conditions (Figure 3.9).

\[ T_g \]

Figure 3.9 Variations of specific volume and initial elastic modulus with temperature
Usually, $T_g$ is not a sharp, well-defined temperature and the changes in temperature dependent properties occur over a range of values around $T_g$.

As the temperature increases, the volume of a rigid polymer sample expands in the usual manner. This involves proportionate increases in the actual volume occupied by the molecules, as they vibrate, and that of the voids between molecules in the amorphous zones and around the chain ends. These voids are called the polymer free volume. Molecular packing in the crystalline state is very compact and ordered so the free volume is a characteristic of the amorphous regions of a polymer. At temperatures above the $T_g$, bond rotations allow sections of the polymer chains to move into voids with increasing ease and thus create new voids. Segmental motion increases rapidly with increasing temperature above $T_g$, increasing the free volume and the coefficient of expansion. Eventually, on continued heating, chain mobility becomes so pronounced that the true liquid state forms at the melting point.

The $T_g$ has considerable significance in textile processing. Two of the most important processes that depend upon a synthetic filament having some plasticity are drawing and texturising. In drawing, newly formed continuous filaments are first wrapped several times around a rotating feed cylinder, and then around a second one running at 4–5 times the linear speed of the first. Provided that the polymer is not at a temperature too far below its $T_g$, the stress applied by the faster running cylinder causes the polymer molecules to unfold and slide by each other in the filament as it extends in length. This aligns the molecules in proximity, increasing the degree of molecular interaction and therefore the strength of the filament. It is in this way, in varying degrees, that the orientation of the molecules of all artificially made fibres improves the filament tenacity and rigidity. If the filament is at a temperature too far below $T_g$, it is too rigid to be drawn uniformly and may even break on application of stress. At temperatures around $T_g$, the filament is sufficiently plastic for drawing to be practicable.

In texturising, the filaments are deformed by application of a transverse stress. The objective is to buckle the initially straight filament so that it develops a permanent crimp. Several technologies for texturising depend on bending the filaments while they are warm and plastic, and then stabilising the crimp by rapidly cooling. The degree of crimping determines whether the fabric handle will be smooth or rough. Texturising increases the bulk of an assembly of filaments trapping more air and improving the insulating power.

When a fabric made from thermoplastic fibres such as nylon or polyester is heated to a temperature around $T_g$, the mobility of the polymer chains allows the
relaxation of any tension. This causes deformation of the shape of the material, usually with considerable shrinkage. It can occur in hot water. The tensions in the polymer molecules can be present from the original drawing of the filaments immediately after their production, from texturising, or from stresses introduced during winding, weaving or knitting. The strained polymer molecules, held in place in the rigid, glassy structure, become mobile once the temperature is above $T_g$. Their movement in the plastic condition eases the stress on them.

Fabric deformation or shrinkage on heating is minimised by a process called heat setting. The speed and separation of two moving parallel chains, which grip the fabric edges as it passes through the setting oven, determine the final dimensions of the relaxed fabric. The setting temperature used is above $T_g$. In heat setting, inter-chain bonds, such as hydrogen and dipole bonds, break. This allows the molecular chains to move and adopt new, stress-free positions. New intermolecular bonds then form with the fabric in a relaxed condition at the setting temperature. After cooling, the polymer molecules in the filaments become frozen in place. The new bonds are stable up to the heat setting temperature. The reorganised internal polymer structure, and the material’s dimensions, will be stable, provided the material is not heated to temperatures above the heat setting temperature.

Most synthetic fibres cannot be dyed at temperatures below the $T_g$ existing under the dyeing conditions. This is because the dye has no mechanism for diffusion into the fibre. The dye can only penetrate into the polymer structure when motion of the polymer chain segments creates sufficient free volume with adequate mobility to allow dye molecules to penetrate into the polymer. The temperature at which polymer chain segment mobility allows a significant increase in the rate of dye diffusion is called the dyeing transition temperature, $T_d$. Dyeing of thermoplastic synthetic fibres always requires temperatures above $T_d$. This poses no problems with nylon and acrylic fibres that have quite low values of $T_d$. The $T_p$ of polyester, however, is around 80–90°C. The diffusion of dyes into polyester filaments is therefore quite slow at 100°C and dyeing must be carried out at temperatures well above this, by dyeing in water above 100°C under pressure. Because of the higher $T_p$, polyester drawing requires warm filaments. Cellulosic and protein fibres do not have a $T_p$. Unlike most synthetics, natural fibres are quite porous, being constituted of many long fibrils laid side by side along the fibre axis. Dyes are able to penetrate into the bulk of these fibres along the many narrow channels permeating them.
This introduction to natural and synthetic polymers briefly outlines the nature of their chemical structures and molecular arrangements. The nature of intermolecular attractive forces and the glass transition temperature were introduced because so many of the properties of synthetic polymers, including their dyeing behaviour, depend upon them. This chapter therefore sets the stage for the following discussions of specific fibres.

REFERENCES

Exact text cannot be provided without the ability to view the actual image content.
Figure 3.4, produced from terephthalic acid (1,4-benzenedicarboxylic acid) and ethylene glycol (1,2-ethanediol), came on the market in 1948, followed by polyacrylonitrile copolymers in 1950.

\[
\text{NH}_2\text{(CH}_2\text{)}_5\text{CO}_2\text{H} + \text{NH}_2\text{(CH}_2\text{)}_5\text{CONH(CH}_2\text{)}_5\text{CO}_2\text{H} \rightarrow \text{NH}_2\text{(CH}_2\text{)}_5\text{CO} \text{NH(CH}_2\text{)}_5\text{CO} \text{NH(CH}_2\text{)}_5\text{CO}_2\text{H} + \text{H}_2\text{O}
\]

Scheme 4.1

All synthetic fibres are produced by extrusion of continuous filaments, either of the molten polymer or of its solution in a solvent, through tiny holes in a metal plate. This is called a spinneret. Extrusion of polymer filaments is called spinning, but must be distinguished from the spinning of yarns of staple fibres by drawing and twisting. In melt spinning, the solid polymer filaments are obtained by rapidly cooling the extruded molten polymer, whereas in solution spinning they remain after evaporation of the solvent, or coagulation in a bath of suitable chemicals.

4.2 NYLON FIBRES

4.2.1 Production of nylon 6.6

Heating the salt of adipic acid and hexamethylene diamine (1, Figure 4.1) in concentrated aqueous solution in the presence of a little acetic acid gives nylon 6,6, or polyhexamethylene adipamide. Once most of the volatile diamine has reacted, water is gradually removed by distillation. Finally, the molten mixture is heated to 260 °C under nitrogen to avoid oxidation. Figure 3.3 illustrates the sequence of condensation reactions. The final liquid polymer is extruded as a thick ribbon, cooled to solidify it, and cut into chips. Using the exact 1:1 stoichiometric ratio of the monomers (from the diacid-diamine salt), and forcing the polycondensation to a high conversion, are important for obtaining the desired high molecular weight of the product. Low values of molecular weight give weak filaments but too high a value results in a more viscous molten polymer that is difficult to extrude. Addition of a small amount of acetic acid in the polymerisation assists in controlling the final molecular weight of the nylon. The added acetic acid functions as a chain stopper by
reducing the number of terminal amino groups in the polymer (Scheme 4.2). The nylon is then less likely to undergo further polycondensation when molten.

The nylon chips are re-melted and the molten polymer extruded to form fine filaments. The melting point of nylon 6.6 is around 250 °C. Melt spinning directly from the polymerisation reactor requires very long holding times at a temperature above the melting point. This changes the polymer molecular weight distribution, as free amino and carboxylic acid groups can continue to react. There is also the risk of thermal and oxidative degradation causing yellowing and liberation of carbon dioxide gas. In melt spinning from nylon chips, the molten polymer is kept under nitrogen. The amount of liquid is so small that the polymer is only molten for a short time. The hot liquid nylon is filtered to prevent particles of polymer from blocking the holes in the spinneret. It is also important to avoid gas bubbles in the molten polymer since their passage through a spinneret hole gives a broken filament. After cooling, the nylon filaments are bone dry and are conditioned in steam before winding onto bobbins. This avoids the slight expansion that occurs when dry filaments absorb water from the atmosphere and which results in unstable bobbins.

The next process is drawing. The nylon filaments are drawn by passing them around and between sets of rotating cylinders of increasing speed (Section 3.4). The newly extruded filaments are relatively easy to extend to about four-fold their original length before the stress begins to increase sharply. Drawing decreases the filament diameter. The elongation causes folded polymer chains to unfold and the chains to slide past each other, gradually increasing the degree of orientation of the polymer molecules along the filament axis. Because of this, there is an increase in crystallinity, giving higher tenacity and reduced elasticity. The glass transition temperature of completely dry nylon 6.6 is probably over 100 °C, but drops considerably in the presence of small amounts of absorbed water. Water will form
hydrogen bonds with both the hydrogen and oxygen atoms in the amide groups, breaking the existing hydrogen bonds between amide groups in different polymer chains (Scheme 4.3). The chains therefore have greater mobility, since the water is acting as a plasticiser. In air at room temperature, the filaments are sufficiently plastic for cold drawing.

Nylon 6.6 fibres are available in many diverse physical and chemical forms for different applications. These include mono-filaments, multi-filaments, regular and high tenacity types (the latter being more extensively oriented by drawing), and a number of varieties with different dyeing characteristics (Section 4.2.4).

Changing the shape of the holes in the spinneret gives filaments with different cross-sections. Filament cross-sections with flatter surfaces, such as trilobal sections, reflect more light and give high lustre and a smooth silky handle. Titanium dioxide pigment added to the molten nylon before extrusion gives filaments with reduced or no lustre. Filaments for staple nylon, which will be blended with other fibres such as cotton, will normally have been texturised before cutting the filaments into short lengths. The crimp improves the adhesion between fibres in a spun yarn. After spinning, chemicals such as lubricants and anti-static agents are applied to the filament surface. Scouring before dyeing effectively removes these spin finishes.

Both nylon 6.6 and 6 are susceptible to degradation by ultraviolet light resulting in yellowing and loss of strength. Lustrous filaments have better ultraviolet resistance than those dulled by pigmentation with titanium dioxide. Ultraviolet stabilisers, which protect the polymer by strongly absorbing ultraviolet light and converting the energy into heat, are added to the nylon before spinning.

4.2.2 Production of nylon 6

Nylon 6 is manufactured similarly to nylon 6.6 by heating caprolactam with a little water, a chain stopper such as acetic acid, and an acid catalyst, gradually removing

---

Scheme 4.3

---
the water by distillation. The water initially hydrolyses some caprolactam to 6-
aminohexanoic acid. This then reacts with caprolactam, opening the ring and
generating a new amino end group. This amino group then undergoes the same
addition reaction with more caprolactam so that the forming polymer chain always
has amino and carboxylate end groups (Scheme 4.1). The polyamide obtained is in
equilibrium with about 10% of unreacted monomer and low molecular weight oligomers. These are removed by water washing after extrusion.

The melting point of nylon 6 is about 215 °C. Molten nylon 6 is therefore more
stable than molten nylon 6.6. The lower melting temperature of nylon 6 allows
filament spinning directly from the polymerisation reactor without undue
decomposition or changes in properties. Nylon 6 may also be extruded as a thick
band, chipped and processed as for nylon 6.6. The chips are preferred for continuous
filament spinning because the denier is more uniform. Direct spinning from the
reactor is satisfactory for staple fibres where denier variations are less important
because the fibres will be well-blended. As for nylon 6.6, the conditioned filaments
have a sufficiently low Tg to be cold drawn to increase the molecular orientation and
crystallinity, giving improved mechanical properties.

4.2.3 Properties of nylon 6.6 and 6

The numbers of repeat units along the polymer chains of nylon 6.6 and nylon 6 are
about 65 and 130, respectively, corresponding to molecular weights of about
15 000 g mol⁻¹. They have similar chemical structures and therefore many
common characteristics and end-uses. There are, however, some important
distinctions.

These nylons are not totally hydrophobic and do absorb water at room
temperature. The standard regains of both nylon 6.6 and 6 are around 4%. These
relatively low moisture contents do not allow effective dissipation of accumulated
static electric charge, which causes handling and soiling problems. This must be
controlled by application of appropriate anti-static chemicals to the fibres, and
grounding devices on machinery may be necessary.

Both types of nylon contain weakly basic amino and weakly acidic carboxylic acid
end groups. The number of terminal amino groups in a nylon can vary from 30 to
100 mmol kg⁻¹. If each nylon molecule with a molecular weight of 15 000 g mol⁻¹
had one amino end group, the number of such groups would be 67 mmol kg⁻¹. The
actual number is usually less than this since some terminal amino groups will have
reacted with the acetic acid chain stopper (Scheme 4.2). Therefore, the number of
carboxylic acid groups in a typical nylon (90 mmol kg⁻¹) is usually greater than the
number of amino groups, but, in a regular nylon, the sum of amino (40 mmol kg\(^{-1}\)) and acetylamino end groups (55 mmol kg\(^{-1}\)) approximately equals that for the carboxylic acid groups.

Nylon is usually dyed with anionic acid dyes in weakly acidic solution. This process can be considered as a simple anion exchange process in which a counter ion such as acetate, associated with a protonated amino group in the nylon, is exchanged for a dye anion (Scheme 4.4). In many instances, the number of available ammonium ion groups limits the amount of anionic dye taken up by a nylon fibre and direct dyeing of deep shades and blacks becomes impossible. On the other hand, the amino and carboxylic acid groups do not influence dyeing with disperse dyes. The nylon acts as a solid solvent in which the disperse dye is soluble, so the nylon extracts it from the aqueous bath. This mechanism is identical to that for dyeing cellulose acetate and other synthetic fibres with disperse dyes (Section 1.1.2). Nylons, however, tend to absorb many kinds of dyes to some extent, so that staining of the nylon component in fibre blends by dyes intended for the other fibres is a problem. Such staining is undesirable since stained fibres have poor fastness properties and may subsequently be difficult to dye on shade with the correct type of dye selected for them.

Scheme 4.4

Nylons are polyamides and are therefore susceptible to hydrolysis. They are hydrolysed by boiling solutions of strong acids. For this reason, dyeing is rarely carried out at pH values below 3.0. They are resistant to short treatments with hot alkaline solutions.

Nylon 6 and nylon 6.6 are strong fibres with moderate elasticity, even after drawing. Nylon 6 has a somewhat lower elastic modulus and better elastic recovery than nylon 6.6 and therefore gives more flexible fabrics of softer handle. Both nylons are available in high tenacity variations for industrial uses. In fact, the mechanical properties can be varied considerably by changes in the polymerisation and drawing conditions.

Nylon fibres and filaments appear remarkably uniform in appearance. This can be misleading. Each nylon filament has a particular heat and tension history arising
from polymer production and textile manufacturing processes. We have already seen that heating nylon to a temperature above its $T_g$ causes rearrangement of the molecular chains in the amorphous regions of the material, and a reorganisation of the intermolecular attractive forces (Sections 3.4 and 4.2.1). Because the nylon polymer molecules are still potentially reactive, strong heating may establish a new polycondensation equilibrium with a new molecular weight distribution and more or fewer amino end groups. Level dyeing with anionic dyes is difficult if thermally induced changes in polymer structure have not been uniform. Filaments under tension undergo a drawing effect that can change the orientation and crystallinity of the polymer. During weaving and knitting, nylon filaments under prolonged mild stress elongate but do not recover their original length on releasing the tension. Variable mechanically and thermally induced stresses can build up in the filaments and may not relax until the fabric is subsequently wetted or heated. This can result in undesirable changes in shape from the shrinkage of filaments. Processes such as drawing, bulk (texturising) and heat setting, in which it is difficult to ensure uniform treatment, can result in physical and chemical variations along the length of filaments that only become visible after dyeing with anionic acid dyes. These effects are the origin of a phenomenon called barré. The extreme case of this is the occurrence of individual filaments in a woven or knitted nylon material that have absorbed less dye than neighbouring filaments and show up as a pale streak on the material surface.

Heat setting of nylon materials may be carried out under dry conditions in hot air at 190 °C for nylon 6, or 205 °C for nylon 6.6. Alternatively, setting is achieved in steam at 120 or 135 °C, respectively. As explained in Section 3.4, this allows relaxation of any strain in the filaments or fibres introduced during manufacture and improves the wrinkle resistance and dimensional stability of a material, avoiding shrinkage when it is heated in water, as in dyeing, or in hot air as in drying. It also stabilises the yarn twist and filament crimp. Heat setting is carried out after dyeing unless the fabric has a tendency to form crease marks.

It is very difficult to obtain accurate data for the $T_g$ values of nylons. In particular, absorption of small amounts of water significantly depresses the value of $T_g$, but it also depends on the extent of drawing and the method of heat setting, and therefore on the degree of orientation and crystallinity. Nylon 6 has a lower $T_g$ than nylon 6.6 for comparable conditions. It also has a less compact internal structure. At a given temperature, nylon 6 will usually have greater and more mobile free volume and therefore it usually has a higher rate and degree of dye absorption. Although dyes diffuse more rapidly into nylon 6 fibres during dyeing, they also diffuse out more
readily on washing. This type of generalisation is useful but it may not always be valid as there are considerable variations of each type of nylon, all with different dyeing and fastness characteristics.

4.2.4 Other nylons

Nylon is also used for a number of speciality fibres such as ‘core and mantel’ and bicomponent varieties (Figure 4.2). In the former, a nylon filament core may be wrapped with a different filament or staple fibre. Combining extruded streams of two different molten nylons, with different characteristics, during spinning produces bicomponent fibres. They form a single filament but have the different nylons on each side. These show different shrinkage when wetted or heated producing a crimped filament. In Chapter 7, we shall see that wool fibres have a similar bicomponent structure that is responsible for its natural crimp.

Normal nylon filaments have a terminal amino group content of around 45 mmol kg\(^{-1}\). In addition, there are varieties with more than double this number of amino groups, which are therefore able to absorb increased quantities of anionic acid dyes. These so-called deep-dyeing nylons have amino groups that are protected during polycondensation by salt formation using p-toluene sulphonic acid or phosphoric acid derivatives.
Nylons dyeable with cationic dyes, but which resist acid dyes, have a smaller number of amino groups. They come from polymerisation of adipic acid with hexamethylene diamine in the presence of 5-sulpho-isophthalic acid (5-sulpho-1,3-benzenedicarboxylic acid, 2, in Figure 4.3). This gives a polymer with a number of anionic sulphonate groups along the molecular chain capable of binding cationic or basic dyes by cation exchange (Section 1.1.2). The deep-dyeing and basic-dyeable nylons are often used in mixtures with regular nylons for the production of two-colour or two-tone effects for carpets and some fabrics. With disperse dyes, these modified nylons usually dye to the same depth as regular nylons since the absorption of this type of dye does not involve any ionic interactions.

\[ \text{5-Sulpho-1,3-benzenedicarboxylic acid} \]

**Figure 4.3** 5-Sulpho-1,3-benzenedicarboxylic acid

### 4.3 POLYESTERS

The first commercial fibre-forming polyester was developed by Dickson and Whinfield working at the Calico Printers’ Association in England in 1941. It was produced by condensation of ethylene glycol (1,2-ethanediol) and terephthalic acid (1,4-benzenedicarboxylic acid) (Figure 3.4). Rights to manufacture this product were bought by ICI and DuPont but, because of the Second World War, fibres were not marketed until 1948. The ICI product was named Terylene and the DuPont product Dacron. This type of polyester, and several variants, are now produced by a number of manufacturers.

#### 4.3.1 Production of PET fibres

The polyester from ethylene glycol and terephthalic acid is called polyethylene terephthalate (PET). Terephthalic acid sublimes on heating and is difficult to purify because it is not particularly volatile or soluble in common solvents. The actual polymerisation process is, in fact, a transesterification reaction starting with ethylene glycol and the ester dimethyl terephthalate. The latter is easily purified by distillation. Initially, dimethyl terephthalate reacts with an excess of ethylene glycol,
in the presence of sodium methoxide as catalyst, forming bis(2-hydroxyethyl)terephthalate. Distillation removes the methanol produced. Subsequent heating induces further transesterification of the bis(2-hydroxyethyl)terephthalate forming the polymer and releasing ethylene glycol, which is removed under vacuum at 280 °C and recovered (Figure 4.4).

Filament production is very similar to that for nylon 6.6. The molten product is extruded as a thick band, cooled and chipped. The blended chips are then re-melted under nitrogen and spun into fine filaments.

The PET filaments are then drawn to about 4–5 times their original length, but at 70 °C rather than at room temperature as for the nylon. This improves the polymer chain orientation and promotes crystallisation. The \( T_g \) of PET is around 80–90 °C and less uniform filaments result on cold drawing because of their low plasticity at

\[
\begin{align*}
\text{HO}_2\text{CC} & \quad \text{O}_2\text{H} \\
& \quad \rightarrow \\
\text{2CH}_3\text{OH} & + \text{2H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O}_2\text{C} & \quad \text{CO}_2\text{H} \\
& \quad \rightarrow \\
\text{2HOCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{HOOCH}_2\text{CH}_2\text{O}_2\text{C} & \quad \text{CO}_2\text{H}_2\text{CH}_2\text{OH} \\
& \quad + \text{2CH}_3\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{2HOCH}_2\text{CH}_2\text{O}_2\text{C} & \quad \text{CO}_2\text{H}_2\text{CH}_2\text{OH} \\
& \quad \rightarrow \\
\text{HOCH}_2\text{CH}_2\text{O}_2\text{C} & \quad \text{CO}_2\text{H}_2\text{CH}_2\text{OH} + \text{HOCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{O}_2\text{C} & \quad \text{CO}_2\text{H}_2\text{CH}_2\text{OH} \\
& \quad \rightarrow \\
\text{O}_2\text{C} & \quad \text{OCH}_2\text{CH}_2\text{O}_2\text{C} + \text{CO}_2\text{H}_2\text{CH}_2\text{O}_2\text{C}
\end{align*}
\]

Figure 4.4 Transesterification reactions in the formation of PET
Like other hydrophobic fibres, accumulation of static electric charge poses some problems in handling and promotes accumulation of dirt. Anti-static spin finishes are invariably applied by the fibre manufacturer. The three major types of PET fibres are high tenacity (highly oriented by drawing), regular tenacity and staple fibre. Large amounts of texturised staple polyester fibres are produced for blending with cotton.

### 4.3.2 Properties of PET fibres

The standard regain of PET is only 0.4% and so it is a hydrophobic material. Even above the $T_g$ water penetration is minimal. Because of this, PET is unaffected by aqueous solutions of ionic dyes. The many ester linkages make it slightly polar and the fibres can be dyed with non-ionic disperse dyes as for cellulose acetate and nylon. Disperse dyes only have very limited water solubility. The dye in the bath is so finely divided that the high specific surface area of the particles allows a rapid equilibrium with the small amount of dye in true solution. This dyeing process involves the fibre extracting the small amount of dye dissolved in the aqueous bath, and more dye dissolving from the reservoir of dispersed particles. At 100 °C, the temperature is not more than 10–15 °C above the value of the $T_g$, the rate of diffusion of dyes into the polyester is very low and dyeing is slow. This is because polymer chains in the amorphous regions of the polymer still do not have adequate mobility to continually create large enough voids into which dye molecules can diffuse. Increasing the dyeing temperature from 100 °C to 130 °C, however, has a very favourable effect on the dyeing rate and dyeing of PET under pressure has become the accepted practice. Even under these conditions, however, the dyes used are invariably of small molecular size in comparison with other types of dyes to ensure an acceptable rate of diffusion into the fibres.

Dyeing at the boil is possible if the $T_g$ of the PET has been lowered by absorption of a swelling agent or carrier. Dyeing carriers are liquids present in emulsified form in the dyebath, which absorb into the PET causing swelling. They act as plasticisers and assist chain movements and create free volume. The use of dyeing carriers is now in decline because of their odour, the difficulties of removing them from the fibres after dyeing, and their adverse effect on the light fastness of some dyes.

Small amounts of cyclic oligomers, such as the cyclic trimer with three glycol and three diacid units, are always by-products of the polycondensation reaction. These oligomers cause complications in dyeing. Although they are not very soluble in water, they leech out of the polyester during high temperature dyeing. On cooling...
the dyebath there is a risk that the oligomers will deposit on the fibre and machine surfaces. For this reason, the exhausted dyeing bath is often drained while still hot.

In PET, the molecular chains are fully extended and relatively rigid because of the repeating benzene rings and the short chains separating them. PET filaments therefore have a higher elastic modulus than the nylons and are less extensible and flexible. They are therefore not suitable for the manufacture of ladies’ silk hose but provide fabrics with good dimensional stability, crease resistance and shape retention, even when wet. Such properties are also improved by heat setting. Because PET is a thermoplastic material, permanent pleats can be introduced by hot pressing. Polyester fibres are strong, easy to dry, and relatively stable to processing conditions. Much of their value is attributable to the excellent textile properties of fabrics of both 100% PET and those in which cotton and polyester are blended.

Even though PET is less extensible than nylon, unset filaments will shrink by relaxation when exposed to dry or wet heat. This is a consequence of the relaxation of tensions built up in the filaments during processing. It can cause consolidation problems with packages of yarn and uneven dimensional changes in fabrics. Materials are usually heat set before exposure to high temperatures. Steam setting can be used for packages, but hot air is preferred for woven fabrics using a pin stenter. In this, small pins mounted on two parallel continuous chains pierce and hold the selvages of the fabric as it passes through a hot air oven. The setting temperature may be as high as 220 °C. If pin marks on the selvages are undesirable, setting on heated cylinders is possible but does not allow width control. Heat setting after dyeing usually involves lower setting temperatures and care in dye selection to ensure that the non-ionic disperse dyes do not vapourise from the fibre surface.

Being an ester, PET is susceptible to hydrolysis but under normal conditions this does not limit its use as a textile. It is, for example, unaffected by treatment with cold, aqueous 20% NaOH solution in the mercerisation of cotton in cotton/polyester blends (Section 5.4.6). PET does hydrolyse and slowly dissolve in hot alkaline solutions, however. Treatment with 3–5% NaOH for 30–60 min at 95 °C gives a considerable weight loss and filaments of decreased denier and softer handle. This type of process led to the deliberate manufacture of fine microfibres (Section 4.3.4). The polymer is reasonably stable to solutions of dilute acids and is stable to pressure dyeing at 130 °C at pH 4.5–6.0, apart from the leeching out of low molecular weight oligomers. PET is more stable to sunlight than nylon and has good resistance to the chemicals used in textile processing. This is partly a consequence of its hydrophobic nature. It is not particularly soluble in common solvents although it may swell somewhat. Methylene chloride (dichloromethane) or aqueous N,N-
dimethylformamide can be used to extract disperse dyes without influencing PET filaments.

Pilling is the name given to the undesirable formation of small bundles of knotted fibres on a fabric surface. These are formed by the matting together of fibre ends that have been rubbed up from the fabric surface by abrasion. This is much easier for the smooth surfaced synthetic fibres than for natural fibres. Because of the high tenacity of synthetic fibres, these knots of matted fibres do not easily break off, as do those of the weaker natural fibres. The balls of fibres therefore accumulate on the fabric surface and produce an unattractive appearance. This can be quite pronounced in fabrics made from 100% PET staple fibre. Decreased fibre tenacity reduces the pilling, as does singeing after dyeing. Optimising the yarn and fabric construction, heat setting, and chemical finishes all help to minimise pilling.

4.3.3 Modified polyesters

As for the nylons, PET type fibres are available in a considerable number of different physical and chemical forms. Besides ethylene glycol and terephthalic acid, other monomers may be added in the polymer-forming reaction. Copolymers produced with ethylene glycol plus other diols (such as 1,4-butanediol), or diacids (such as suberic acid, 1,8-octanedicarboxylic acid), have a lower melting point and \( T_g \) and improved dyeing properties. The introduction of longer alkyl groups into the polymer chain gives it greater flexibility and the fibres absorb disperse dyes at the boil without use of a carrier. They also give less fibre pilling on abrasion. Incorporation of halogenated or phosphonated derivatives gives polyesters with improved flame resistance.

Polyester dyeable with cationic acid dyes has some terephthalic acid units replaced by 5-sulphoisophthalic acid (2, Figure 4.3). This again decreases the regularity of the PET chains and also the crystallinity and orientation so that dyeing can be carried out at the boil by a cation exchange mechanism. Similarly, dyeing with anionic dyes is possible if an acid such as 1,5-pyridinedicarboxylic acid (3, in Figure 4.5) is used as a comonomer. Basic and acid-dyeable PET are used for special colour effects.

All these chemically modified PET fibres have lower \( T_g \) values. They all absorb disperse dyes at the boil without the use of a carrier.

Kodel fibres (Eastman Chemical, USA) are also polyesters produced by ester exchange between dimethylterephthalate and a mixture of cis- and trans-1,4-bis(hydroxymethyl)cyclohexane. The polymer is called poly-1,4-cyclohexylene-dimethylene terephthalate or PCDT (4). In many respects, this polymer is very
similar to PET in its physical and chemical properties. It is also produced by melt extrusion and drawing. PCDT fibres have lower tenacity than PET and are more elastic, with superior recovery. They give less pilling and are useful where resilience and bounce are required.

Shell have recently introduced a new polyester fibre called Corterra. This is a polyester called polytrimethylene terephthalate (PTT) based on terephthalic acid and 1,3-propanediol [2]. This development came about as a result of a new, efficient method of synthesis of the diol in which ethylene oxide reacts with carbon monoxide and hydrogen. It is produced similarly to PET and can be spun into filaments from pre-melted polymer chips. Its properties are similar to those of other polyesters. Because of the somewhat longer trimethylene unit between the benzene rings along the polymer chain, PTT gives filaments that are more elastic than those from PET and the fabrics produced from them are softer and have good elastic recovery. In addition, the increased chain flexibility permits dyeing with disperse dyes at lower temperatures than for PET, typically at 100–110 °C.

4.3.4 Microfibres

The usual definition of a microfibre is one that has a count of less than 1.0 denier or decitex. A typical PET yarn might contain 30–50 filaments, each with a denier in the range 2.0–3.0. A microfibre yarn may have well over a hundred filaments of 0.5 denier. A number of manufacturers are now producing such microfibres. In fact, there has been a continuing trend of denier reduction from around 7 to 2–3 dpf (denier per filament) for polyester filaments since the early 1980s. Low denier filament fabrics have been most popular in Japan, where the name Shin Goshen meaning ‘new synthetic fibre’ is used. Microfibres only have a small share of the total polyester market but this is growing quite rapidly.
As outlined in Section 4.3.2, the treatment of PET filaments with hot aqueous NaOH solution hydrolyses and dissolves the filament surface, reducing the filament diameter. Copolymers of PET hydrolyse more rapidly, but the reaction of the homopolymer can be catalysed with cationic auxiliary products. The resulting fabrics of denier-reduced PET have a warm silky handle with increased scroop (the attractive sound that silk fabric gives when it is compressed and released). In Japan, where this technique has been most popular, weight losses of as high as 40–50% are not uncommon, but are in the range 10–20% in other countries.

Some microfibres can be spun directly while others are bicomponent or matrix types (Figure 4.6). After spinning of the filaments, the individual microfibres are liberated by splitting, or by chemical treatments to remove the supporting matrix.

Microfibre filaments give lightweight fabrics with a soft handle and good drape. The fabrics produced are attractive and comfortable for fashion and sports applications. Because of the high number of filaments in each yarn, closely woven microfibre fabrics have high covering power. A variety of finishing processes enhances their natural properties. The fabric can be made to be breathable with adequate permeability to air and moisture, but yet easily waterproofed. Finishing
processes (such as differential shrinkage of warp and filling filaments, sanding or sueding to give the fashionable 'peach skin' look, or napping and shearing) produce special surface appearances. A variety of chemical finishes are used to impart water or oil resistance, soil release, and resistance to pilling. The application of anti-static lubricants is common.

Fabrics of microfibres are delicate and require careful treatment. They also pose a number of problems in wet processing and dyeing not found with those produced from higher denier filaments. The extra fine filaments have a much higher specific surface area than regular filaments. A major consequence of this is the much higher reflection of light from the filament surface. A higher dye concentration in the filaments is therefore needed to produce a given depth of shade. The greater fibre surface area also results in higher rates of dyeing at lower temperatures, and decreased fastness to light, crocking (fastness to rubbing), water and ozone. These problems will be more fully discussed in Section 15.7.5.

4.4 ACRYLIC FIBRES

4.4.1 Polyacrylonitrile

Radical polymerisation of acrylonitrile (cyanoethene) in aqueous solution, using sodium persulphate (Na₂S₂O₈) and bisulphite (NaHSO₃) as initiators, gives polyacrylonitrile (PAN) with sulphate (SO₄⁻) and sulphonate (SO₃⁻) end groups (Figure 3.2). The homopolymer decomposes on heating before it melts. Melt spinning, as carried out for polyamide and polyester fibres, is therefore impossible. In addition, the homopolymer has limited solubility in common solvents so solution spinning of filaments was not a simple option for commercial fibre production. Pure PAN also proved to be very difficult to dye because of its compact, crystalline structure and a \( T_g \) above 100 °C.

Commercial acrylic fibres are copolymers obtained by polymerisation of acrylonitrile in the presence of other monomers, usually in aqueous solution or emulsion. An acrylic fibre consists of polyacrylonitrile containing at least 85% by weight of acrylonitrile units. The presence of other types of monomer unit along the polymer chain destroys the regularity of the structure and decreases the crystallinity. Non-ionic comonomers such as vinyl chloride or acetate, or methyl esters of acrylic or methacrylic acids (propenoic and 2-methylpropenoic acids), lower \( T_g \) to around 75 °C and considerably improve the dyeability of the polymer. The disruption of the regular repeating structure by a different comonomer not only increases dye diffusion.
rates but also renders the copolymers more soluble in solvents such as dimethylformamide (DMF; 5, in Figure 4.7) or ethylene carbonate (cyclic ester of 1,2-ethanediol and carbonic acid; 6). Such solutions can be spun into filaments either by evaporation of the solvent (hot DMF) in steam or hot nitrogen, or by coagulation of the polymer in an aqueous bath of appropriate chemicals. The filaments may then be stretched in steam or hot drawn.

The anionic sites in the polymer arising from the sulphonate and sulphate end groups give a fibre that can be dyed by an ion exchange mechanism using cationic dyes (Scheme 4.5).

![Scheme 4.5](image)

Surprisingly, dyeings of PAN fibres with cationic dyes show much better fastness to light than these dyes give on natural fibres. In fact, today, PAN dyeing is the major textile consumer of cationic dyes, despite some difficulty in obtaining level dyeings. The early types of PAN were difficult to dye and a special dyeing technique, in which cuprous ion was absorbed by the fibres, was developed so that it could be dyed with acid dyes capable of forming a complex with the metal. This procedure is obsolete partly because of the problem of copper in the dyehouse effluent.

Some PAN fibres contain anionic comonomers such as allyl sulphonate (2-propenylsulphonic acid; 7, in Figure 4.8) or acrylic acid (propenoic acid; 8) to improve the uptake of cationic dyes by ion exchange. Others have added vinyl chloride (chloroethene), or vinylidene chloride (1,1-dichloroethene) to improve the flame resistance. Potential cationic comonomers, such as 2-vinylpyridine (2-ethenylpyridine) that promote substantivity for anionic dyes by ion exchange have also been used but have been less successful (Acrilan, Chemstrand Corp.). Coagulated filaments are more porous and accessible to dyes than those obtained by evaporation of the solvent in solution spinning. There is a wide range of acrylic fibres
that differ in dyeability. PAN fibres are hydrophobic (regain 1–3%) and can also be dyed with disperse dyes by the solution mechanism. The disperse dyes, however, only build up to give pale or medium shades of moderate fastness properties.

![Chemical Structures](image)

**Figure 4.8**

PAN fibres do not have the high tenacity of nylon and polyester, but the strength is sufficient for most textile applications. PAN fabrics can be heat set but, unlike nylon and PET, this does not increase the crystallinity. The filaments are easily stretched when hot. This causes increased chain alignment but not much plastic flow since the latter is limited by the polymer crystallites. Hot stretching thus builds up some tension in the filaments. On heating, these tensions relax and there is shrinkage to the length that existed before hot stretching. This leads to considerable bulking of the filaments. Vast quantities of high-bulk acrylic fibres are produced by initial hot stretching and subsequent steam relaxation. Bicomponent fibres with each component having different shrinkage on heating are used for some bulked fibres. To take advantage of the effects of chain alignment on hot stretching of acrylic filaments, they must be annealed to give fibres of high tenacity. Although PAN fibres come way behind polyester and nylon in consumption, the bulked fibres give fabrics with a warm, soft handle that provide good thermal insulation. Because of this, and the relatively easy care required, they have largely replaced wool for knitted goods. Carpets and non-woven blankets are also significant outlets.

The large number of possible variations in manufacture has resulted in a large number of commercial acrylic fibres with different properties. These depend upon the type and amount of the comonomer used, the spinning method (wet or dry) and the drawing. The base polymers are produced by different polymerisation methods and may then be dry or wet spun, the latter giving better dyeability. The wet spun fibres produced by coagulation have more pores and are therefore more accessible to dyes and chemicals. They will be drawn, heat set, bulked or textured by different methods. A wide range of physical forms is available. Most products are of low crystallinity but have a high order of polymer chain orientation. They have good mechanical properties and have excellent resistance to light showing little or no yellowing on exposure. PAN fibres are generally inert and have good resistance to chemicals including dilute solutions of acids and alkalis. They are, however, soluble in polar aprotic solvents such as DMA.
4.4.2 Modacrylic fibres

Modacrylic fibres have between 35 and 85% acrylonitrile units in the polymer chain. Fibres with such high relative proportions of comonomers such as vinyl chloride (chloroethene), along with the acrylonitrile, provide specific properties such as improved flame resistance or chemical resistance. Because of the wide variations in comonomer type and proportions, fibres with a wide range of properties can be produced. The dyeing characteristics of modacrylics are much like those of regular PAN. They are usually more soluble in common solvents such as acetone, which may be used for solution spinning. Some of the fibres of this type, with a high proportion of a comonomer, may have lower softening temperatures and care is required to avoid creasing in dyeing.

4.5 OTHER SYNTHETIC FIBRES

The three major synthetic fibre types are the nylons, polyesters and acrylics, with polyesters predominating. In addition, there are a number of other kinds used to a much lesser extent in textiles. These include a variety of addition polymers made from vinyl compounds. Fibres from polypropylene are relatively cheap but quite difficult to dye. Large quantities are coloured by pigmentation of the molten polymer before spinning. This provides cheap coloured filaments of good fastness properties but only in a restricted range of colours. Additives can be incorporated into the polypropylene before spinning that are capable of increasing dye substantivity and the rather poor heat and light resistance of this polymer.

Polyvinyl fibres have limited textile application. Polyvinyl and polyvinylidene chlorides are valued for their high resistance to chemicals and their low-flammability, and have specialised applications. They tend to have low softening temperatures and shrink on heating. This polymer is soluble in water and filaments of it are used as support yarns in the construction of delicate materials. Washing the final article dissolves out the polyvinyl alcohol leaving the delicate structure of the other yarns behind.

Polyurethane elastomeric fibres are being used more and more. The generic name of such fibres is Spandex. They have the unusual characteristic of high elasticity and elastic recovery. Such elastomeric fibres are essentially block copolymers consisting of strong, rigid polymer segments among weaker more flexible segments. The flexible segments are composed of low molecular weight aliphatic polyesters or polyethers. These are reacted with a di-isocyanate and the resulting product is reacted with an appropriate diamine (Figure 4.9). The urethane and urea type groups produced are
capable of strong inter-chain hydrogen bonding and provide the strong rigid segments of the matrix. On initial stretching, the flexible coiled segments of the polyester or polyether uncoil, but the bonded urethane segments remain immobile. On releasing the stress, the flexible chains recoil, and since the rigid segments have not permitted any extensive chain slippage, the flexible chains return to their original positions. Since they have amino end groups derived from the diamine, the dyeing of segmented polyurethane fibres is similar to that of the nylons.

REFERENCES
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CHAPTER 5

Natural cellulosic fibres

5.1 INTRODUCTION
Cotton is, by far, the most important textile fibre. This chapter discusses the chemical and physical properties of cotton, related to the preparation, dyeing and finishing of fabrics containing this fibre. In Sections 1.1.2 and 3.1, we saw that cotton consists of cellulose, a polymer of glucose. Cellulose is the basic building material of all types of vegetation and many different plants are sources of cellulose fibres. Linen and ramie are cellulosic fibres of lesser importance than cotton. Purified cotton consists almost exclusively of cellulose, whereas fibres such as linen and ramie contain other materials besides this polymer. Other types of cellulosic fibres, such as hemp and jute, are used for sacks and cord but these are not usually dyed.

Chapter 6 deals with regenerated cellulose (viscose) and cellulose acetate, mentioned in Section 1.1.2. Although cotton and viscose are almost pure cellulose, they have quite different physical properties because of their distinctive morphologies and molecular arrangements. Even though cotton and viscose fibres can be dyed with the same types of dyes, using similar methods, their dyeing characteristics are different.

5.2 COTTON [1,2]

5.2.1 Production of cotton
Cotton comes from the seed pod of plants in the Gossypium family cultivated in a number of subtropical climates. The fibres grow out of the seeds in the closed pod. In the initial phase, they form long, thin-walled cells filled with protoplasm. Later, as the growth in length ends, the cell walls increase in thickness as rings of cellulose are deposited on the inner surface of the cell wall. When the pod or boll bursts, the cotton fibres, whose function is to aid seed transport in the wind, dry out. Once the remaining protoplasm has evaporated, the cotton bolls are harvested mechanically and the fibres removed from the seeds by a process called ginning. This must be carefully controlled to avoid over-cutting of the fibres. Cotton 'linters', the short lint hairs not removed from the seeds by ginning, are
also an important source of pure cellulose. Pressing the residual seeds gives cotton seed oil.

5.2.2 Structure and constituents of cotton fibres

Microscopic examination of cotton fibres reveals that they are single cells with a closed tip but open at the end where they were cut from the seed. They have the appearance of flat, twisted ribbons. This characteristic shape develops as the cotton fibres dry out and collapse in the open boll. The fibre cross-section has a bean shape and often shows the presence of a central canal or lumen.

The morphology of a cotton fibre is extremely complex. The cuticle, or outer cell wall, is relatively hydrophobic. It contains some cellulose but accompanied by fats and waxes. It will be broken and more or less removed during processing to render the fibres more water-absorbent. Beneath the cuticle is the primary cell wall composed of criss-crossed fibrils of cellulose and containing some pectins. The next layer inside this, the secondary wall, constitutes the bulk of the fibre. It is built up of successive layers of fibrils. These are long structures, in each growth layer, that spiral around the fibre in a helical manner. From time to time, the spirals reverse direction and are responsible for the characteristic convolutions of the cotton fibre that develop on first drying. The fibrils, in turn, are composed of smaller microfibrils, the smallest being a combination of cellulose molecules. The numerous channels between the fibrils result in a fibre porosity of about 6% and an internal specific surface area of the order of 100 m² g⁻¹. The lumen, the cavity that may remain after the protoplasm in the cell interior has evaporated, has proteins, colouring matter and minerals deposited on its walls.

Figure 5.1 Scanning electron micrographs of raw cotton fibres (Source: BTIG, Manchester)
The complex arrangement of cellulose fibrils leads to a fibre structure of uneven accessibility. Dye absorption tends to be greatest on the inside surface of the curved bean-shaped cross-section and least on the ends. These differences in dye absorption are evident on microscopic examination of cross-sections of dyed fibres and illustrate the great heterogeneity of cotton. Fortunately, they are not visible to the human eye [3].

Table 5.1 Typical composition of raw cotton

<table>
<thead>
<tr>
<th>Component</th>
<th>Main location</th>
<th>Relative amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>Secondary wall</td>
<td>86.8</td>
</tr>
<tr>
<td>Oils, waxes</td>
<td>Cuticle</td>
<td>0.7</td>
</tr>
<tr>
<td>Pectins</td>
<td>Primary wall</td>
<td>1.0</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>Primary wall</td>
<td>0.5</td>
</tr>
<tr>
<td>Proteins</td>
<td>Lumen</td>
<td>1.2</td>
</tr>
<tr>
<td>Salts</td>
<td>Lumen</td>
<td>1.0</td>
</tr>
<tr>
<td>Water</td>
<td>Lumen</td>
<td>6.8</td>
</tr>
<tr>
<td>Other</td>
<td>Lumen</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 5.1 shows a typical composition of raw cotton. During manufacture of cotton materials, they are boiled with solutions of NaOH, which serves to emulsify waxes, hydrolyse fats and proteins, and solubilise mineral salts. Some low molecular weight non-cellulosic carbohydrates are also removed. This alkaline treatment gives a loss in weight of around 7%. Subsequent bleaching eliminates the natural yellowish colour of cotton. Dry, purified cotton therefore consists of essentially pure cellulose. Alkali boiling and bleaching always involves some degree of cellulose hydrolysis and oxidation, decreasing the average molecular weight of the polymer. Process conditions must minimise this, while ensuring adequate removal of those impurities such as waxes that make the fibres difficult to wet.

5.2.3 Properties of cotton

Cellulose is a polyalcohol, but the strong hydrogen bonds between hydroxyl groups in neighbouring polymer molecules do not easily break, even in the presence of water. In fact, water does not penetrate into the compact, crystalline regions of cellulose and therefore it is not soluble in water. Cotton is, however, a relatively
hydrophilic, water-absorbent fibre. Its porous structure allows ready penetration of water molecules between the fibrils and into the amorphous regions of the polymer where they can easily form hydrogen bonds with free cellulose hydroxyl groups. The standard regain is about 8% and rises to around 25–30% water at 100% relative humidity, at room temperature. Water absorption causes swelling of the secondary wall but little fibre elongation. The wet fibres become softer and more pliable. Cotton is unusual in that water absorption increases the fibre strength. Although absorbed water acts as a plasticiser, it also cements the cellulose chains and fibrils together by hydrogen bonding.

Cellulose shows remarkable stability towards strongly alkaline solutions in the absence of oxygen, even at high temperatures. This is significant in the alkali boiling process mentioned above. Cellulose is, however, very sensitive to mineral acids. These catalyse hydrolysis of the bonds between the glucose units and cause depolymerisation eventually leading to the monomer glucose (Section 5.3.2).

Cellulose is a carbohydrate and, despite its alkali stability, it is a sensitive biopolymer. On heating, cotton’s behaviour is like that of sugar. Browning and hardening of the fibres becomes more pronounced at temperatures above 150 °C. If processing requires higher temperatures, shorter treatment times avoid thermal damage. Unlike synthetic fibres, damp cotton readily supports the growth of bacteria and moulds. These first generate an unpleasant odour and leave coloured marks on the fabric that are often difficult to remove. In bad cases, the fibres may become substantially weakened. Warm, damp conditions foster the growth of mildew, but application of an appropriate anti-fungal agent to the cotton material prevents this problem.

Cotton is a natural vegetable fibre and exhibits considerable variability in properties, even among fibres from the same seed. Cotton is available in a variety of qualities based on the fibre length or staple, and the colour. The longest fibres are usually the finest. Cotton fibre fineness is often evaluated by measuring the pressure drop across a pad of cotton fibres of given weight that is required to produce a given air flow rate. The pressure drop is related to the total fibre surface: the finer the fibres, the greater the pressure drop [4]. Cottons from different geographical regions are quite distinctive. The top quality cottons, such as Sea Island, are 25–65 mm long (12 µm diameter). The bulk of the cotton produced consists of medium quality fibres 12–33 mm long (15 µm diameter). The courser Asiatic grades are only 10–25 mm long (18 µm diameter). The major producing countries are the USA, Russia, China and India.

Cotton fibres from the same harvest do not all have the same degree of
maturity. The thickness of the secondary wall of cellulose, deposited during the second phase of growth of the fibres, can vary over a wide range. Mature fibres will have a thick secondary wall and more convolutions per unit fibre length. Immature fibres are those with thinner secondary walls, because of restriction of their growth, and so-called dead fibres have essentially only the primary cell wall. Because of their higher elasticity, immature and dead cotton fibres readily form small bundles of entangled fibres during the mechanical processes producing yarns. These are called neps. The thin secondary wall of nep fibres makes them more opaque and they appear much paler than mature cotton fibres after dyeing. Dead fibres remain undyed. Neps can therefore be readily seen on the fabric surface. Dyeing tests are frequently used to evaluate the content of dead and immature fibres in a cotton sample. Such fibres are always present, typically constituting about 20% of the total weight. Immature cotton fibres will swell in 20% NaOH solution during mercerisation (Section 5.4.6). This decreases the colour contrast between the dyed neps and mature fibres.

5.3 CELLULOSE

5.3.1 Molecular structure of cellulose

Careful hydrolysis of cellulose gives an almost quantitative yield of glucose, confirming that the former is a polymer of this sugar. 2,3,6-Trimethylglucose (Figure 5.2) is the predominant product of the hydrolysis of cellulose in which all the hydroxyl groups have been initially methylated. Therefore, the hydroxyl groups attached to carbon atoms C-2, C-3 and C-6 in the glucose units in cellulose are free and the oxygen atom linking the glucose units must be between carbon atoms C-1 and C-4. The numbering of the glucose ring is shown in Figure 5.2. Cellulose is a polymer of β-D-glucose, with the specific configuration shown in Figure 5.2. This distinguishes it from starch (a polymer of α-D-glucose) in which the 1-hydroxyl group has the alternative configuration. The correct name for glucose is glucopyranose which indicates that the glucose molecule has five carbon atoms and one oxygen atom in a ring, as in pyran. α- and β-D-glucopyranose must also be distinguished from the respective L-glucopyranoses, their non-superposable mirror images (enantiomers), which are not found in natural carbohydrates.

In the cellulose molecule, each successive glucose unit is rotated 180° around the molecular axis. This gives a linear polymer chain that is almost flat. This structure allows the close approach of neighbouring cellulose molecules necessary
Figure 5.2 Relationships between the structures of cellulose, starch and their monomers; see next page for starch
Figure 5.2 Relationships between the structures of cellulose, starch and their monomers; see previous page for cellulose.
for the development of crystalline regions. In these, the cellulose molecules are held together by intermolecular hydrogen bonds between hydroxyl groups. X-ray diffraction studies of ramie fibres show that the repeat distance in crystalline cellulose corresponds very closely to the length of a cellobiose molecule. Cellobiose is the dimer of glucose (Figure 5.2). The molecules in cellulose are oriented along the fibre axis passing through regions varying from fully crystalline to amorphous. Whenever the molecules are in proximity, hydrogen bonds will form between pairs of adjacent hydroxyl groups.

The arrangement of \( \alpha \)-glucose units in starch is less regular. Unlike cellulose, molecules of amylose, one component of starch, are not flat and crystallinity is totally suppressed. In amylpectin, the other major \( \alpha \)-glucose polymer in starch, the polymer molecules are branched. The oxygen atom at C-1 at the end of one chain links to a C-6 in the middle of a neighbouring chain.

Cellulose is soluble in a solution of cuprammonium hydroxide, Cu(NH\(_3\))\(_4\)(OH)\(_2\). The viscosity of this solution depends on the average molecular weight of cotton cellulose and can establish if any depolymerisation has occurred during processing. The DP (degree of polymerisation) of purified cotton is around 1000–3000. The dissolution of cotton in cuprammonium hydroxide solution is quite slow and protection of the solution from light and oxidation during the procedure is essential. The quantity usually determined is the fluidity or inverse of the viscosity [5]. The higher the molecular weight or DP of the cellulose, the higher the viscosity, and the lower the fluidity of the cuprammonium solution. Any process such as hydrolysis or oxidation that reduces the length of the molecular chains, causes a loss in fibre strength and an increase in the fluidity.

5.3.2 Chemical properties of cellulose

Cellulosic fibres absorb large amounts of water (25–30% regain at 100% relative humidity and 25 °C). Water molecules, however, do not penetrate into the crystalline regions of cotton. Even though cellulose has a large number of hydroxyl groups per molecule, it is not soluble in water, unlike glucose. Even quite large molecules, such as those of typical cotton dyes, easily penetrate into the accessible interfibrillar and amorphous regions of the fibres. The high molecular weight and crystallinity of cotton cellulose are thus responsible for its good mechanical properties, and the fibrillar structure and amorphous regions for its hydrophilic character and absorptivity. Starch, in which the arrangement of glucose units
prevents crystallinity, is much more accessible to water and the unbranched amylose is soluble.

Cellulose is susceptible to hydrolysis by hot dilute solutions of mineral acids. Initially, this breaks the polymer chain at the oxygen atoms between C-1 and C-4 of adjacent glucose units, causing a dramatic drop in DP, and a loss of fibre strength called tendering. The lower molecular weight insoluble celluloses obtained from such partial hydrolysis are called hydrocelluloses. If hydrolysis continues, the eventual product is the soluble monomer glucose. Because of this sensitivity towards acids, cellulose fibres are never dyed at a pH below 3–4. For the same reason, wet cellulose must never be heated, dried or stored when it contains residues of mineral acids. After treatment of a cellulosic material with an alkaline solution, acetic acid is the preferred acid for neutralisation. This is a weak acid that will vaporise during drying before it concentrates to the point at which the pH becomes low enough to result in hydrocellulose formation.

Glucose is a mild reducing agent. The α- and β-configurations of D-glucopyranose interconvert in aqueous solution by way of the open chain aldehyde (Figure 5.3). This process is called mutarotation, after the changes in optical activity that occur. In fact, glucopyranose is a hemi-acetal, formed by the intramolecular reaction of aldehyde and alcohol groups at C-1 and C-5, just as for a simple aldehyde and alcohol (Figure 5.3). Although the actual concentration of the aldehyde form is very small, the equilibrium is quite rapid in acidic or alkaline

---

**Figure 5.3** Mutarotation of glucose via the non-cyclic aldehyde form
solution. Glucose therefore readily gives some reactions typical of aldehydes, such as easy reduction of copper(II) or silver(I) ion complexes, or derivative formation with hydrazines.

One end of a cellulose molecule ends in a C-1 hydroxyl group and can form a terminal aldehyde group like glucose. Cellulose is therefore a reducing agent, but a weak one since the number of such reducing end groups is limited. Because of this, dyeing of cellulosic fibres with some azo dyes at high temperatures under weakly alkaline conditions is not always feasible. The aldehyde of the reducing end group can reduce the azo dye, destroying its colour. This problem is more serious for regenerated cellulosic fibres since they have a considerably lower DP and therefore a higher proportion of potential aldehyde end groups. There are a number of chemical tests that are used to establish the reducing power of cellulose. They provide a measure of its DP. For example, the 'copper number' is the weight in grams of cupric ion in Fehling’s solution reduced to the salmon coloured \( \text{Cu}_2\text{O} \) by 100 g of cellulose [5] (Scheme 5.1). Such tests are useful for detecting the formation of hydrocellulose.

\[
\text{Cellulose} + 2\text{Cu}^{2+}(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 4\text{H}^+(\text{aq}) + 2\text{Cu} \text{O}(\text{aq}) + \text{CO}_2\text{H}(\text{s})
\]

**Scheme 5.1**

Cellulose is also susceptible to oxidation of the primary alcohol group at C-6 and at the linkage between C-2 and C-3. Like all alcohols, it is sensitive to oxidation by oxygen under hot alkaline conditions, such as those used in alkali boiling to eliminate non-cellulosic impurities. In such processes, oxygen must be excluded.

To destroy the natural yellowish colouring matter of cotton, and produce a white material, cotton is usually bleached. This is not necessary if it is going to be dyed in a dull or a deep shade. Bleaching agents include alkaline sodium hypochlorite (NaOCl) and alkaline hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) solution, both of which are quite powerful oxidising agents. Neutral solutions of sodium hypochlorite, in particular, readily over-oxidise cellulose and produce oxycellulose. This increases the number of aldehyde and particularly of carboxylic acid groups; for example, at C-6. Oxidation between C-2 and C-3 of the glucopyranose ring and subsequent hydrolytic reactions dramatically reduce the DP. Pure cellulose does not adsorb cationic dyes from solution because the fibres lack anionic sites to bind the positively charged dye molecules. When carboxylic acid groups are
present, however, the cellulose will contain negatively charged carboxylate groups at pH values above 4–5 and these can bind cationic dye molecules. Staining of cotton with a cationic dye such as Methylene Blue (1, in Figure 5.4) is a common test for oxycellulose.

![Methylene Blue](image)

In the absence of oxygen, cellulose exhibits excellent stability towards alkaline solutions. Treatment with hot dilute NaOH solution at the boil, or even under pressure at higher temperatures, has no ill effects. This is extremely valuable for eliminating a number of impurities from cotton. Treatment of cotton with concentrated NaOH solution, in a process called mercerisation, causes a change in internal structure of the cellulose but no degradation (Section 5.4.6).

## 5.4 COTTON PROCESSING

### 5.4.1 Preparation of cotton [6]

In preparation for dyeing and finishing, a number of impurities must be removed from cotton fibres. Table 5.1 lists the major natural contaminants. Other chemicals present, such as warp size or knitting oil that assist manufacturing processes, must also be eliminated. Many of the natural and synthetic contaminants are hydrophobic and hinder wetting of the fibres. The objective of preparation is to remove the bulk of these impurities so that the cotton readily and uniformly absorbs the aqueous solutions used in dyeing and finishing. Complete elimination of the undesired impurities is not practical and uniformity of the prepared material is the critical requirement. Any uneven distribution of residual warp size, oil or wax will result in uneven dye absorption and be immediately visible.

Although the operations used in the preparation of cotton differ widely in practice, depending upon the type and quantity of material to be processed, the
same basic principles apply. For bulk production of woven goods, fully continuous preparation of open-width and rope forms is common. A woven cotton fabric may undergo singeing, desizing, alkali boiling and bleaching treatments, followed possibly by mercerisation, before it is ready for dyeing (Section 2.4). Knitted materials do not require singeing or desizing. Because knitted fabric stretches easily, handling with minimum tension is essential to avoid excessive elongation. There are therefore many different types of equipment. For more specialised, low volume materials, and in commission dyehouses that dye only small lots, preparation is often a batch process carried out in the dyeing machine.

5.4.2 Preliminary processes for woven cotton fabric

The first process in the preparation of woven cotton materials is singeing. The full-width fabric passes rapidly through a flame issuing from a long gas burner. This burns off the short fibre ends projecting from the fabric surface without any damage to the fabric. These exposed fibres arise from the abrasion of the yarns during weaving. The result is a much smoother fabric surface.

The fabric is then ready for desizing, the removal of the sizing material covering the warp yarns [7]. Warp size consists of a film-forming polymer and hydrophobic lubricants; its effective removal is essential for rapid and uniform wetting of the cotton fibres. A sizing formulation must coat each warp yarn with a flexible polymer film and lubricants, and good adhesion of the film to the yarn surface is vital. Starch-based products are widely used for sizing cotton warps, since their chemical similarity to cellulose ensures good film adhesion. However, although starches have excellent sizing characteristics and low price, they are often difficult to remove by simple washing. The fabric is therefore usually treated with a suspension of an enzyme capable of depolymerising the starch molecules to the point at which they become water-soluble.

Like cellulose, the terminal glucose units of the starch have a reducing action. Unless the starch is effectively removed from the cotton material, it will reduce the oxidising agent used in bleaching, increasing its consumption.

Because of the sensitivity of enzymatic systems, desizing proceeds at a temperature and pH where the enzyme has high activity. The fabric is then well washed to remove the starch degradation products. Alternatively, the starch size may be degraded by oxidation with hydrogen peroxide in alkaline solution.

It is now common practice to size warps of cotton/polyester with polyvinyl alcohol. This polymer is water-soluble and easily removed by simple washing in hot
5.4.3 Alkali boiling of cotton [8]

Treatment of cotton with boiling dilute NaOH solution hydrolyses the natural fats in the fibre, producing soaps that then aid in emulsifying the cotton wax. The latter is resistant to hydrolysis. The classical method of kier boiling involves heating cotton with about 2% aqueous NaOH solution under pressure. Besides NaOH, the solution may also contain soaps and solvents such as pine oil, which aid wax removal from the fibre cuticle. Uniform plaiting of the rope of fabric into the kier boiler avoids channeling of the circulating liquor and non-uniform treatment. Before the boiler is closed to develop pressure, the steam from the boiling solution is vented, thus removing air from the system. This avoids any oxidation of the alkaline cotton. For the same reason, after several hours of boiling under pressure, oxygen must not enter the hot boiler. After the initial cooling, the dirty alkaline solution is slowly drained off but replaced with water to completely cover the hot, alkaline goods and avoid direct contact with the air. Provided oxygen is absent, the cellulose is unaffected by the hot alkaline solution.

Continuous alkali treatment involves impregnating the cotton fabric with NaOH solution and then heating it in a sealed pressurised steamer. Because continuous processes have a shorter treatment time, a more concentrated solution of NaOH is used.

The final step, after either batch or continuous alkaline boiling, is good rinsing with much hot water to remove the soluble and emulsified impurities. The process results in a 5–8% loss of weight from emulsification of the cotton wax, hydrolysis of fats, and the solubilisation of precipitates, organic acids, cellulose oligomers and mineral salts, as well as any residues of sizing material. Again, the effect of these chemicals on the BOD of the effluent is of concern.

5.4.4 Cotton bleaching [9]

The objective of cotton bleaching is to eliminate the yellowish natural colouring matter in the fibres. This is only present in very small amounts and its chemical
nature is not known. For the production of high quality white fabrics, and for those that will be dyed in pale or medium, bright shades, bleaching is essential. It is not necessary for dull or dark shades provided the fabric is already of adequate and uniform absorbency. The types of chemicals used include hypochlorites, chlorites and peroxides, hydrogen peroxide being by far the chemical of choice.

The traditional use of bleaching powder (calcium hypochlorite, Ca(OCl)₂) for cotton bleaching is now almost obsolete. Bleaching cotton with alkaline solutions of sodium hypochlorite (NaOCl) was once common. Hydrogen peroxide (H₂O₂) has taken its place. A successful continuous method of bleaching with hypochlorite was never developed. Even in a batch process, careful control of the temperature and a pH above 10 were essential to avoid over-oxidation of the cellulose. In hot, neutral hypochlorite solution, oxycellulose formation is rapid. In addition, effective alkali boiling was essential as starch residues and proteins both react with hypochlorites. The free amino groups in proteins (R–NH₂) react with hypochlorite, forming chloramines (R–NHCl). On heating the fabric, these groups liberate hydrogen chloride, causing rapid depolymerisation of the cellulose with a drastic loss of fibre strength (Scheme 5.2). After bleaching with chlorine-based oxidising agents, complete removal of residual chlorine and chloramines is essential, using a mild reducing agent such sodium bisulphite solution. In more recent times, there has also been concern about the presence of chlorinated organic chemicals in the bleaching plant effluent.

\[
\begin{align*}
R–NH₂ + Cl₂ & \rightarrow R–NHCl + HCl \\
R–NHCl + H₂O & \rightarrow R–NH₂ + HCl \\
2HCIO + R–CHO & \rightarrow Cl₂ + R–CO₂H + H₂O \\
Cl₂ + H₂O & \rightarrow HCl + HCl
\end{align*}
\]

Scheme 5.2

Cotton and cotton/polyester materials are now invariably bleached with an alkaline solution of hydrogen peroxide. This usually involves impregnation of the goods with a stabilised, alkaline solution of hydrogen peroxide followed by steaming. The goods are finally well washed in hot water. Neutralisation of any residual NaOH in the cotton using dilute acetic acid is a key step before the final rinse and drying. For small batches of cotton fabric, bleaching with alkaline hydrogen peroxide solution may be carried out in a dyeing machine.
The active species in bleaching with hydrogen peroxide is probably the hydroperoxyl anion (HO$_2^-$). Hydrogen peroxide is quite unstable in alkaline solution, particularly on heterogeneous surfaces and in the presence of many transition metal ions. The bleaching liquor normally contains a silicate, polyphosphate or protein stabiliser. These probably function by sequestering (complexing) metal ions in the water, such as Fe$^{3+}$, and by coating rough surfaces. Thus the stabiliser suppresses catalysis of the decomposition of the peroxide.

Hydrogen peroxide bleaching of cotton offers a number of advantages:

1. A range of continuous, semi-continuous and batch bleaching processes are possible;
2. The complete removal of proteins from the cotton is not essential since chloramine formation is not possible with peroxide;
3. For some materials, the combining of alkali boiling and bleaching, or even of desizing, alkali boiling and bleaching, into a single operation is possible;
4. There is a reduced risk of over-bleaching and oxycellulose formation.

On the negative side, careful control of the bleaching pH is necessary and heavy metal ions such as those of copper and iron, which catalyse rapid peroxide decomposition, must be complexed with an appropriate sequestering agent such as a stabiliser or ethylenediamine tetra-acetic acid (EDTA) (Section 8.3.3). The use of buffers and stabilisers is rather critical. The presence of magnesium ions in the water is essential for effective peroxide stabilisation by silicates. Silicate stabilisers tend to deposit on the yarns or fabric and form silica particles on drying. These can give a rough handle to a fabric and considerable friction of yarns with their guides during knitting. Protein stabilisers are preferred over silicates for a softer, smooth handle.

In the preparation of cotton yarn packages for knitting, a one-step process is common (combined mild alkali boiling and bleaching). Pressurised alkali boiling promotes swelling of the yarns and can create excessive pressure in the package interior.

Much of the success of hydrogen peroxide bleaching is a consequence of the development of rapid processes combining some or all of the three preparation operations, allowing considerable economies in labour, time, steam and hot rinsing water. Good water absorbency only requires rupture of the cotton fibre cuticle wall and not necessarily complete removal of the cuticle so vigorous alkali boiling, as in a kier, is not always essential. On the other hand, the traditional enzyme desizing, kier boiling and hypochlorite bleaching give the whitest cotton. Continuous
preparation operations, and particularly those where stages are combined, although often giving acceptable results, are less effective and give a white of lower quality. Semi-continuous pad–batch methods, with cold or hot storage, are also used. Section 21.6.6 discusses evaluation of the degree of whiteness of a fabric.

Cotton may also be effectively bleached with weakly acidic solutions of sodium chlorite (NaClO₂), more widely used in bleaching wood pulp. The acid liberates the toxic gas ClO₂, which is the real bleaching agent. This, however, promotes corrosion of steel and a corrosion inhibitor such as sodium nitrate is needed in the solution.

5.4.5 Fluorescent whitening agents [10]

One remarkable way of improving the apparent whiteness of a cotton fabric is to treat it with a fluorescent whitening agent (FWA), sometimes also called an optical whitenner or optical bleach. These chemicals are colourless or very pale yellow. They do not absorb visible light significantly, but do absorb ultraviolet light with wavelengths around 340–380 nm. Some of the absorbed ultraviolet energy is re-emitted as blue fluorescence in the 430–450 nm wavelength range. The absorbed ultraviolet light has greater energy than the re-emitted fluorescence, the remainder being converted into heat. This is illustrated in Scheme 5.3. In this, FWA and FWA* represent the normal and excited electronic states of the fluorescent chemical, respectively, ν and λ are the frequency and wavelength of the absorbed or emitted light, h is Planck’s constant, and c the speed of light.

\[
\text{FWA} \rightarrow h\nu (360\text{nm}) \rightarrow \text{FWA}^* \\
\text{FWA}^* \rightarrow \text{FWA} + h\nu (440\text{nm}) + \text{heat}
\]

\[
\text{Energy of light} = h\nu = \frac{hc}{\lambda}
\]

Scheme 5.3

A perfectly white material will reflect all wavelengths of white light to the same high degree. Most textile fabrics requiring bleaching, however, have a slight cream or yellowish appearance because they preferentially absorb blue light and therefore have lower reflectance in the 400–500 nm region of the spectrum. The blue
fluorescence of the FWA compensates for this. In fact, it may over-compensate, and it is possible that the sum of the reflected light and fluorescence at 400–500 nm may give an apparent reflectance exceeding 100% in this wavelength region (Figure 5.5). The effect is a very bright white, the ‘whiter than white’ of the detergent advertisements. However, these compounds are only functional if the light source has a sufficient proportion of ultraviolet light to activate the blue fluorescence. They are therefore much less effective in light from a tungsten filament lamp (Section 21.2) than in normal daylight. The presence of a FWA is easily detected by illumination in the dark with a long-wave ultraviolet mercury lamp, when only the blue fluorescence can be seen.

Figure 5.5 Reflectance spectra of unbleached, bleached and optically brightened cotton (treated with a fluorescent whitening agent)

An FWA is a colourless dye, and must have some substantivity for the fibre on which it is to be used. For use with different types of fibres, therefore, there are anionic, cationic and non-ionic types available (Figure 5.6). The Colour Index lists over 250 such chemicals under the generic name fluorescent brighteners. Their chemical constructions resemble those of dyes but they often lack electron-attracting and electron-donating groups and the direct conjugation between them. Figure 5.6 compares the chemical structures of some FWAs with various anionic,
Figure 5.6 Chemical structures of some FWAs and closely related dyes
NATURAL CELLULOSE FIBRES

cationic and non-ionic dyes. The types for cotton behave as colourless anionic
direct dyes whereas the non-ionic types are similar to disperse dyes. Use of these
compounds at low concentrations of 0.1 g l⁻¹ or less is usual, with application
procedures closely resembling the analogous dyeing processes. Many of these
compounds are stable in alkaline solutions of hydrogen peroxide commonly used in
beaching and their presence in the bleaching bath allows milder bleaching
conditions. They often have poor fastness to washing and light but this is not a
problem since most synthetic washing detergents contain FWAs and reproduce
the whitening effect after each wash.

5.4.6 Mercerisation

Mercerisation is a process named after its discoverer, John Mercer (1850). He
treated cotton cloth with cold 20% aqueous NaOH solution, without any applied
tension, and then washed out the alkali. This caused considerable fibre swelling
and shrinkage of the fabric, but increased its strength, elasticity and ability to
absorb cotton dyes. Later, around 1890, Horace Lowe showed that if the material
was held under tension during the treatment, and until most of the NaOH had
been washed out, no shrinkage occurred and the fibres developed an attractive,
subdued lustre. The development of this lustre is still one of the purposes of
modern mercerisation.

During the process, absorption of NaOH by the cotton fibres causes acidic
dissociation of a significant number of hydroxyl groups. The concentration of ionic
sites within the cotton fibres is high in comparison to the ion concentration in the
external solution. A considerable pressure develops in the fibres as water is
absorbed by osmosis and the fibre swells, loosing the characteristic convolutions.
After washing out of the alkali, the fibres have a much rounder cross-section and
therefore higher lustre. Today mercerisation is also appreciated because mercerised
cotton absorbs larger amounts of dyes and gives a higher rate of dyeing. The more
uniform swollen fibres absorb more and scatter less light so that a given amount of
dye produces a deeper shade than on regular cotton. This is significant when the
dyes are expensive. In addition, the swelling of immature fibres, with thin
secondary walls, during mercerisation results in improved dye absorption and a
depth of colour close to that of normal fibres, so that the paler dyed neps are less
obvious.

The effects on the dyeing properties and the changes in mechanical properties
are a consequence of the fibre swelling and changes in the crystalline structure of
the cellulose, giving a more open accessible structure. Obviously, dissociation of the hydroxyl groups gives sufficient swelling for water and hydroxide ions to penetrate into the crystalline regions. The cellulose chains then rearrange into a new, more stable pattern, which is preserved after washing out the alkali.

Identification of mercerised cotton is quite easy by microscopic observation of its characteristic rounder fibres, without convolutions. Alternatively, a small region of a fabric sample may be wetted with 20% NaOH solution for a few minutes. After washing, the whole sample is dyed with a direct cotton dye such as Benzopurpurine 4B (CI Direct Red 3). If the treated zone dyes deeper than the remainder of the sample, the cotton was not mercerised. The greater accessibility of mercerised cotton is also evaluated from the increased absorption of chemicals such as iodine and barium hydroxide.

Large quantities of bleached cotton fabric, and to a lesser extent cotton/polyester, are mercerised by a technique called chain mercerisation. The wet fabric coming directly from bleaching is mangled, and possibly vacuum extracted. The objective is to remove as much water as possible from the goods, but to ensure a uniform distribution of the residual water. The material then passes into the first bath of the mercerisation unit, containing 22% NaOH. The solution may contain an alkali-stable wetting agent to assist penetration of the solution into the cotton yarns. It is squeezed, to remove excess liquid, and then passes over a series cold metal cylinders to allow time for the solution to absorb into the fibres. This impregnation is repeated with a second bath and series of ‘timing cans’. Then, clips grip the selvages of the fabric and pull it to the required width. The clips run down each edge of the fabric in continuous chains. The tension in the fabric is determined by the speed of the chains and their separation. Further along the chain, the washing process begins, using dilute NaOH solution originating from the countercurrent flow of the wash water that enters at the chain end. Suction boxes below the fabric pull the washing solution through it and circulate the liquid upstream. The NaOH in the cotton is diluted to a concentration below 5% before the clips release the fabric at the end of the chain. Further washing in a wash box, neutralisation with acetic acid solution and final rinsing and drying complete the series of operations. The entire process must be conducted under conditions giving uniform mercerisation from side to side and end to end of the fabric. The residual alkalinity should be negligible. Table 5.2 lists some of the effects of this process.

Cotton yarn, in hanks held by a pair of rollers, can also be mercerised under tension. This is usually a batch operation. In the Prograde process, cotton yarn is treated under tension with liquid ammonia at its boiling point (−34 °C), washed
with hot water, and dried in a continuous process. The effects are similar to those of mercerisation. Ammonia treatment also gives improved strength, elasticity and dye uptake, but the degree of fibre swelling is less. There are also processes in which cotton fabric is treated with liquid ammonia and the bulk of the ammonia is allowed to evaporate. The liquid ammonia treatments may take place after dyeing, give softer fabrics with a more resilient handle, and allow use of lower amounts of crease-resist agents.

### Table 5.2 Effects of the chain mercerisation of cotton fabric

<table>
<thead>
<tr>
<th>Property</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric lustre</td>
<td>Increased</td>
</tr>
<tr>
<td>Dye uptake</td>
<td>Increased</td>
</tr>
<tr>
<td>Dye consumption</td>
<td>Economy of 30-50%</td>
</tr>
<tr>
<td>Fibre strength</td>
<td>Increased</td>
</tr>
<tr>
<td>Standard regain</td>
<td>Increased from 6 to 10%</td>
</tr>
<tr>
<td>Fibre cross-section</td>
<td>Increased and rounder</td>
</tr>
</tbody>
</table>

5.5 OTHER VEGETABLE FIBRES

In addition to cotton, there are a number of minor vegetable fibres, the most important being linen, which is derived from flax. The stalks of the plants are harvested and soaked in water under various conditions, in a process called retting. This softens the ligneous material holding the stalk fibres together. A considerable amount of processing is required to produce clean linen fibres. Linen materials also tend to crease easily. For finishing with crease-resist chemicals, mercerisation of the linen helps to minimise the decrease in resistance to abrasion (Section 25.4.1). Ramie, from China grass, is another vegetable fibre used for textiles. These different types of cellulosic fibres have different morphologies to cotton and are a less pure form of cellulose. They have similar dyeing behaviour but will not dye to the same depth of shade as cotton with a given amount of the same dye.
REFERENCES

CHAPTER 6

Artificially made fibres based on cellulose

6.1 THE FIRST REGENERATED CELLULOSE FIBRES

The first artificially made filaments of regenerated cellulose were produced by Chardonnet in 1884. These were named artificial silk because of their form and appearance. The production method involved extrusion of a solution of cellulose nitrate and regeneration of the cellulose by hydrolysis, as outlined in Section 1.1.2. Although this fibre was produced commercially until 1949, the quantity was always limited by the difficulties of controlling the reactions involved and the high flammability of nitrocellulose and the solvents used. Nevertheless, Chardonnet was the first to demonstrate that extrusion of a polymer solution and evaporation of the solvent, a technique now called dry spinning, was a feasible method of fibre production on a large scale.

Cuprammonium viscose (then called cuprammonium rayon) was first manufactured commercially in 1899. According to the US Federal Trade Commission, a rayon (viscose) is a fibre of regenerated cellulose in which other substituents have replaced not more than 15% of the hydroxyl groups. Cuprammonium viscose is also called cupro or Bemberg viscose. Purified cotton linters, or wood pulp, are dissolved in a solution of cuprammonium hydroxide and sulphate. This is a mixture of copper sulphate, ammonia and sodium hydroxide (Scheme 6.1). Before this solution can be forced through the holes in the spinneret plate to form filaments, the usual filtering and degassing are necessary (Section 4.2.1). The filaments are produced by a wet spinning technique, extruding the cuprammonium solution into running water. This dilutes the solution and coagulates the cellulose filaments. They pass down a converging funnel and the shear forces developed by the concurrent flow of water stretch the still plastic filaments. This increases the orientation of the cellulose chains along the filament axis and thus improves the fibre strength. A bath of dilute sulphuric

\[
\text{CuSO}_4 + 2\text{NaOH} + 4\text{NH}_3 \rightarrow \text{Cu(NH}_3\text{)}_4(\text{OH})_2 + \text{Na}_2\text{SO}_4
\]

Scheme 6.1
acid washes out the remainder of the copper and neutralises the ammonia. Copper salts are sufficiently expensive to make recovery and recycling of the copper necessary. The filaments are finally well washed and dried.

The smooth, round filaments of this viscose tend to adhere together so that twisting is not necessary. This adhesive quality is used in forming slub yarns. These have thicker areas along the even yarn consisting of an accumulated mass of fibres. For these, the filaments running continuously from one spinneret are intermittently combined with accumulated filaments from another, to produce yarn with slubs. The physical and chemical properties of cuprammonium viscose are very similar to those of viscose fibre discussed in the next section. Despite the silky appearance, fine denier, soft handle and good draping properties of fabrics made from it, cuprammonium viscose has always been a minor fibre compared to regular viscose.

6.2 VISCOSE FIBRE [1,2]

6.2.1 Production of regular viscose fibre
Cross and Bevan in the UK discovered the viscose method for the production of regenerated cellulose in 1892. This was later developed by Courtaulds Ltd. After wet spinning of a dilute NaOH solution of the xanthate ester of cellulose into an acidic spinning bath, the cellulose filaments reform by coagulation and hydrolysis of the ester. Scheme 6.2 outlines the basic chemistry of this process.

![Scheme 6.2](image)

The major starting material for viscose fibre is high-grade wood pulp in the form of pressed sheets. These consist mainly of cellulose with a reasonably high DP. Treatment of the sheets with warm 18% aqueous NaOH solution causes dissociation of some of the hydroxyl groups in the cellulose and the formation of...
artificially made fibres based on cellulose

its sodium salt, called alkali- or soda-cellulose (Scheme 6.2(ii)). Pressing out the excess NaOH solution removes some soluble carbohydrates, and the moist, solid product is next broken up into crumbs and allowed to age. During this period, oxidation in the presence of air causes some depolymerisation. The crumbs of alkali-cellulose are then churned with about 10% of their weight of carbon disulphide, forming sodium cellulose xanthate (Scheme 6.2(iii)). Addition of dilute aqueous NaOH gives a viscous, brown solution, from which the name 'viscose' was derived.

The viscose solution is then left to ripen. The viscosity gradually increases as some of the xanthate ester groups hydrolyse back to hydroxyl groups (Scheme 6.2 (iii)). The degree of substitution (DS) of the hydroxyl groups of cellulose represents the number of hydroxyl groups per glucose unit that have undergone chemical substitution. The value of the DS varies from 0, for cellulose, up to a maximum of 3.0. The initially formed sodium cellulose xanthate has a DS of just less than 1.0 but during ripening this falls to about 0.33. Too large a decrease in the DS results in precipitation of cellulose.

During ripening, the average DP also decreases further. The depolymerisation of the cellulose in the ageing and ripening stages of viscose production determines the viscosity of the final spinning solution. This is important for controlling the filament integrity on initial extrusion into the coagulating bath. The low DP of the final cellulose is, however, the major reason for the weakness of this fibre.

The ripe viscose solution is finally degassed and filtered in preparation for wet spinning. Extrusion of the solution into a bath containing acid and salts first coagulates the cellulose xanthate, which then hydrolyses to reform cellulose (Scheme 6.2(iii)). The still plastic filaments pass around and are stretched between rotating pulleys. Stretching produces finer filaments, but also orients the cellulose molecules along the filament axis so that they begin to interact with each other by hydrogen bonding. Without such orientation, viscose filaments would be too weak for textile use. The drawn filaments may be collected in a Topham box (a rotating cylindrical container in which the filaments press against the walls as a result of centripetal force), or wound up on perforated tubes to form bobbins.

The filaments produced require a number of aftertreatments such as desulphurising, bleaching if necessary, washing, drying and oiling. The aftertreatment and washing processes are carried out on batches of cakes or bobbins. Washing with Na₂S solution removes any precipitated elemental sulphur from the filaments, which tends to cause a yellow coloration. Like bleaching, this
is not always necessary. Thorough washing finally eliminates all the residual chemicals. The cakes or bobbins may also be dyed at this stage, before drying.

Manipulation of numerous cakes and bobbins is time-consuming and these batch operations limit the rate of production. Fully continuous aftertreatment and washing, immediately after spinning, is much more productive. For each treatment, the extruded and stretched filaments wind around, and advance along, a pair of rollers with convergent axes while being sprayed with the appropriate washing solution.

Wood pulp, and the other chemicals used, are relatively cheap and viscose has become the predominant regenerated cellulose fibre. However, viscose production involves an extremely lengthy series of operations requiring strict control. Large volumes of water are necessary and the alkali, soluble carbohydrates and sulphur compounds in untreated effluent pose an environmental problem. A newer type of regenerated cellulose (called lyocell) is now being manufactured by a process generating less water pollution (Section 6.2.4).

6.2.2 The morphology, properties and uses of viscose

The cellulose in cotton has a DP of around 2000 and a degree of crystallinity of up to 70%. For regular viscose, the DP (250–400) and crystallinity (25–30%) are much lower. The crystallites in viscose are also 4–5 times smaller than in cotton and have a lower degree of orientation. It is therefore not surprising that viscose is a much weaker fibre than cotton. Crystalline zones in a fibre are responsible for strength and rigidity, whereas the amorphous regions provide accessibility, flexibility and extensibility. Wet spinning involves extrusion of a solution of free, individual cellulose molecules. These tend to orient themselves along the filament axis during extrusion and this continues during stretching after coagulation. The molecules are not, however, aligned to the same extent as in cotton.

Regular viscose fibres are weaker than those of cotton, particularly when wet (Figure 6.1). They are much less rigid and much more plastic. Elongation under a stress of more than 2% can cause displacement of the cellulose molecules and therefore permanent elongation. The strength of viscose filaments is improved by stretching them after extrusion, while they are still plastic. Even so, the strength of wet viscose may be as much as 50% lower than when dry. Because the filaments have low crystallinity and high accessibility, water absorption causes fibre swelling and increases the extensibility by 20%. Swelling of viscose filaments can be a
problem when treating wound packages. The swelling tends to close the channels through which dye or chemical solutions are flowing and thus increases the internal pressure.

These properties are in direct contrast to those of cotton, which is much stronger and only swells slightly in water. Cotton fibres are still quite rigid even when wet. Fabrics of viscose do not, therefore, have the good resistance and washability of those made with cotton. During processing and use, viscose fabrics must be handled with care to avoid stretching, creasing and even tearing. The limp handle of fabrics made from viscose contrasts sharply with the crisp handle of cotton materials. Resin finishes are widely used on viscose materials to improve the poor wet strength and provide better dimensional stability (Section 25.4).

The low DP of viscose results in a much higher number of reducing end groups and therefore a higher copper number than for cotton (Section 5.3.2). Because of this, the problem of dye reduction, when dyeing under hot alkaline conditions, is more pronounced for regenerated cellulosic fibres. The low DP and crystallinity of viscose fibres make them much more accessible to solutions of chemicals than fibres of cotton. Viscose has about the same accessibility as mercerised cotton, as shown by the regain values at 25 °C and 100% relative humidity (cotton 25%, viscose 45% and mercerised cotton 50%).

Since it is essentially pure cellulose, viscose has the same chemical properties as cotton. In its chemical reactions, it will, however, react more rapidly than cotton.
Because of its lower DP and crystallinity, and higher accessibility, viscose even tends to be reactive under conditions where cotton is quite stable. For example, cold, concentrated or hot dilute NaOH solution will attack and tend to dissolve viscose, so it requires milder processing conditions. Viscose also has a higher number of carboxylate groups than cotton and will absorb cationic dyes by ion exchange.

The composition of the aqueous coagulating bath significantly influences the properties of the viscose filaments. A typical bath might contain dilute sulphuric acid, sodium sulphate, glucose and zinc sulphate. The salts promote rapid coagulation and dehydration of the coagulated sodium cellulose xanthate by osmosis. The acid present in the bath catalyses hydrolysis of the cellulose xanthate back to cellulose. Cellulose is generated either by transformation of the sodium cellulose xanthate into cellulose xanthate, and its subsequent hydrolysis, or similarly by the slower reaction of the zinc cellulose xanthate. Scheme 6.3 shows the two different routes by which cellulose is reformed.

In regular viscose filaments, there is a distinct difference between the skin and the core of the filament. Since the acid in the spinning bath penetrates into the core of the coagulated sodium cellulose xanthate more rapidly than zinc ions, the cellulose skin is formed via the zinc salt and more slowly than the cellulose core forms from the sodium salt. Rapid coagulation of the filament surface, using a higher concentration of zinc sulphate in the bath, produces a pronounced filament skin. During these processes, the more rapidly regenerated cellulose core shrinks and the skin becomes wrinkled, giving the filaments of viscose their characteristic serrated cross-section (Figure 6.2).
The cellulose molecules in the skin layer are more highly oriented along the filament axis than those in the core and the crystallinity is therefore higher. This is partly because of the friction of the solution with the walls of the spinneret hole. The core of a regular viscose filament therefore absorbs dyes faster than the skin. Dyes also tend to bleed more rapidly from the core on washing. These effects provide a means of seeing the skin thickness on microscopic examination of cross-sections of dyed fibres.

Viscose filaments from wood pulp are relatively cheap and available in large quantities. The normal filaments have an attractive lustre. Titanium dioxide is added to the viscose solution during ripening to give matte filaments. Alternatively, coloured pigments may be added. Despite a limited choice of colours, pre-pigmented or dope-dyed viscose filaments are useful when high fastness to washing and light are essential. As for other artificially made fibres, a wide variety of forms and properties are available. These differ in denier, cross-section, lustre, tenacity, and so on. In addition, hollow filaments or filaments containing air bubbles are produced. These give high bulk and good thermal insulating power. They have high moisture absorption. A number of modified viscoses have non-cellulosic polymers or crosslinking agents added to the viscose solution before spinning.

Large quantities of viscose are produced as staple fibre. Blending with other fibres such as polyester provides cost-effective water absorbency and softness. Because of the blending of staple fibres, they do not need to have the same
uniformity as continuous filaments and large scale production of staple fibre gives better economics. For staple fibres, combination of the output of several spinnerets forms a band or tow of filaments, which can then be cut into short lengths. Before cutting, the filaments may be crimped to improve the adhesion of the short fibres for yarn spinning. Crimping may be achieved mechanically or by coagulating under conditions that produce an asymmetric cross-section, with more skin on one side of the filament than the other. When wet, the asymmetric fibres swell more on the thin-skinned side and tend to curl. Bicomponent fibres of two different kinds of viscose behave similarly.

6.2.3 Improved forms of viscose

As we have seen, the cellulose skin in regular viscose has better orientation and strength. So, to produce high tenacity viscose, less acid and a high concentration of zinc sulphate in the spinning bath are used. Then, all the cellulose is regenerated slowly and the filament is all skin. These filaments have no core, do not shrink during regeneration of the cellulose, and have a uniform cross-section. Alternatively, regeneration of the cellulose is delayed by using a very dilute acid bath. This allows time for better stretching and improved orientation.

High tenacity viscose fibres are used for tyre belts, hoses, and industrial applications. They are rarely dyed. There are various ways of controlling the coagulation process with bath additives. A higher degree of stretching produces filaments with greater orientation and crystallinity. This gives filaments that may be up to three times stronger than regular viscose, but still with acceptable extensibility. High tenacity viscose has lower water absorption and swelling but higher wet strength.

A variety of other high-strength viscose filaments are also produced whose mechanical properties are much closer to those of cotton. These are called high wet modulus (HWM), modal and polynosic viscoses but there are various definitions of these names. The word ‘polynosic’ is presumably derived from ‘polymer’ and ‘cellulosic’ and refers to viscoses with a fine micro-fibrillar structure resistant to cold 8% aqueous NaOH solution. The generic name ‘modal’ is used to describe viscoses having high tenacity and a high wet modulus; ‘polynosic’ usually refers to the type with the highest values of wet modulus. The elastic modulus is the stress that must be applied to produce a unit elongation. The higher the value, the more rigid the fibre. All the HWM viscoses have higher wet strength than regular viscose, increased resistance to swelling by alkali solution, a higher DP and
a more fibillar internal structure similar to cotton. Their properties are therefore
much closer to those of cotton. Compared to regular viscose, they are more
crystalline and oriented, imbibe less water and swell less.

HWM viscose is used as staple for blending with other fibres using the cotton
carding system. The fibres consist of cellulose fibrils and have no skin. The
average DP is 500–600, and the fibres are 50–60% crystalline with larger
crystallites than in cotton. Because of this, and the higher orientation than in
regular viscose, HWM viscose fibres are less likely to deform under wet conditions.
On water absorption, the swelling is intermediate between that of regular viscose
and cotton. For many materials, HWM viscose competes with cotton, but, unlike
cotton, it has a soft silky handle, with an attractive subdued lustre. It can be used
for materials where regular viscose would be inappropriate because of its poor wet
strength. It is blended with cotton to a large extent and also with polyester staple.

Polynosic fibres have a higher DP of around 500–700, compared to the value of
250–400 for regular viscose. The higher values of the DP for HWM and polynosic
fibres are achieved by curtailing the ageing of the soda-cellulose and the ripening
of the viscose solution to avoid depolymerisation. The viscose solution is prepared
under much milder, neutral conditions. Regeneration is also slowed down by
spinning into a dilute sulphuric acid solution without salts. Other additives are
also present to retard coagulation. The filaments exhibit a high degree of internal
fibrillation and their properties are much closer to those of cotton.

6.2.4 Lyocell fibres [3]
The lyocell fibres developed by Courtaulds and Lenzing appear to have solved the
two major problems of viscose production: the excessive environmental pollution
and the poor wet strength of the viscose filaments. The generic name ‘lyocell’ is
from the Greek verb λυεῖν meaning ‘to dissolve’, and is used for fibres of
regenerated cellulose produced directly from a solution of cellulose rather than
from a cellulose derivative. Courtaulds’ product is called Tencel.

Few details of the manufacture of this type of fibre have been divulged but the
following steps seem likely. Firstly, an aqueous suspension of ground cellulose
(13%) in water (20%) and N-methylmorpholine-N-oxide (67%) is prepared. The
solvent is obtained by oxidation of N-methylmorpholine with hydrogen peroxide
(Scheme 6.4). Thin film evaporation of the water then increases the cellulose
solubility and a true solution is obtained in the amine oxide solvent. This solution
is stabilised by an anti-oxidant such as propyl gallate (propyl-3,4,5-
trihydroxybenzoate) and a little NaOH. After the usual filtration, the hot solution is extruded through a spinneret. Before entering the aqueous coagulation bath, the liquid filaments pass through an air gap where the final filament shape is determined. The water in the spinning bath precipitates solid cellulose filaments. The filaments are then washed to remove the amine oxide and dried. The beauty of the lyocell technology is the re-use of the recovered solvent and of much of the process water. In addition, the number of process steps is much smaller than in production of viscose.

Staple lyocell fibres can be ring or open-end spun, alone or in mixture with other natural or synthetic fibres. They can be used for clothing and also for technical textiles. In comparison to viscose, lyocell filaments have a round cross-section and are relatively homogeneous throughout. The core–skin character typical of viscose is absent. Lyocell filaments have higher tenacity and slightly greater extensibility than cotton fibres. The wet strength is 2–3 times greater than for regular viscose filaments, being comparable to that of cotton. The mechanical properties are slightly better than those of most HWM viscoses and are a consequence of the high crystallinity of the filaments and the high degree of polymer chain orientation in the amorphous regions.

The fibres have a fibrillar structure and these fibrils will separate when the fibres are wet and under tension. Fibrillation is the longitudinal splitting of a fibre into a bundle of microfibres of smaller diameter, typically 1–4 μm. This will occur predominantly on the exposed fibre surface. Because of the high transparency of the fibres, the fabric has a white or frosty surface appearance. Fibrillation usually occurs during rope wet processing, as in winch or jet dying (Sections 12.4.1 and 12.4.4), being much less pronounced when fabric is treated in open-width form. The degree of fibrillation can be controlled during fabric processing.

Fibrillation allows the production of very attractive fabric surface effects with a soft, pleasant handle, such as the peach skin effect. To produce these attractive effects, a number of processes is required. A typical procedure is to singe off any loose fibrils and then fibrillate by rope scouring. The surface fibrils are then removed by a cellulase enzyme treatment. Cellulase is an enzyme capable of digesting cellulose. Because the fibrils expose a large surface area, it is possible to
clean them off the fibre surface without digesting the bulk of the more compact fibre. A second fibrillation is next carried out on the cleared fibre surface but only on the exposed areas. This avoids any problems of pilling and fibril entanglement. It is preferable that dyeing follow these processes. If a fabric is required with a clean surface appearance, fibrillation must be minimised by using high liquor ratios, a lubricant in the bath or by low temperature processing. To minimise fibrillation of Tencel, Courtaulds recommend the use of a proprietary chemical applied under hot alkaline conditions. It functions as a crosslinking agent and prevents fibrillation.

6.2.5 Dyeing regenerated cellulose fibres

All the various forms of viscose are composed of cellulose and therefore have similar chemical properties. The different types of viscoses, however, have different dyeing properties. They can all be dyed with the same types of dyes used for dyeing cotton, but the dyeing rate and amount of dye absorbed may vary from one type of viscose to another. If a viscose/cotton blend is dyed with a typical cotton dye, it is usual that the viscose will be more deeply coloured. Even in the case of fibrillar viscoses, which closely resemble cotton, it is unlikely that the two different cellulosic fibres in the blend will be dyed to the same depth. Dyed lyocell fibres have a colour yield (the depth of colour obtained for a given amount of dye) that is higher than that for dyed viscose, but lower than for mercerised cotton. These differences are not surprising since viscose morphology can be quite varied, depending upon the manufacturing conditions. From the dyeing point of view, all they have in common with each other, and with cotton, is their cellulosic nature. Dyeing trials are therefore recommended.

6.3 CELLULOSE ACETATES [2,4]

Cellulose acetates are esters of cellulose in which a large fraction or even all the hydroxyl groups have been esterified using acetic anhydride (Scheme 6.5). The two major types of cellulose acetate have about 55 and 62% of combined acetic acid. These values correspond to cellulose with degrees of substitution (DS) of 2.48 and 3.00, respectively. The latter is correctly called cellulose triacetate, but the name cellulose diacetate for the former is somewhat misleading, its composition being intermediate between the di- and triacetate.

These fibres in no way resemble fibres of cellulose. Both cellulose diacetate and
triacetate are relatively hydrophobic and thermoplastic. The standard regain of cellulose di- and triacetate are 5.0 and 2.5%, respectively. They hardly swell in water. Once superficial water has been removed by centrifugation, vacuum or mangling, fabrics from these fibres are easy to dry, unlike cotton. Both cellulose acetates are resistant to dilute solutions of acids but are sensitive to alkaline solutions, which cause hydrolysis of the acetate ester to hydroxyl groups, especially at higher temperatures. The triacetate is more hydrophobic and more compact and crystalline than the diacetate and has better resistance to alkaline solutions and to solvents.

The dyeing properties of cellulose acetates are quite different from those of cellulose fibres and different types of dyes must be used. Although much of the work on development of these polymers was carried out by Henry and Camille Dreyfus, working in England during the First World War, full commercial exploitation was not possible before the problem of dyeing these fibres had been solved. Cellulose di- or triacetates have no ionic groups. They are quite hydrophobic fibres. When introduced in the 1920s, cellulose diacetate was initially difficult to dye satisfactorily with existing ionic dyes. Fine dispersions of simple, non-ionic azo and anthraquinone compounds, of limited water solubility, however, efficiently dyed this fibre. These so-called disperse dyes are slightly soluble in water and are extracted from the aqueous solution by the solid fibre in which the dyes are quite soluble (Figure 1.7).

6.3.1 Cellulose diacetate

In the production of cellulose acetates, wood pulp is first pretreated either with glacial acetic acid or with the vapour of an acetic acid–water mixture to swell the cellulose fibres. This makes them more accessible for acetylation. The fibres are then treated with a mixture of acetic acid and acetic anhydride containing a small amount of sulphuric acid as catalyst. Cooling prevents an increase in temperature of the mixture that will promote excessive hydrolysis of the cellulose. The cellulose triacetate produced becomes soluble in the reaction medium. This initial product is called primary cellulose acetate. Cellulose diacetate is obtained directly from the triacetate by partial hydrolysis. Rather than precipitate the triacetate, by
addition of a large amount of water; a small amount of dilute aqueous acetic acid is added to the cellulose triacetate solution. The water reacts with the excess of acetic anhydride and hydrolyses some of the acetate to hydroxyl groups. The final product is called secondary cellulose acetate which is synonymous with cellulose diacetate. Once the DS has fallen to the required value of about 2.5, the cellulose diacetate becomes soluble in acetone. It is then precipitated by addition of water.

Because of its good solubility in acetone, filaments of cellulose diacetate can be produced by extrusion and evaporation of this solvent. This is the dry spinning process, which has the advantage over wet spinning that no additional treatments such as washing are needed. Recovery of the evaporated acetone and of the acetic acid is required for economical operation.

For dry spinning, a filtered and degassed acetone solution, containing a small amount of water, is extruded through a spinneret. To ensure constant properties of the filaments, the acetone solution is prepared from several blended batches of the solid cellulose diacetate because of their slight variations in properties. If required, pigmentation of the solution with TiO₂ at this stage will decrease the lustre of the filaments produced. The solution is spun into a rising current of hot air at 100 °C. Some stretching occurs during this phase while the filaments are still quite plastic. Lubricants are then sprayed or wiped on and the filaments wound up.

Cellulose diacetate is available in a range of deniers, as single or multi-filaments, and as staple fibre. The denier depends on the solution pumping rate, the spinneret hole size and the filament speed that causes drawing. Staple fibre is produced by cutting a tow of mechanically crimped filaments. Slub yarns can be made by combination of two different sets of extruded filaments.

The acetylation procedure, under acidic conditions, results in a large decrease in the DP of the cellulose to about 300. This is controlled by pre-swelling of the cellulose fibres, by cooling the reaction mixture and by careful hydrolysis of the primary acetate. The large acetate side-groups prevent close packing of the polymer chains and the development of crystallinity. Even though the filaments are drawn during spinning, the degree of polymer chain orientation remains fairly low. Filaments of cellulose diacetate are therefore not particularly strong. The fibre is weaker and more extensible when wet but it does not lose as much strength as viscose when wetted. Fabrics easily deform if over-stretched. Because this polymer is thermoplastic, it requires careful handling when in contact with hot solutions to avoid stretching and creasing of the material. Fabrics from this fibre have good drape, a crisp handle, and reasonable dimensional stability and wrinkle resistance if they are handled carefully and not over-heated.
Cellulose diacetate filaments have an almost round cross-section with several lobes, with ridges between them that run along the filament length. The unpigmented filaments have high sheen that is valued for linings, lingerie and dress fabrics, ribbons, and for some furnishing fabrics. Few of these have high fastness requirements. Yarns made from multi-filaments, however, do tend to slip easily over each other and chemical finishes may be needed to avoid this effect and to stabilise a fabric. Cellulose diacetate is produced mainly as continuous filament even though it is more difficult to dye level.

The temperature of materials of cellulose diacetate should not exceed 85 °C when wet, and should be less than 140 °C in dry heat. Because bright filament is easily delustered in hot water above 85 °C, partly by surface hydrolysis of acetyl groups, dyeing temperatures rarely exceed this value, even if the filament has been delustered with TiO₂. The fibre surface is very easily hydrolysed by mild alkaline scouring. This sensitivity to heat and alkaline hydrolysis should always be born in mind. Cellulose diacetate softens on heating and fabrics can be embossed with a pattern using heat and pressure. It is produced with almost no natural colour and rarely requires bleaching. It is soluble, or swells considerably, on contact with a number of common solvents.

6.3.2 Cellulose triacetate

Cellulose triacetate is obtained as described in the previous section. Before precipitation, reaction with magnesium acetate and a little water removes any sulphuric ester groups (Cell–OSO₃H). The triacetate is then precipitated by addition of water, filtered and washed. Alternatively, acetylation procedures are used in which the fibrous wood pulp preserves its form and does not dissolve. The product is soluble in chloroform but this toxic solvent is not used for dry spinning. A solution of the triacetate in methylene chloride (dichloromethane) containing a little ethanol is used. The safety of even this chlorinated solvent is in question and the production of triacetate is decreasing because of this.

Fibres of the triacetate are more hydrophobic than those of secondary acetate and they have higher chemical resistance. They are much more stable to hot water and dilute alkali than secondary acetate. Dyeing temperatures are close to the boil and even as high as 120 °C. Because of the more regular structure, the crystallinity of triacetate is higher than that of the diacetate and it is more solvent resistant.

Cellulose triacetate is thermoplastic and fabrics can be heat set or permanently
pleated using dry heat or steam. Heat setting of triacetate fabrics improves their dimensional stability so they do not shrink or wrinkle on dyeing, or on washing, but the process increases the crystallinity and the rate of dyeing is reduced. The mechanical properties of triacetate fibres are close to those of the secondary acetate but it does not lose a great deal of strength when wet. It gives fabrics with a firm crisp handle, less soft than that of the diacetate.

REFERENCES
CHAPTER 7

Protein fibres

7.1 INTRODUCTION

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

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

7.2 STRUCTURE OF WOOL FIBRES

7.2.1 Keratins and wool proteins

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

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

Wool consists of about 82% of a protein called keratin, but this has various

![Figure 7.1 L2,3-dihydroxypropanal (1); L-serine (2); D-serine (3)](image)

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

Because of resonance, the amide or peptide groups in a protein molecule are
planar, the carbon–nitrogen bond having some double bond character and
restricted rotation. The different 2-amino acid substituents, or side-chains, vary in
Table 7.1 Structure and amount of major amino acids in wool [2]

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Structure</th>
<th>Mol % (from two sources)</th>
<th>Nature of side-chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>H_2N_2\H_2C_O_2H</td>
<td>8.6 8.2</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Alanine</td>
<td>CH_2N_2\H_2C_O_2H</td>
<td>5.3 5.4</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>CH_2N_2\H_2C_O_2H</td>
<td>2.9 2.8</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Valine</td>
<td>H_2C_O_2H _2H_2C_O_2H</td>
<td>5.5 5.7</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Leucine</td>
<td>H_2C_O_2H _2H_2C_O_2H</td>
<td>7.7 7.7</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>H_2C_O_2H _2H_2C_O_2H</td>
<td>3.1 3.1</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Serine</td>
<td>H_2O_2H _2H_2C_O_2H</td>
<td>10.3 10.5</td>
<td>Polar</td>
</tr>
<tr>
<td>Threonine</td>
<td>H_2O_2H _2H_2C_O_2H</td>
<td>6.5 6.3</td>
<td>Polar</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>H_2O_2H _2H_2C_O_2H</td>
<td>4.0 3.7</td>
<td>Polar</td>
</tr>
<tr>
<td>Aspartic acid(a)</td>
<td>H_2O_2H _2H_2C_O_2H</td>
<td>6.4 6.6</td>
<td>Acidic</td>
</tr>
</tbody>
</table>
Table 7.1 continued

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Structure</th>
<th>Mol % (from two sources)</th>
<th>Nature of side-chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glutamic acid (c)</td>
<td>HOOCHCHCONH2</td>
<td>11.9 11.9</td>
<td>Acidic</td>
</tr>
<tr>
<td>Histidine</td>
<td></td>
<td>0.9 0.8</td>
<td>Basic</td>
</tr>
<tr>
<td>Arginine</td>
<td>HCONHCHCONH2</td>
<td>6.8 6.9</td>
<td>Basic</td>
</tr>
<tr>
<td>Lysine</td>
<td>HCONHCONH2</td>
<td>3.1 2.8</td>
<td>Basic</td>
</tr>
<tr>
<td>Methionine</td>
<td>HOSCHCONH2</td>
<td>0.5 0.4</td>
<td>Sulphur-containing</td>
</tr>
<tr>
<td>Cystine (d)</td>
<td>HOOCHCHSSCHCONH2</td>
<td>10.5(e) 10.0(e)</td>
<td>Sulphur-containing</td>
</tr>
<tr>
<td>Tryptophan</td>
<td></td>
<td></td>
<td>Heterocyclic</td>
</tr>
<tr>
<td>Proline</td>
<td></td>
<td>5.9 7.2</td>
<td>Heterocyclic</td>
</tr>
</tbody>
</table>

(a) Shading indicates identity of side-chain
(b) Includes asparagine residues
(c) Includes glutamine residues
(d) Includes oxidation by-product, cysteic acid
(e) Values are for half-cystine
size and chemical nature and project outwards from the main polymer chain. There are six main types:
(1) non-reactive hydrocarbon groups, as in alanine;
(2) polar groups such as alcoholic or phenolic groups, as in serine and tyrosine;
(3) basic groups, as in lysine, that influence the maximum amount of acid with which the wool combines and the absorption of anionic acid dyes (Section 1.1.2)
(4) acidic groups, as in glutamic acid;
(5) covalent crosslinking groups, as in cystine, that influence the solubility, swelling and mechanical properties of wool;
(6) heterocyclic groups, as in proline.

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

![Figure 7.2 Types of inter-chain linkages in wool](image-url)
water. Exactly the same types of interactions occur between different parts of the same molecule, as between different molecules. These various types of interactions are responsible for stabilising the particular configuration that a protein molecule adopts and for many of its chemical and physical properties.

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

\[
\text{NH}_3\text{Wool} \rightarrow \text{CO}_2\text{H} \quad \text{NH}_3\text{Wool} \rightarrow \text{CO}_2\text{NH}_2 \quad \text{NH}_3\text{Wool} \rightarrow \text{CO}_2\text{H}^{-}
\]

\[\text{Scheme 7.1}\]

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

X-ray diffraction of unstretched wool fibres shows a pattern characteristic of \(\alpha\)-keratin, in which the individual protein molecules have a helical configuration and wrap around each other in a helix. On stretching the wool fibre, the X-ray diffraction pattern changes to that of \(\beta\)-keratin, in which the chains are fully
Extended and form sheets of molecules bonded together (Figure 7.3). In this conversion, the intramolecular hydrogen bonds holding the helix together are broken and, once the protein chains are extended, new intermolecular hydrogen bonds form between neighbouring chains. Wool is not, however, very crystalline because the bulky side-groups along the polymer chains prevent the molecules from becoming aligned.

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

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

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

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

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

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

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

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

<table>
<thead>
<tr>
<th>Table 7.2</th>
<th>Approximate composition of raw wool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>%</td>
</tr>
<tr>
<td>Wool</td>
<td>45</td>
</tr>
<tr>
<td>Wool wax</td>
<td>18</td>
</tr>
<tr>
<td>Suint</td>
<td>10</td>
</tr>
<tr>
<td>Water</td>
<td>12</td>
</tr>
<tr>
<td>Debris</td>
<td>15</td>
</tr>
</tbody>
</table>

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

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

7.3 PHYSICAL AND CHEMICAL PROPERTIES OF WOOL

7.3.1 Wool quality

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

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

Virgin wool is very expensive, particularly for the better qualities. The chemical treatments that prevent shrinkage and felting on repeated washing of wool fabrics add to the cost. Wool consumption is now only a small fraction of the total for all fibres, and, because of its high price, many articles contain recycled wool. Wool is used for three major types of fabrics: woollen, worsted and felts. The latter have fibres matted and pressed together with a random arrangement. Woollen and worsted materials are produced using different carding and spinning systems and have quite different appearances and characteristics (Table 7.3).

### Table 7.3 Different characteristics of woollen and worsted yarns

<table>
<thead>
<tr>
<th>Woollen yarn</th>
<th>Worsted yarn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short fibres</td>
<td>Long fibres</td>
</tr>
<tr>
<td>Only carded</td>
<td>Carded and combed</td>
</tr>
<tr>
<td>Low twist</td>
<td>High twist</td>
</tr>
<tr>
<td>Coarse, soft and voluminous</td>
<td>Fine, smooth and solid</td>
</tr>
<tr>
<td>Medium strength</td>
<td>High strength</td>
</tr>
</tbody>
</table>
7.3.2 Wool properties

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

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

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

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

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

7.3.3 Effects of acids and alkalis on wool

Aqueous solutions of acids and alkalis initially influence wool by changing the degree of dissociation of carboxylic acid and ammonium ion groups in the fibre.
For wool, the numbers of amino and carboxylic acid groups are nearly equal, being about 820 and 770 mmol kg\(^{-1}\), respectively. In electrically neutral wool, these are present as ammonium and carboxylate ion groups.

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

<table>
<thead>
<tr>
<th>Group</th>
<th>Isoelectric point</th>
<th>Acidic (+ 820 mmol kg(^{-1}) H(^{+}))</th>
<th>Alkaline (+ 770 mmol kg(^{-1}) HO(^{-}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino, NH(_2)</td>
<td>50</td>
<td>0</td>
<td>820</td>
</tr>
<tr>
<td>Ammonium ion, NH(_3)(^{+})</td>
<td>770</td>
<td>820</td>
<td>0</td>
</tr>
<tr>
<td>Carboxylic acid, CO(_2)H (^{−})</td>
<td>0</td>
<td>770</td>
<td>0</td>
</tr>
<tr>
<td>Carboxylate ion, CO(_2)(^{−})</td>
<td>770</td>
<td>0</td>
<td>770</td>
</tr>
</tbody>
</table>

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

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

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

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

7.3.4 Setting of wool

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

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

\[
\text{Wool} + \text{H}_2\text{O} \rightarrow \text{Wool} + \text{H}_2\text{O}
\]

\[
\text{Wool} + \text{SH} + \text{H}_2\text{O} \rightarrow \text{Wool} + \text{H}_2\text{O}
\]

Scheme 7.2

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

\[
\text{Wool} + 2 \text{SH} + \text{CO}_2 \rightarrow \text{Wool} + 2 \text{SH} + \text{CO}_2
\]

\[
2 \text{Wool} + \text{SH} + 2 \text{O}_2 \rightarrow 2 \text{Wool} + 2 \text{SH} + 2 \text{O}_2
\]

Scheme 7.3

7.3.5 Felting of wool

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

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

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

7.4 WOOL PROCESSING [4]

7.4.1 Scouring wool fabric

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

7.4.2 Means of eliminating wool shrinkage

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

1. modification of the scale structure of the fibre cuticle to decrease the directional friction effect – this can be achieved by chemical treatments that either partially remove the scales or cover them with a smooth film of polymer;

2. reduction of fibre mobility by adhesion of fibres and yarns at their points of contact and by decreasing fibre elasticity by means of intermolecular crosslinking.

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

\[
2\text{HCl} + \text{NaClO} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} + \text{NaCl}
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} + \text{NaHSO}_3 \rightarrow \text{NaHSO}_4 + 2\text{HCl}
\]

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

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

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

Figure 7.5 Hydrolysis of dichloroisocyanuric acid

The objective of the reaction with chlorine is to modify the scales of the cuticle rather than the cortex. The scales, particularly the tips, are attacked and their mutual friction is reduced thus decreasing the degree of shrinkage on washing. Chlorination also oxidises disulphide crosslinks in the cuticle proteins to sulphonic acid groups (Scheme 7.5). These are strongly solvated by water and the cuticle
therefore swells and becomes softer. Chlorination also generates some watersoluble peptides from the proteins in the cuticle, which also contribute to softening the scales. The anti-shrink effect of chlorination may not be permanent if these proteins are gradually removed from the fibre surface on washing and the scales harden.

A number of other so-called subtractive or destructive wool shrink-resist processes are known. These also modify the scale structure. In particular, the process based on treatment of wool with permonosulphuric acid (H$_2$SO$_5$) merits mention. It will be of increasing importance as concern for pollution by organochlorine compounds increases.

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

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

A variety of other polymer deposition processes is used for producing shrink-resistant wool. These act by coating the fibre scales and reducing the frictional
effect, and by welding fibres together at their contact points. The polymer can be a polyamide produced by interfacial polymerisation, or a silicone or polyurethane coated onto the fibres using an organic solvent. A curing step is usually needed to fix the film of polymer onto the surface scales.

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

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

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

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

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

7.4.4 Moth-proofing wool

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

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

Moth-proofing agents are usually applied during dyeing, some, such as Mitin FF (Figure 7.7), acting rather like colourless acid dyes. They have adequate fastness to washing and light to maintain their moth-proofing effect over the life of the
wool article. Alternatively, the wool may be treated during scouring but the degree of penetration of the agent into the fibres is smaller and the fastness properties are inferior to those obtained by dyebath application.

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

7.5 SPECIALITY ANIMAL FIBRES

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

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

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

The amino acid composition of fibroin is quite different from that of keratin. Fibroin has only four major amino acid components – glycine, alanine, serine and tyrosine – containing long sequences of alternating glycine and alanine residues. It has fewer amine and acid side-chains and contains no cystine. Silk only absorbs about 1.50 mmol kg$^{-1}$ of acid compared to about 8.20 mmol kg$^{-1}$ for wool. Compared to wool, silk is somewhat less sensitive to alkalis but more sensitive to acids. Treatment with dilute mineral acid solutions causes shrinkage and is used to produce crepe effects. Organic acids harden the fibre surface and increase the scroop, the crunching noise made when the fabric is crumpled. The protein chains in fibroin are fully extended in the $\beta$-configuration and silk therefore has lower elasticity than wool. It is, however, sufficiently resilient to give fabrics that retain their shape and resist wrinkling. It is still considered the luxury fibre.

REFERENCES
CHAPTER 8

Water treatment

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

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

8.1 WATER QUALITY FOR THE DYEHOUSE

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

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

The various salts present in water depend on the geological formations through which the water has flowed. These salts are mainly the carbonates (\(\text{CO}_3^{2-}\)), hydrogencarbonates (\(\text{HCO}_3^-\), more commonly named bicarbonates), sulphates (\(\text{SO}_4^{2-}\)) and chlorides (\(\text{Cl}^-\)) of calcium (\(\text{Ca}^{2+}\)), magnesium (\(\text{Mg}^{2+}\)) and sodium (\(\text{Na}^+\)). Although calcium and magnesium carbonates in limestone are relatively insoluble, the action of dissolved carbon dioxide in rain water can leach them out in the form of the more soluble bicarbonates (Scheme 8.1). Hard water contains
calcium and magnesium ions and gives an immediate precipitate with soap. Soap is a water-soluble sodium salt of a high molecular weight carboxylic acid, such as stearic acid. Its calcium and magnesium salts are much less soluble and give a gummy precipitate with a soap solution in hard water (Scheme 8.2). When this happens, the cleaning efficiency of the soap decreases dramatically. The dirt in suspension, as well as the precipitated calcium and magnesium soaps, can deposit back onto the material being washed. This gives a dingy fabric with a poor handle that will be difficult to dye in a level shade.

\[
\text{CaCO}_3(s) + \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(HCO}_3\text{)}_2(aq)
\]

Scheme 8.1

\[
2\text{CH}_3\text{(CH}_2\text{)}_{16}\text{CO}_2\text{Na}^+(aq) + \text{Ca}^{2+}(aq) \rightarrow \text{(CH}_3\text{CH}_2\text{CO}_2\text{)}_{2}\text{Ca}^{2+}(s) + 2\text{Na}^+(aq)
\]

Scheme 8.2

Besides dissolved salts of natural origin, water may contain a variety of other salts from human or industrial activity. These include nitrates (NO\textsubscript{3}\textsuperscript{−}), phosphates (HPO\textsubscript{4}\textsuperscript{2−} and H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}) and various metal ions. The ions of certain transition metals, such as those of iron, copper and manganese, can precipitate dyes, or form complexes with them, dulling or even changing their shade. In addition, many of these ions catalyse the decomposition of hydrogen peroxide in bleaching baths. It is not uncommon for a particle of iron rust on the surface of a cotton fabric to generate such rapid peroxide decomposition that the cellulose is totally oxidised and a hole results. These transition metal ions may be present in the natural or municipal water, or, in the case of iron, come from corrosion within pipelines. Both dissolved and colloidal silica in boiler feed water can lead to the formation of a hard resistant scale on the boiler’s internal surfaces, considerably decreasing heat transfer efficiency. Organic compounds from the decomposition of vegetable matter in the water, or from sources of pollution, can be very varied. They can have such high concentrations that the water is coloured. Table 8.1 illustrates the quality of water usually considered acceptable for textile processing and steam generation.

Water entering a textile dyeing or finishing plant usually passes through a grill to eliminate floating debris. Small particles in suspension must also be removed.
The water may pass from the primary source into a settling pond, from which water can be drawn after any small particles have settled to the bottom, or it may be filtered by passage through a bed of fine sand. For particles smaller than about 0.02 mm, a coagulant aids sedimentation and clarification of the water. Addition of small quantities of sodium aluminate (NaAlO₂) or aluminium sulphate, and adjustment to around pH 7, give a gelatinous precipitate of aluminium hydroxide that imprisons the small particles and accelerates sedimentation or filtration. Addition of a flocculant, such as a polyacrylic acid-polyacrylamide copolymer, gives better particle adhesion and a higher rate of sedimentation. This type of treatment also improves the colour of the water. Soluble impurities in the water, such as iron, pollutants, and organic matter, are a real problem. Good aeration of the water will usually convert iron into Fe³⁺, which precipitates as ferric hydroxide unless the water is quite acidic.

8.2 WATER HARDNESS [1]

8.2.1 Consequences of using hard water

The use of hard water in a textile dyeing or finishing mill can have some serious consequences. These include:
1. precipitation of soaps;
2. redeposition of dirt and insoluble soaps on the fabric being washed – this can cause yellowing and lead to unlevel dyeing and a poor handle;
3. precipitation of some dyes as calcium or magnesium salts;
4. scale formation on equipment and in boilers and pipelines;
5. reduction of the activity of the enzymes used in desizing;

<table>
<thead>
<tr>
<th>Table 8.1 Typical dyehouse water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>Hardness</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Manganese</td>
</tr>
<tr>
<td>Silica</td>
</tr>
<tr>
<td>Alkalinity to pH 4</td>
</tr>
<tr>
<td>Dissolved solids</td>
</tr>
</tbody>
</table>
decreased solubility of sizing agents;
(7) coagulation of some types of print pastes;
(8) incompatibility with chemicals in finishing recipes.

8.2.2 Definitions

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

Hardness is defined as the presence of soluble calcium and magnesium salts in the water. If these are present in the form of bicarbonates, the hardness is temporary. Heating hard water containing bicarbonates eliminates dissolved carbon dioxide and the reverse of Scheme 8.1 causes precipitation of calcium carbonate. Magnesium carbonate is slightly soluble in water but heating will cause its hydrolysis into the much less soluble magnesium hydroxide (Scheme 8.3).

Simply boiling and filtering the water therefore eliminates temporary hardness. In regions where water has high temporary hardness, and is used directly without treatment, it is not uncommon to see hot water rinsing and washing baths with a generous crust of chalk (CaCO₃) on the inner surfaces. This type of precipitation inside a boiler is also undesirable because the scale reduces the efficiency of heat transfer.

\[
\text{Mg(HCO}_3\text{)₂(aq)} \rightarrow \text{MgCO}_3\text{(s) + CO}_2\text{(g) + H}_2\text{O)}
\]

\[
\text{MgCO}_3\text{(aq) + H}_2\text{O} \rightarrow \text{Mg(OH)}_2\text{(s) + CO}_2\text{(g)}
\]

Scheme 8.3

Permanent hardness arises when water contains soluble salts of calcium and magnesium such as chlorides and sulphates. It is unaffected by boiling the water. The total hardness of water is determined by the amount of dissolved calcium and magnesium, but expressed in the form of CaCO₃. This is possible because calcium and magnesium carbonates have identical stoichiometry. Therefore, water that contains 1.0 mm calcium and 0.5 mm magnesium ions, has a total concentration
of 1.5 mM. Since the molecular weight of CaCO₃ is 100 g mol⁻¹, 1.5 mM corresponds to 150 mg l⁻¹ of CaCO₃, or 150 ppm (parts per million), assuming that 1.0 l of the water has a mass of 1.0 kg. The permanent hardness is that remaining after the water has been boiled and filtered to remove the precipitated calcium and magnesium carbonates and magnesium hydroxide. The temporary hardness is the difference between the total and permanent hardness. Occasionally, hardness due to magnesium alone is of interest, again expressed as the equivalent amount of CaCO₃. For the water mentioned above, 0.5 mM of magnesium ions is equivalent to 50 mg l⁻¹ or 50 ppm CaCO₃.

Understanding water hardness values is often a tedious exercise in manipulation of units. In the past, the hardness of water was given in units called degrees. The definition of one degree of hardness, however, varied from one country to the next (Table 8.2). It is much simpler to express hardness in mg l⁻¹ or ppm of CaCO₃.

<table>
<thead>
<tr>
<th>Unit of water hardness</th>
<th>ppm CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 British degree</td>
<td>14.3</td>
</tr>
<tr>
<td>1 American degree</td>
<td>17.2</td>
</tr>
<tr>
<td>1 French degree</td>
<td>19.0</td>
</tr>
<tr>
<td>1 German degree</td>
<td>17.9</td>
</tr>
<tr>
<td>1 mmol l⁻¹ CaCO₃</td>
<td>100</td>
</tr>
</tbody>
</table>

8.2.3 Determination of water hardness

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

Scheme 8.4
is equivalent to 0.01 mmol Ca\(^{2+}\). Thus, if a 100.0 ml sample of water is titrated with 0.02 M potassium oleate solution to just give a permanent foam after addition of V ml of soap, equivalent to V \(\times 0.01\) mmol Ca\(^{2+}\), the hardness will be V \(\times 10\) ppm CaCO\(_3\).

Despite the simplicity of this method, it is not always possible to detect precisely the point at which a layer of foam persists. Hardness is therefore more usually determined by titration with a standardised solution of the disodium salt of ethylenediamine tetra-acetic acid (EDTA). EDTA forms very stable, soluble complexes with calcium and magnesium ions (Figure 8.1). EDTA is a tetraprotic acid and the various acid–base forms are usually abbreviated by H\(_4\)Y, H\(_3\)Y\(^-\), H\(_2\)Y\(^{2-}\), HY\(^{3-}\), and Y\(^{4-}\), as the degree of dissociation progresses. Scheme 8.5 illustrates complex formation with calcium and magnesium ions. The equilibrium constants are large and ensure quantitative formation of the colourless complexes on addition of EDTA to a solution containing calcium and magnesium ions.

The titration involves gradual addition of standardised EDTA solution (Na\(_2\)H\(_2\)Y) to the water sample, buffered at pH 10 with an ammonia–ammonium buffer.

![Figure 8.1 Structure of EDTA and its complex with calcium ion](image)

\[\begin{align*}
\text{EDTA} & \quad + \quad \text{Ca}^{2+} \\
\text{CaY}^{2-} & \quad \text{K} = 5.0 \times 10^{10}
\end{align*}\]

\[\begin{align*}
\text{EDTA} & \quad + \quad \text{Mg}^{2+} \\
\text{MgY}^{2-} & \quad \text{K} = 4.9 \times 10^{8}
\end{align*}\]

Scheme 8.5
chloride solution. The indicator is a dye that changes colour on complexing with calcium or magnesium, such as Eriochrome Black T (CI Mordant Black 11). At the beginning of the titration, the large concentrations of calcium and magnesium ions ensure that all the dye indicator is in the form of the red complexes with these metals (Ca–Dye, Scheme 8.6). Very close to the equivalence point, the free Ca$^{2+}$ and Mg$^{2+}$ ion concentrations become so low that the added EDTA begins to remove the metals from their red complexes with the dye. This liberates the blue dye ion. The colour of the solution therefore changes from red (dye–metal complex) to blue (free dye anion) at the end-point.

\[
\begin{align*}
\text{Ca}^{2+} + \text{H--Dye}^2\text{–} & \rightarrow \text{Ca--Dye}^–(\text{red}) + \text{H}^+ \\
\text{Ca--Dye}^–(\text{red}) + \text{Y}^4\text{–} + \text{H}^+ & \rightarrow \text{CaY}^2\text{–} + \text{H--Dye}^2\text{–}(\text{blue})
\end{align*}
\]

Scheme 8.6

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

8.2.4 Water alkalinity
Various dissolved salts in natural water give it an alkaline pH. These are mainly carbonates, bicarbonates and phosphates (Scheme 8.7). The alkalinity of a water sample can be determined by titration with
standardised sulphuric acid solution. With phenolphthalein as the indicator, the equivalence point occurs at about pH 8.3. At this point, all free hydroxide ion is neutralised, carbonate converted into bicarbonate, and phosphate (PO$_4^{3-}$) into monohydrogen phosphate (HPO$_4^{2-}$). The alkalinity to pH 8.3 is calculated in ppm CaCO$_3$ based on Scheme 8.8. Therefore, each millimole of sulphuric acid required corresponds to 1.00 mmol CaCO$_3$ in the water sample. If the titration of a 100.0 ml water sample with 0.01 M sulphuric acid consumes $V$ ml of acid, the alkalinity is given by:

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

$$= 10 \times V \text{ ppm CaCO}_3 \tag{1}$$

At the phenolphthalein end-point of pH 8.3, the water is still slightly alkaline and it is therefore common practice to titrate the sample to a methyl orange end-point, corresponding to about pH 4.5. This ensures that all carbonate is in the form of carbonic acid and all phosphate is present as dihydrogenphosphate (H$_2$PO$_4^-$). The alkalinity to pH 4.5, often called the total alkalinity, is given by the same equation as above, but, of course, the volume of sulphuric acid solution may be greater.

$$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- (\text{aq}) + \text{HO}^- (\text{aq})$$
$$\text{HCO}_3^- (\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{HO}^- (\text{aq})$$
$$\text{PO}_4^{3-}(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} (\text{aq}) + \text{HO}^- (\text{aq})$$
$$\text{HPO}_4^{2-} (\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_4^- (\text{aq}) + \text{HO}^- (\text{aq})$$

Scheme 8.7

$$\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$$

Scheme 8.8

Table 8.3 relates the total (T) alkalinity and phenolphthalein alkalinity (P) of various types of water to the dissolved salts that are present. In the absence of phosphate ions, there will be some correlation between the alkalinity caused by bicarbonate and the temporary hardness. For example, if the alkalinity to
phenolphthalein is zero \((P = 0)\), the total alkalinity, assuming no phosphates or weakly acidic pollutants, will be caused by bicarbonate ion and the total alkalinity in ppm \(\text{CaCO}_3\) will equal the temporary hardness. The alkalinity of water fed to boilers must not be too high because of the risk of corrosion of non-ferrous fittings.

### 8.3 WATER SOFTENING

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

#### 8.3.1 The lime-soda process

The old lime-soda process is now obsolete but was very useful for the treatment of large volumes of hard water. Addition of lime (\(\text{CaO}\)) and soda (\(\text{Na}_2\text{CO}_3\)) to the hard water precipitates calcium as the carbonate, and magnesium as its hydroxide. The amounts of the two chemicals required are easily calculated from the analysis of the water and stoichiometry of the reactions (Scheme 8.9). Since calcium
carbonate and magnesium hydroxide are not completely insoluble, the water obtained has a residual hardness of not less than 20 ppm CaCO\textsubscript{3}. A major problem of this type of process is the disposal of the sludge of precipitated calcium carbonate and magnesium hydroxide.

8.3.2 Ion exchange methods

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

\[
\begin{align*}
\text{CaO(s)} & \rightarrow \text{H}_2\text{O} \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \\
\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) & \rightarrow \text{CaCO}_3(\text{s}) \\
\text{Mg}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) & \rightarrow \text{Mg(OH)}_2(\text{s})
\end{align*}
\]

Scheme 8.9

\[
\begin{align*}
2(2\text{Na}^+(\text{s}) + \text{Ca}^{2+}(\text{aq})) & \rightarrow (2\text{Na}^+(\text{s}) + 2\text{Ca}^{2+}(\text{aq})
\end{align*}
\]

Scheme 8.10

Many zeolites occur in nature but they can also be manufactured. The removal of the alkaline earth metal ions is more effective the greater the surface area of the zeolite particles in contact with the water. For this reason, softening involves percolation of the water down a packed column of the finely ground zeolite, followed by periodic regeneration. Although the calcium and magnesium ions in the water are replaced by sodium ions, these are relatively harmless in textile processing.
The chemical structures of aluminosilicates are based on the structure of silica. This consists of a three-dimensional network of SiO$_4$ units, in which the oxygen atoms have a tetrahedral arrangement around the central silicon atom. These tetrahedra may have common corners or faces. In an aluminosilicate, a number of aluminium atoms replace silicon atoms in the silica structure. The aluminium atoms are bonded to four tetrahedral oxygen atoms but because their atomic number is one less than silicon, each aluminium atom introduced has a negative charge, balanced by incorporation of a cation such as Na$^+$ or K$^+$. It is these cations that are available for exchange.

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

![Figure 8.2 Chemical structures of cation and anion exchangers based on cross-linked polystyrene](image)

Scheme 8.11

$$2(\text{Polymer} - \text{SO}_3^- \text{Na}^+) (s) + \text{Cu}^{2+} (aq) \rightarrow (\text{Polymer} - \text{SO}_3^- \text{Cu}^{2+}) (s) + 2\text{Na}^+(aq)$$

$$2(\text{Polymer} - \text{SO}_3^- \text{Na}^+) (s) + \text{Ca}^{2+} (aq) \rightarrow (\text{Polymer} - \text{SO}_3^- \text{Ca}^{2+}) (s) + 2\text{Na}^+(aq)$$
The so-called weak acid cation exchangers are usually polymers containing carboxylic acid groups, such as vinyl polymers containing acrylic acid (ethenoic acid) units (1), in Figure 8.3). These are used in the form of their sodium salts. They do not exchange hydrogen ions for cations below pH 5 since the free carboxylic acid groups are barely dissociated at low pH values (Scheme 8.12).

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

\[
\begin{align*}
2\text{Polymer} &-\text{CO}_2\text{Na}^+(s) + \text{Ca}^{2+}(aq) & \rightarrow & \text{Polymer} -\text{CO}_2\text{Ca}^{2+} (s) + 2\text{Na}^+(aq), \text{pH}>5 \\
\text{Polymer} & -\text{CO}_2\text{Na}^+(s) + \text{H}^+(aq) & \rightarrow & \text{Polymer} -\text{CO}_2\text{Ca}^{2+} (s) + \text{Na}^+(aq), \text{pH}<5
\end{align*}
\]

Scheme 8.12

Figure 8.3 Weak acid cation exchanger, containing acrylic acid (ethenoic acid) units (1); strong basic anion exchange resin, containing quaternary ammonium hydroxide groups (2); weakly basic anion exchange resin with protonated secondary amino groups (3).
Therefore, a strongly basic quaternary ammonium ion resin is regenerated using NaOH solution, and a secondary amine type with NaCl or HCl solution.

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

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

Water can be totally demineralised by firstly exchanging all cations using a strongly acid form of a cation exchanger. Thus, a solution of salts M\(^+\)X\(^-\) becomes a solution of acid H\(^+\)X\(^-\), the M\(^+\) ions being retained by the resin. Subsequent percolation through a packing of a strongly basic form of an anion exchanger absorbs the X\(^-\) ions and liberates HO\(^-\) ions into the water. These then neutralise the H\(^+\) ions from the first step. The result is retention of all anions and cations and the neutralisation of H\(^+\) and HO\(^-\) to form water (Scheme 8.14). Thus, the
water has been demineralised. It may, however, still contain organic material and dissolved carbon dioxide from the reaction of carbonate and bicarbonate with the acid from the resin. A thorough aeration eliminates the carbon dioxide. Demineralisation is important for water fed to very high pressure boilers.

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

![Processes for water softening and regeneration using a cation exchanger]

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

### 8.3.3 Sequestering agents

Transition metal ions in the water supply can pose difficult problems in a dyehouse. Firstly, many of these ions catalyse the decomposition of hydrogen peroxide in bleaching baths. In addition, transition metals often give insoluble
salts with dyes, or form complexes that are invariably duller and even different in shade. If the amounts are excessive, the water may be unusable without treatment. On adequate aeration of the water at pH values around 7, iron precipitates as insoluble Fe(OH)₃ and can be removed. There is always concern about the possibility of iron from corrosion inside the water pipes in a textile plant.

Addition of a sequestering agent to the water avoids many problems from relatively low concentrations of undesirable metal ions. Sequestering agents react with the metal ions to form very stable complex ions. Examples of such chemicals used in textile processing include EDTA, and related aminocarboxylic acids, as well as polyphosphates such as sodium tetrametaphosphate Na₄P₂O₁₀. EDTA is a most effective sequestering agent, particularly in neutral or weakly alkaline solution. It forms such stable complexes with metal ions that it often removes the metal ion from a metal–complex dyestuff molecule, to give the EDTA–metal complex and uncomplexed dye.

Polyphosphates can bind alkaline earth metal ions and thus decrease the effects of water hardness. The product Calgon, sodium hexametaphosphate Na₆P₆O₁₈, is widely used for this purpose. Calcium ions replace sodium in the hexametaphosphate, forming a stable complex. The free calcium ion concentration in the water is then so low that calcium soaps do not precipitate. Polyphosphates are frequently present in domestic washing powders for the same reason.

8.4 BOILER WATER

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

Temporary hardness in boiler feed water gives an accumulation of chalk scum in the boiler and scale on the walls and heating tubes. Deposition on the latter greatly reduces the rate of heat transfer and the boiler becomes increasingly less efficient. At high temperatures and pressures, both calcium and magnesium carbonates and magnesium hydroxide are much less soluble than under ambient conditions and contribute to scaling. Simple phosphates such as Na₂HPO₄, added to boiler feed water, will precipitate insoluble calcium and magnesium phosphate in a form that does not form a crust on the boiler walls and pipes. Polyphosphate
Sequestrants are less helpful since they tend to hydrolyse rapidly to simple phosphates in boiling water. Treatment with simple phosphates also ensures absorption of colloidal silica. This is significant, since silica scale on pipes and walls is very difficult to remove.

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

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

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

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

\[
\begin{align*}
2\text{Na}_2\text{SO}_3 + \text{O}_2 & \rightarrow 2\text{Na}_2\text{SO}_4 \\
\text{N}_2\text{H}_4 + \text{O}_2 & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Scheme 8.15
8.5 DYEHOUSE EFFLUENT AND ITS TREATMENT [2]

8.5.1 Contaminants in dyehouse effluents

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

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

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

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

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

A measure of the amount of oxygen it will consume for oxidation of the organic chemicals it contains. This point is important because depletion of oxygen in water has a negative impact on aquatic life. The biological oxygen demand (BOD) \[1\] is the amount of oxygen (mg l\(^{-1}\) or ppm) consumed in 5 days at 20°C by growth of bacteria from a culture added to the water. The chemical oxygen demand (COD) \[1\] is based on a much faster chemical oxidation of organic compounds with hot sodium dichromate solution. The two values are often close but not equivalent. Many organic compounds are readily oxidised by hot dichromate but are resistant to microbial oxidation at ambient temperature. It is typical of textile effluent that the COD is much higher than the BOD. The COD is less affected by the usual effluent treatment processes, and is thus more persistent in the environment. Values range from 200–3000 mg O\(_2\) l\(^{-1}\) for BOD and from 500–5000 mg O\(_2\) l\(^{-1}\) for COD. The total organic carbon (TOC) in the water serves as an alternative to BOD and COD. All these can be determined by standardised analytical procedures.

Floating insoluble chemicals, mainly insoluble oils and solvents.

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

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

<table>
<thead>
<tr>
<th>Water pollutants</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy metals</td>
<td>Chromium, copper, zinc</td>
</tr>
<tr>
<td>Organochlorine compounds</td>
<td>Moth-proofing agents</td>
</tr>
<tr>
<td>Insecticides</td>
<td>Aldrin</td>
</tr>
<tr>
<td>Sulphides</td>
<td>Sodium sulphide from dyeing</td>
</tr>
<tr>
<td>Colour</td>
<td>Dyes</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Detergents, dispersing agents</td>
</tr>
<tr>
<td>Oils</td>
<td>Emulsions from scouring</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>Starch sizing</td>
</tr>
<tr>
<td>Solvents</td>
<td>Degreasing solvents from scouring</td>
</tr>
<tr>
<td>Acids and alkalis</td>
<td>Dyeing assistants</td>
</tr>
</tbody>
</table>
to a considerable degree of colour in a dyehouse effluent. Dyes are not easily biodegraded since, by design, they have good stability towards light and various chemical treatments. Most dyes are not of high toxicity and are eventually removed from water by oxidation or adsorption on sediment, but presence of colour in the water from a dyehouse is undesirable. It is a strong indicator of the presence of much higher quantities of dyeing assistants, almost all of which are present in the effluent. Even a simple chemical such as acetic acid can significantly increase the BOD.

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

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

8.5.2 Effluent treatment

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

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

(1) re-use of excess dye solution remaining at the end of a process – this can be incorporated into other dyeing recipes;
(2) mixing acidic and alkaline effluents before discharge to avoid excessive acidity or alkalinity;
(3) replacing starch-based sizing materials with polyvinyl alcohol, which can be recovered by membrane separation techniques and recycled;
Various types of processes are used in textile effluent treatment. Dyehouse effluent has a composition that is highly time-dependent in terms of both the types and quantities of contaminants. A first stage in treatment is often an equalising lagoon. Equalisation involves holding the combined process effluents for a given period to allow stabilisation of pH and BOD, and time for sedimentation of some solids. This considerably reduces fluctuations in the composition of the water leaving the dyehouse, which can upset downstream processes such as activated sludge treatment.

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

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

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

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

CHAPTER 9

Auxiliary chemicals for wet processing and dyeing

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

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

Many of these auxiliary chemicals are surfactants; they are chemicals exhibiting surface activity. This means that their molecules tend to accumulate at the surface separating two immiscible materials such as water and a fibre, or water and oil. The concentration of the surfactant at the interface may be more than 500 times greater than in the bulk of the aqueous solution. Surfactant molecules have two key structural features. One part of the molecule is a hydrophobic ‘tail’, such as a long alkyl chain (C15H31–); the other part is a hydrophilic polar or ionic group, or ‘head’, such as a carboxylate ion (–CO2–). Substances such as C15H31CO2–Na+ are slightly soluble in water, strongly adsorbed at phase boundaries, and have a pronounced tendency to aggregate in solution. The aim of this chapter is to introduce these surface-active chemicals and to examine how they function in processes such as scouring and dyeing.
9.1 IMPURITIES IN TEXTILE FIBRES

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

Natural fats and oils are esters of glycerol (1,2,3-propanetriol) and high molecular weight carboxylic acids called fatty acids. Since glycerol has three hydroxyl groups, and each can be esterified, its esters are called triglycerides. The fatty acids usually have an unbranched chain of up to about 20 carbon atoms with a carboxylic acid group on the end carbon atom. In saturated fatty acids the carbon atoms (other than that of the terminal carboxylic acid group) form only single bonds, either to other carbon atoms or to hydrogen atoms, in an unbranched chain. A typical example is stearic acid, CH₃(CH₂)₁₆CO₂H (octadecanoic acid). The triglycerides of saturated fatty acids are usually solids at room temperature.

Unsaturated fatty acids have at least one carbon–carbon double bond along the unbranched carbon chain, as in oleic acid cis-CH₃(CH₂)₇–CH=CH–(CH₂)₇CO₂H (cis-9-octadecenoic acid). Their triglycerides are usually oils at room temperature, but catalytic hydrogenation produces the solid saturated fats (Scheme 9.1). Unsaturated fats rapidly turn rancid on exposure to air. Their reactive carbon–carbon double bonds are sensitive to air oxidation. This causes yellowing and decomposition. Because fibres can absorb the rancid odour, unsaturated oils are not used in textile processing.

\[
\text{CH}_3\text{(CH}_2\text{)}_7\text{CH=CH(CH}_2\text{)}_7\text{CO}_2\text{H} + \text{H}_2 \xrightarrow{} \text{CH}_3\text{(CH}_2\text{)}_7\text{CH}_2\text{CH}═\text{CH(CH}_2\text{)}_7\text{CO}_2\text{H}
\]

Oleic acid Stearic acid

Scheme 9.1

In natural fats and oils, the glycerol is usually esterified with a mixture of fatty acids. Hydrolysis of fats in hot alkaline solution produces glycerol and a mixture of the alkali salts of the fatty acids. This hydrolysis reaction is called saponification because, when these fatty acid salts have about 12–20 carbon atoms, the alkali metal salts are soaps. Figure 9.1 shows the major products of the saponification of
castor and olive oils, and of mutton tallow. Palmitic acid (CH_{3}(CH_{2})_{14}CO_{2}H, hexadecanoic acid) and stearic acid occur as triglycerides in many animal fats and their sodium salts are often major components of common soap.

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

Figure 9.2 Linoleic acid (1) and linolenic acid (2)
Waxes are often either high molecular weight alcohols (fatty alcohols) or their esters with fatty acids. They are solids with high melting points and very low water solubility. The fatty alcohols do not hydrolyse in alkaline solution and their esters are much more resistant to hydrolysis than triglycerides. Other types of waxes are mixtures of high molecular weight inert alcanes such as paraffin wax.

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

9.2 SURFACE ACTIVITY OF DETERGENTS

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

\[
\text{Scheme 9.2}
\]

\[
\text{R}-\text{CO}_2^- + \text{H}_2\text{O} \rightarrow \text{R}-\text{CO}_2\text{H} + \text{HO}^- 
\]
The major disadvantages of natural soaps are that they precipitate in acidic solution at below pH 5, forming the insoluble free fatty acid, and also in hard water forming the calcium and magnesium salts (Section 8.1). They also readily precipitate in the presence of excess sodium ions. Although modern synthetic surfactants have almost completely replaced natural soaps in textile wet processing, a simple soap solution is a suitable point to begin a discussion of surface activity.

9.2.1 Basic thermodynamics

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

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln(K) \]  

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

\( \Delta S^0 \) is the change in entropy for the process. Entropy is a measure of how molecules are able to disperse the total energy available to them and increases whenever molecules have higher speeds and greater freedom of movement. As a substance passes from solid to liquid to gas, the entropy increases. It also increases with increasing temperature, because the broader distribution of molecule speeds allows better distribution of the total molecular energy. In the above
One of the fundamental principles of thermodynamics is that all favourable processes increase the overall entropy of the system and its surroundings. $\Delta S^0$ is the change in the Gibbs free energy for the process. It is a measure of the total overall change in entropy of the system and surroundings when the process takes place under standard conditions. A negative value corresponds to a large equilibrium constant and a favourable change. This is promoted by an increase in entropy for the process (positive value for $\Delta S^0$) and an exothermic change (negative value for $\Delta H^0$). In fact, the value of $\Delta H^0$ is a measure of the change in entropy of the process surroundings. Any released heat from an exothermic change, increases the temperature of the molecules in the surroundings. The increased molecular speeds correspond to a gain of molecular freedom and thus increased entropy. The overall free energy equation above therefore states that the overall entropy change of the system and surroundings resulting from a given process $(-\Delta G^0/T)$ is the sum of the entropy change for the process ($\Delta S^0$) plus that of the process surroundings $(-\Delta H^0/T)$.

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

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 = 44000 - 298 \times 119 = +8500 \text{ J mol}^{-1}$$

Thus, water evaporation at 25 °C is not an overly favourable process and the extent of vapourisation at equilibrium is small.
9.2.2 Surface activity and micelle formation

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

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

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

Surface adsorption and micelle formation are governed by the laws of thermodynamics. The ordering of the soap molecules at a phase boundary, or in a micelle, represents the most stable state of these molecules in the solution. When a soap molecule passes from the aqueous solution into a micelle, the structured cage of hydrogen-bonded water molecules surrounding the alkyl chain collapses. Thus, hydrogen bonds will be broken but the water molecules gain considerable
freedom of movement. The alkyl group of the soap molecule, which had no bonding interaction with the water molecules, now forms weak bonds with other alkyl groups in the micelle but the molecule has lost much of its freedom of movement. For micelle formation, $\Delta G^0 = +2 \text{ kJ mol}^{-1}$, indicating that the bond energy liberated from the hydrophobic interaction of the alkyl chains with each other in the micelle almost offsets that needed to break the hydrogen bonds when the structured water cage around the alkyl groups collapses. Micelle formation is, however, favourable because $\Delta S^0 = +77 \text{ J mol}^{-1} \text{ K}^{-1}$, a substantial increase in entropy. The soap molecules give up a considerable degree of freedom on aggregating in the micelle. The entropy increase for the process is, however, dominated by the collapse of the structured cage around each alkyl group of a soap molecule in solution, when it goes into a micelle. Many water molecules that were bonded into the cage wall are therefore free and more mobile. This is the driving force for micelle formation.

Figure 9.3 Surface activity and micelle formation in an aqueous soap solution
The formation of micelles is an important facet of surface activity. It occurs quite suddenly once the phase boundaries are saturated with a monolayer of surfactant molecules and the total concentration in solution increases above a critical value called the critical micelle concentration or CMC. The CMC is a characteristic property of a given surfactant. Its value is often lower than 1.0 g l\(^{-1}\). The formation of micelles depends on:

1. the preference of the surfactant alkyl groups to interact with each other, in their own hydrophobic environment, rather than remain exposed to the water;
2. the freeing of water molecules from the hydrogen-bonded cage around the hydrophobic groups when the surfactant molecules aggregate together.

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

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

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

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

9.2.3 Emulsification, detergency and wetting

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

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

---

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

\[ \gamma = \gamma_{\text{water-air}} + \gamma_{\text{water-fibre}} - 2 \cos \theta \]

**Key**
- \( \theta \) = Contact angle
- \( \gamma \) = Surface tension for the fibre–air \( (\gamma_{fa}) \), water–fibre \( (\gamma_{wf}) \) and water–air \( (\gamma_{wa}) \) interfaces
causes extension of the droplet with a decrease in the contact angle. The water drop therefore spreads out over the surface.

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

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

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

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

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

9.3 SYNTETIC SURFACTANTS

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

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

9.3.1 Anionic surfactants

This is the major group comprising almost 70% of commercial surfactants. Anionic surfactants are invariably the sodium salts of either aliphatic or aromatic...
sulphonic acids (R–SO₃Na, sulphonates), or of the sulphuric or phosphoric acid esters of alcohols (R–O–SO₃Na, sulphates; R–O–PO₃Na, phosphates). They are derived from both natural and synthetic chemicals.

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

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=&\text{CH}-(\text{CH}_2)\text{CO}_2\text{R} + \text{H}_2\text{SO}_4 \\
\text{OH} & \\
\text{CH}_3\text{CH}_2\text{CH}=&\text{CH}-(\text{CH}_2)\text{CO}_2\text{R} + \text{H}_2\text{O} \\
\text{SO}_3\text{H} & \\
\text{Turkey Red oil}
\end{align*}
\]

Scheme 9.3

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

\[
\begin{align*}
\text{C}_8\text{H}_{17}\text{O}_2\text{C}=\text{CH}=&\text{CH}-(\text{CH}_2)\text{CO}_2\text{H} + \text{NaHSO}_3 & \text{C}_8\text{H}_{17}\text{O}_2\text{C}=\text{CH}=&\text{CH}-(\text{CH}_2)\text{CO}_2\text{H} + \text{SO}_3\text{Na} \\
\text{Di-octyl maleate} & & \text{Di-octyl sulphonosuccinate}
\end{align*}
\]

Scheme 9.4
Other important types of anionic surfactants include sulphuric and phosphoric acid esters of the products of partial polymerisation of ethylene oxide onto the hydroxyl groups of alkylphenols or alcohols (4, in Figure 9.7). Since phosphoric acid is a triprotic acid, its esters may have one, two or three alkyl groups (5, in Figure 9.7). The products are invariably complex mixtures. Many of the sulphate and sulphonate surfactants are sodium salts but some are salts with amines such as triethanolamine. The latter are oil-soluble and excellent emulsifiers.

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

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

9.3.2 Cationic surfactants

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

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

Cationic auxiliaries are not usually compatible with anionic products and they are rarely used together. The two types interact with each other to form an insoluble organic salt. This is often rather gummy and difficult to remove if deposited on the fibre surface. Emulsification with excess surfactant or a non-ionic dispersing agent avoids this precipitation. Cationic agents are often used to aftertreat dyeings where anionic dyes of poor washing fastness have been used.
The cationic product interacts with the anionic dye in the fibres, forming a high molecular weight organic salt of decreased water solubility and much reduced diffusion rate. The washing fastness is therefore improved. Unfortunately, many of these products decrease the light fastness of the aftertreated dyeing.

9.3.3 Non-ionic surfactants

This is the second most important group of surfactants. They are mainly chemicals whose molecules have the usual hydrophobic ‘tail’ connected to a short polyethylene oxide chain. This will usually have about five to twenty -CH₂CH₂O- units linked together and forms the polar hydrophilic ‘head’ to whose oxygen atoms water molecules can hydrogen-bond. A wide range of products is available with different types of hydrophobic groups and varying degrees of polymerisation of the polyethylene oxide chain. Some have polypropylene oxide ‘heads’, usually promoting oil solubility. The non-ionic surfactants are produced from natural or synthetic carboxylic acids, alcohols, phenols, amines and amides, and ethylene oxide (for example, 10, 11, and 12, in Figure 9.9). Polyethylene oxide derivatives obtained by polyethoxylation of thiols give good detergents with high biodegradability, a factor that is becoming of increasing importance. All the precursors, such as alcohols, phenols and thiols, have a reactive hydrogen atom capable of adding ethylene oxide and initiating its partial polymerisation. The products are mixtures with molecules having polyethylene oxide chains of varying lengths.

![Figure 9.9 Structures of some typical non-ionic surfactants](image)

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

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

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

Non-ionic surfactants are usually excellent wetting agents and detergents. Those based on polyethylene oxide are usually water-soluble while those from polypropylene oxide are oil-soluble. Their major disadvantages are considerable
foaming, and clouding at higher temperatures and salt concentrations. To some extent, a low cloud point can be overcome by blending the non-ionic surfactant with an anionic product that serves as an emulsifiant.

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

**Scheme 9.6**

\[
RCH(CH_2O)nCH_2CH_2OH + H_2SO_4 \rightarrow RCH(CH_2O)nCH_2CH_2OSO_3H
\]

**Scheme 9.7**

9.3.4 Amphoteric surfactants

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

**Figure 9.10** Structure of an amphoteric surfactant – both cationic and anionic sites in the same molecule
Advantages and disadvantages of synthetic surfactants

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

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

Surfactants must always be evaluated under the conditions that prevail during their use, particularly to establish that they are stable. This is essential for processes in which the solution is strongly acidic or alkaline, or if high concentrations of salts are present. It is also important, in many applications, that
rinsing removes surfactant residues from a fabric. This is essential before application of water-repellent finish to a fabric.

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

9.4 OTHER APPLICATIONS OF SURFACTANTS

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

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

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

9.4.1 Dyeing levelling agents

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

\[
\text{Acrylic} + SO_3^- Na^+ + R_4N^+ \rightarrow \text{Acrylic} - SO_3^- R_4N^+ + Na^+
\]

\[
\text{Acrylic} + SO_3^- R_4N^+ + \text{Dye}^+ \rightarrow \text{Acrylic} - SO_3^- \text{Dye}^+ + R_4N^+
\]

Scheme 9.9

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

REFERENCES
An introduction to dyes and dyeing

10.1 DYES

10.1.1 The molecular structures of dyes

The structures of dye molecules are complex in comparison with those of most common organic compounds. Compare the molecular formula of acetic acid, \( \text{C}_2\text{H}_4\text{O}_2 \), with that of even a simple dye such as Orange II, \( \text{C}_{16}\text{H}_{11}\text{N}_2\text{SO}_4\text{Na} \) (Figure 1.2). Despite their complexity, dye structures have a number of common features. Most dye molecules contain a number of aromatic rings, such as those of benzene or naphthalene, linked in a fully conjugated system. This means that there is a long sequence of alternating single and double bonds between the carbon and other atoms throughout most of the formal written structure. This type of arrangement is often called the chromophore or colour-donating unit. The conjugated system allows extensive delocalisation of the \( \pi \) electrons from the double bonds and results in smaller differences in energy between the occupied and unoccupied molecular orbitals for these electrons. At least five or six conjugated double bonds are required in the molecular structure for a compound to be coloured. The wavelength of the absorbed light able to excite an electron from an occupied orbital to the first unoccupied molecular orbital then corresponds to visible light. The smaller the energy difference, the longer the wavelength of the light absorbed, according to the Planck equation:

\[
\Delta E = h\nu = \frac{hc}{\lambda}
\]

In this equation, \( \Delta E \) is the energy difference between the implicated molecular orbitals, \( h \) is Planck’s constant, \( \nu \) is the frequency and \( c \) is the speed of the absorbed light, and \( \lambda \) is its wavelength. Conjugation results in a framework with all the atoms lying in the same plane. Figure 10.1 shows some typical examples of dye structures with different chromophores.

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

10.1.2 Composition of commercial dyes

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

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

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

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

10.1.3 Dye selection

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

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

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

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

10.2 DYEING METHODS

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

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

1. Direct dyeing, in which the dye in the aqueous solution in contact with the material is gradually absorbed into the fibres because of its inherent substantivity;

2. Dyeing with a soluble precursor of the dye, which forms an insoluble pigment deep within the fibres on treatment after dyeing;

3. Direct dyeing followed by chemical reaction of the dye with appropriate groups in the fibre;

4. Adhesion of the dye or pigment to the surface of the fibres using an appropriate binder.

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

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

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

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

10.3 DYEBATH AND FABRIC PREPARATION

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

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

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

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

10.4 TERMS USED IN DIRECT EXHAUST DYEING

10.4.1 Exhaustion

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

\[
\% \text{ Exhaustion} = \frac{C_0 - C_s}{C_0} \times 100
\]  

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

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

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

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

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

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

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

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

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

$$K = \frac{C_f}{C_s} \frac{(C_s - C_s) \times L}{C_s} = \frac{(C_s - C_s) \times C_s}{C_s} \times L \frac{(E \times L)}{(L - E)}$$

(3)

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

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

(4)

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

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

10.4.4 Rate of dyeing and strike

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

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

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

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

Materials composed of finer fibres have a much larger specific surface (m² kg⁻¹) and a higher dyeing rate, even though the equilibrium exhaustion may not be significantly different from that of a material made of coarser fibres of the same polymer. If the dyeing rate is proportional to the fibre surface area per unit mass, it will be inversely proportional to the square root of the fibre tex.

\[
\text{Dyeing rate} = \frac{\text{area}}{\text{mass}} = \frac{2\pi}{\pi} \frac{r}{r^2} = \frac{1}{r}
\]

\[
\text{Fibre tex} = \pi r^2
\]

\[
\text{Dyeing rate} = \frac{1}{\sqrt{\text{tex}}}
\]

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

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

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

10.4.5 Migration and levelling

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

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

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

![Figure 10.4](image)

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

### 10.4.6 Effect of temperature on exhaustion and dyeing rate

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

In some cases, as for some direct dyes on cotton, the final exhaustion increases as the temperature of dyeing increases. This is because of the effect of temperature on the aggregation of the dye in solution. A dilute solution of a dye does not necessarily consist of a collection of individual dye molecules surrounded by water molecules. Many dyes, in solutions at lower temperatures or at high salt concentrations, exist as micelles or aggregates containing many molecules. Their behaviour is identical to that of surfactant molecules. Only individual dye
molecules, however, are able to diffuse into the fibres. A rapid equilibrium exists between single molecules and aggregates in solution. Aggregation is slightly exothermic. As the dyeing temperature increases, the aggregates gradually break up (heat absorbing) so that more individual molecules are available for penetration into the fibres. The exhaustion thus increases with increasing temperature. Eventually, if the dyeing temperature increases further, and aggregation is no longer significant, the final exhaustion will begin to decrease with increasing temperature. In the dyeing of synthetic fibres with disperse dyes, the dye bath exhaustion often apparently increases with increasing temperature at temperatures around the dyeing transition temperature. This is more of a kinetic effect related to the rate of dye diffusion, controlled by polymer chain segment mobility. Practical dyeing rarely reaches equilibrium. A rapidly dyeing dye may soon reach equilibrium and dyeing may only require a relatively short time ((a), in Figure 10.5). For such a dye, dyeing at lower temperatures gives the best exhaustion ((a), at temperature T2), assuming that dyeing is still reasonably rapid. For a slowly dyeing dye ((b) in Figure 10.5), the best exhaustion normally occurs at higher dyeing temperatures ((b), at temperature T1) because dyeing is far from equilibrium and the exhaustion depends on the rate of dyeing and the time.

10.4.7 Dye compatibility

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

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

10.5 CONTINUOUS DYEING

10.5.1 Introduction

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

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

Most continuous dyeing processes can be divided into four stages:

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

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

10.5.2 Padding

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

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

![Figure 10.7 Schematic of a padder](image)

The fabric first passes through the pad trough, where it is saturated with dye solution, and then between the rollers, where the pressure squeezes air out of the fabric and the solution into it. The nip is the zone where pressure is applied to the wet fabric. The material should be well prepared and very absorbent because the wetting time in the pad bath may be as short as 0.5 s. Dry fabrics of cotton and cotton/polyester are sometimes difficult to wet quickly and re-wetting agents are often dried into the material at the end of preparation. The fabric must, of course, be free of creases and have flat selvages. It is accurately centred on the rollers and runs under moderate tension.
The greater the applied pressure at the nip, the smaller the amount of dye solution retained by the fabric. The latter is called the wet pick-up, the weight of dye solution retained per 100 g of dry fabric. It should be high enough that there is sufficient solution to adequately wet the fibres and yarns and allow the dye to uniformly reach the fibre surfaces, but not so high that there is excessive migration on drying (Section 10.5.3). The wet pick-up cannot be decreased below a certain limit, no matter how high the nip pressure because it is not possible to squeeze out the water absorbed by the fibres and that adhering to the fibre surfaces. When the nip pressure decreases, after passage of the fabric, some of the expressed water is always re-absorbed. The minimum wet pick-up is usually around 55–60% for cotton/polyester materials, 60–70% for cotton, and higher for fabrics of the more absorbent viscose.

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

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

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

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

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

10.5.3 Fixation procedures

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

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

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

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

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

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

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

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CHAPTER 11

Dyeing theory

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

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

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

11.1 DYEING EQUILIBRIA

In the study of dyeing equilibria, the fibre and dye solution are heated at constant temperature until a state of equilibrium is reached. After the initial increase in the degree of exhaustion, it eventually becomes constant, but a true equilibrium implies that the dye is also uniformly distributed throughout the fibres. On heating for the extended period required to reach a true equilibrium, there is always a risk of some decomposition of the fibre, or of the dye.
It is common practice to determine the amount of dye in the fibre from the initial quantity added to the bath, less that remaining in solution at equilibrium. The latter is readily obtained by spectrophotometric analysis of the dye solution (Chapter 24). A mass balance, however, is a necessary prerequisite to ensure that there are no losses of dye from decomposition. This involves completely extracting the dye from the fibre, or dissolving the dyed fibres and determining the dye in the polymer solution. Again, the dye should not decompose during these processes.

11.1.1 Adsorption isotherms

An adsorption isotherm gives the concentration of a substance adsorbed on a solid surface in relation to its concentration in the surrounding fluid when the system is at equilibrium at a constant temperature. The graph representing a dyeing adsorption isotherm has the adsorbed dye concentration \( C_f \) in g kg\(^{-1}\) or mol kg\(^{-1}\) plotted against the solution concentration \( C_s \) in g l\(^{-1}\) or mol l\(^{-1}\).

Adsorption isotherms are useful for the information they provide on the dyeing mechanism. There are three main types of dyeing adsorption isotherm, usually referred to as the Nernst, Langmuir and Freundlich isotherms. Most dyeing systems involving only adsorption are completely reversible. Equilibrium isotherms, established by adsorption of dye from solution onto initially undyed fibres, are identical to those obtained by desorption of dye from dyed fibres into an initially blank dyebath.

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

\[
C_f = k C_s
\]  

(1)

where \( k \) is a constant. This is also the equation describing the distribution or partition of a solute between two immiscible solvents. The graph of \( C_f \) against \( C_s \) is linear up to the point corresponding to the dye saturating the fibre and the water.

The dyeing of many synthetic fibres with disperse dyes follows this type of isotherm (Figure 11.1). The fibre, in which the dye is soluble, extracts the disperse dye from the aqueous bath, in which it is only slightly soluble.

The Langmuir isotherm applies to adsorption on specific sites in the solid, of which there are often only a limited number. Such a situation exists in the dyeing of nylon with simple acid dyes by an ion exchange mechanism. The counter ion associated with an alkylammonium ion group in the nylon, under weakly acidic conditions, is exchanged for a dye anion (Scheme 4.4). The Langmuir adsorption
isotherm is easily derived. The rate of desorption depends only on the fraction of occupied sites \( \frac{C_f}{C_{\text{max}}} \). The rate of adsorption of dye onto the fibre from solution, however, depends upon the fraction of unoccupied sites \( 1 - \frac{C_f}{C_{\text{max}}} \) and the concentration of dye in the solution \( C_s \). At equilibrium, the two opposing rates are equal and:

\[
k_1 \left(1 - \frac{C_f}{C_{\text{max}}} \right) C_i = k_{-1} \frac{C_i}{C_{\text{max}}}
\]

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

\[
\frac{C_f}{C_{\text{max}}} = \frac{K C_s}{1 + K C_s}
\]

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

$$\frac{C_s}{C_f} = \frac{C_s}{C_{f\text{max}}} \left(1 + \frac{1}{K C_{f\text{max}}} C_s\right)$$

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

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

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

$$C_f = k C_s^n$$

or

$$\log(C_f) = \log(k) + n \log(C_s)$$
where \( k \) is a constant, and the exponent \( \alpha \) often has a value around 0.5 for the adsorption of anionic dyes on cellulosic fibres (Figure 11.1). The amount of dye adsorbed by the cotton fibres depends upon the available pore surface area. Initially, the dye molecules adsorb on the surfaces of the most accessible pores, but increasingly the dye must penetrate into the less accessible areas, so adsorption becomes more difficult. The dye molecules may even adsorb onto a layer of dye molecules already adsorbed on the pore surfaces. The equation for the Freundlich isotherm cannot be derived, as was the equation for the Langmuir isotherm.

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

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

### 11.1.2 Standard affinity of a dye

Chemical equilibria are usually discussed in terms of the change in the standard Gibbs free energy for the transformation that comes to equilibrium. The Gibbs free energy is, however, an extensive quantity depending upon the amounts of substance, and therefore varies with change in the composition. In treating dyeing equilibria, the alternative chemical potential is used. The chemical potential is defined as the change in free energy of a system that occurs when the composition changes by a unit molar amount of substance, all other variables such as the temperature, pressure and the amounts of other components remaining constant. It is a property akin to temperature or voltage. These determine the direction and rate of heat transfer, or the direction and size of charge transfer (current), respectively.
A transformation, at constant temperature and pressure, occurs so that the
substance transfers from the state of higher to lower chemical potential until
equilibrium is attained. In the case of dyeing, if the chemical potential of the dye
in solution is higher than in the fibre, the dye will transfer to the fibre. The
chemical potential in the solution falls; that in the fibre increases. At equilibrium,
the chemical potential of the dye in the fibre is equal to the chemical potential of
the dye in the solution. These are given by:

\[ \mu_s = \mu_s^0 + RT \ln(a_s) \quad \text{and} \quad \mu_f = \mu_f^0 + RT \ln(a_f) \]  

(6)

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

\[ \mu_s - \mu_f = 0 = \mu_s^0 - \mu_f^0 + RT \ln \left( \frac{a_f}{a_s} \right) \]  

(7)

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

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

(8)

where \( K \) is the equilibrium constant for dyeing.

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

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

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

(9)

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

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

(10)

Figure 11.4 Adsorption isotherms for dyeing polyester with CI Disperse Red 15
(Source: [1])
This value for the standard affinity indicates a favourable equilibrium for dyeing. At equilibrium at 100 °C, the dye is almost 900 times more soluble in the polyester than it is in water.

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

\[
\gamma_i = [\text{Dye}^{b+}] [\text{Na}^+]^b
\]  

This is derived from:

\[
\text{Dye} \text{(SO}_3 \text{Na})_3(s) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Dye} \text{(SO}_3 \text{)}_3(\text{aq}) + 3\text{Na}^+(\text{aq})
\]  

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

\[
-\Delta \mu^0 = \ln \left( \frac{C_a}{C_i} \right) + z \ln \left( \frac{N_a}{N_i} \right) - (z+1) \ln(V)
\]  

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

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

\[
-\Delta \mu^0 = -\Delta G^0 = -\Delta H^0 + T\Delta S^0 = RT \ln(K)
\]  

The enthalpy of dyeing \(\Delta H^0\) can be derived from the temperature dependence of the standard affinity using the above free energy equation. A graph of \(\ln(K)\) versus \(1/T\) will be linear with a slope of \(-\Delta H^0/R\). The data in Table 11.1 are derived from
Figure 11.4. The graph of ln(K) as a function of 1/T (a), in Figure 11.5) has a slope $-\Delta H^\circ/RT$ of 7393 K so that the enthalpy of dyeing $\Delta H^\circ$ is $-61.5$ kJ mol$^{-1}$. As is usual, the enthalpy of dyeing is negative since dyeing is exothermic. This means

$$\Delta H^\circ = -61.5 \text{ kJ mol}^{-1}$$

### Table 11.1

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

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility $C_s$ (g l$^{-1}$)</th>
<th>Solubility $C_f$ (g kg$^{-1}$)</th>
<th>$K = C_f/C_s$</th>
<th>$-\Delta H^\circ$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.3</td>
<td>0.0207</td>
<td>30.89</td>
<td>1492.0</td>
<td>22.02</td>
</tr>
<tr>
<td>100.0</td>
<td>0.0402</td>
<td>34.81</td>
<td>865.2</td>
<td>20.98</td>
</tr>
<tr>
<td>120.0</td>
<td>0.1449</td>
<td>44.27</td>
<td>305.3</td>
<td>18.71</td>
</tr>
</tbody>
</table>

Figure 11.5 Graphs of ln(K) versus $1/T$ (a), and of standard affinity versus $T$ (b), for the determination of the enthalpy and entropy of dyeing.
that the dye bonds to the fibre more strongly than it bonds to water in the external aqueous solution. The enthalpy of dyeing in this case corresponds to the enthalpy change for transfer of the dye from the aqueous solution into the fibre. It does not include the enthalpy change associated with dissolution of the dye solid in the water.

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

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

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

\[
-\Delta G^0 = -\Delta H^0 + T \Delta S^0 = RT \ln(K) \tag{16}
\]

Alternatively, the graph of \(-\Delta G^0\) versus \(T\) has a slope of \(\Delta S^0\), which gives the same value ((b), in Figure 11.5):

\[
-\Delta H^0 = -\Delta G^0 = -\Delta H^0 + T \Delta S^0 \tag{17}
\]

The value of \(\Delta S^0\) provides a measure of the change of molecular freedom arising as a consequence of dye absorption. It seems reasonable that the immobilisation of the dye in the fibre, relative to its freedom of movement in the aqueous solution, would give a substantial decrease in entropy in agreement with the negative value of \(-108 \text{ J mol}^{-1} \text{ K}^{-1}\) for \(\Delta S^0\) in the above example.
In some cases, the entropy of dyeing is positive. This indicates an increase in molecular freedom as a consequence of the dyeing process. This probably involves an increase in freedom of water molecules that were initially in a highly structured, hydrogen-bonded cage surrounding the hydrophobic dye molecules in the solution. This cage collapses when the dye molecules transfer into the fibre, releasing water molecules. This is the same effect that causes the entropy of micelle formation to be positive (Section 9.2.2). Thus, the freedom gained by the liberated water molecules more than offsets that lost by the adsorbed dye.

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

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

11.2 DYEING KINETICS

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

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

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

![Exhaustion curves](image)

Figure 11.6 Graphs of exhaustion versus time to show variations in the time of half dyeing.
Exhaustion isotherms can be described by different empirical equations. One or other of the following two equations sometimes gives a reasonable description of the dyebath exhaustion during the dyeing process.

$$\frac{E_t}{E_{eq}} = 1 - e^{-kt} \quad \text{or} \quad \frac{1}{E_{eq} - E_t} - \frac{1}{E_{eq}} = kt$$  \hspace{1cm} (18)

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

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

Fick’s equations describe the diffusion of a dye within a fibre. Fick’s second law states that the rate at which the dye diffuses across a unit area in the fibre ($\frac{dQ}{dt}$ in mol m$^{-2}$ s$^{-1}$) is proportional to the concentration gradient across that area ($\frac{dC}{dx}$ in mol m$^{-3}$ m$^{-1}$), the proportionality constant being the diffusion coefficient $D$ (m$^2$ s$^{-1}$).
The negative sign gives a positive value of the diffusion coefficient because the concentration gradient is negative; the concentration decreases along the x axis, in the direction of diffusion. Considerable effort has been devoted to measuring diffusion coefficients and their correlation with dyeing kinetics. Diffusion coefficients are larger for dyes with lower molecular weights and for more porous, less compact fibre structures.

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

$$C_t = C_0 \sqrt{\frac{D t}{\pi}}$$ \hspace{1cm} (20)

A diffusion coefficient calculated from the slope of a graph of $C_t/C_0$ against $\sqrt{t}$ gives an average apparent value that will differ from that obtained from a steady-state experiment at a constant concentration of dye in the material. One of the major problems in this field is that the diffusion coefficient of the dye in the fibre depends upon the amount of dye already present.

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

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

The practical significance of all this is that reproducible dyeing requires that the rates of mass-transfer are also reproducible. This means that a dyeing machine only gives reproducible dyeings when the relative rate of contact of fibre and solution is constant. High-speed circulation of dye liquor under pressure through a wound package of yarn in a large dyeing machine does not give the same mass-
transfer conditions as stirring a small sample in a laboratory dyeing pot. For this reason, dyeing recipes prepared on the basis of laboratory dyeings do not always give the same shade when the recipe is used in a large dyeing machine.

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

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

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

### 11.3 AGGREGATION OF DYES

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

11.4 CONCLUSION

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

REFERENCES

CHAPTER 12

Dyeing machinery

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

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

12.1 BASIC FEATURES OF BATCH DYEING MACHINES

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

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

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

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

12.2 DYEING MACHINES FOR LOOSE FIBRE AND SLIVER

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

Similar types of dyeing machine serve for dyeing raw stock and various types of sliver. The most common types hold the goods in a conical pan with perforated inward sloping sides, or in a perforated cage. The fibres are gradually packed into the pan, then wetted and compressed by screwing down a solid plate laid on the top. The top plate prevents the dye solution from flooding the top of the pack. A flange on the bottom of the pan fits onto a central pipe delivering dye solution from the pump to the inside of the fibre mass. The entire pan or cage sits in an
outer container, also with a closed lid, which collects the dye liquor that has flowed out through the fibres and returns it to the pump (Figure 12.1).

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

Before further processing of dyed loose fibre or sliver, drying is necessary. Centrifugation in a hydroextractor removes the bulk of the adhering or unbound water. It is a slow batch process requiring considerable manipulation and does not eliminate absorbed or bound water. Thermal drying is therefore essential. This can be done by forcing hot air through a bed of fibres held on a continuously moving chain that passes through an oven. Sucking hot air through the fibres held on the surface of perforated drums is also effective.
There are also machines for the continuous dyeing of loose fibre and sliver. For loose fibre dyeing, suction onto a perforated drum or wire cage holds the fibres in place during application of the dye solution and subsequent heating with a mixture of steam and hot air to bring about dye fixation. This type of process requires large runs of one colour for economic operation. Only dyes that absorb and fix rapidly are suitable. In continuous sliver dyeing machines, the band of parallel fibres is impregnated with dye solution and then passed through a heated tunnel. The tunnel may be sectioned so that dyeing at high temperature occurs in the first section, washing-off of unfixed and surface dyes takes place in the second, and the fibres are dried in the third.

12.3 MACHINES FOR DYEING YARN

12.3.1 Hank dyeing

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

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

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

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

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

### 12.3.2 Package dyeing machines

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

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

The dye liquor is pumped into the base of the frame and up through the perforated spindles. Solid spacer plates seal the ends of each package on a spindle and force the circulating liquor to flow out horizontally through the package. Because of their regular cylindrical shape, however, cheeses on compressible formers can often be mounted on the spindles without spacer plates, and compressed together. At the top of the spindles, a screw-on plate presses the cheeses down and gives a good seal between them. Cones cannot be compressed lengthways to the same extent as cheeses and usually require solid spacer plates between them. Even then, the liquor flow through a cone is not usually as uniform as through a more regularly shaped cheese. The dye liquor flows up the perforated spindle and flows outward through the packages of wound yarn. It then flows back down over the outside of the frame and back to the pump. Heating is usually with super-heated steam in coils situated just below the frame carrying the spindles. The same coils, or a different set, can be used for cooling.
Fully filled, closed machines allow bi-directional flow that assists level dyeing. Even though the walls of a package may be of uniform thickness, the surface area of the package increases with distance from its centre. With in-to-out flow, this results in a decrease in the volume flow rate towards the outer edges of the package. To obtain level dyeing of the yarn throughout the package, the initial dye strike must be controlled. Less level dyeing dyes, of higher washing fastness, are used than when dyeing hanks. Frequent flow reversal gives improved levelness with such dyes of low migration ability. Package dyeing has many advantages over hank dyeing. It allows higher loads, lower liquor ratios, more rapid dyeing and easier unwinding of the dyed yarn.

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

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

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

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

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

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

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

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

12.4 MACHINES FOR DYEING FABRIC

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

![Figure 12.3 Illustration of a winch dyeing machine with Autoloda](image-url)
friction and its own weight. Covering the winch with polypropylene or polyester tape increases the friction.

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

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

As for all forms of rope dyeing, the fabric must be fairly resistant to lengthways creasing. Ideally, there should be constant lengthways folding and unfolding of the rope as it cycles around the machine. Lubricants are often added to the dyebath to promote this. A wide variety of materials that do not readily crease can be dyed using the winch machine. The good mechanical action promotes crimp in the yarns and improves the loop length of knitted materials. It gives thicker fabrics with a fuller handle. Open-width threading of the fabric in a winch machine is possible for heavy materials such as carpets and for fabrics that might be crushed in rope form.
Several ropes of equal length (50–100 m) are usually dyed side by side, being kept apart by pegs in a long rail below the fly roller. The hinged peg rail lifts if a tangled rope arrives, automatically turning off the winch drive. Short lengths of individual ropes require more sewing and more time to locate the seams for unloading. There is an obvious advantage if one long, continuous spiral of rope advances through the machine from one side to the other. It then returns to the start by way of a sloping trough or tube filled with dye solution at the back of the machine. In this case, a continuous helical metal spiral, whose pitch determines the loop spacing, replaces the peg rail. This type of loading is more uniform and allows a lower liquor-to-goods ratio.

12.4.2 Jig dyeing machines

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

The bath can be rapidly heated by live steam from an open perforated pipe, the perforations pointing down and away from the fabric. Closed-coil steam heating is slower but gives better temperature control during dyeing and avoids dilution of the liquor. As in winch dyeing, the fabric moves through a stationary bath, which is stirred only by the movement of the fabric through it. The bulk of the dyeing is usually carried out with a constant bath temperature. In the widest machines,
stirring the bath ensures uniformity of its temperature. During dyeing, the machine lid should be closed. This helps to maintain a high and uniform roll temperature and reduces heat loss and steam consumption. Any condensation on the lid must run into the dyebath without drops falling onto the fabric rolls. The lid limits air access and avoids rapid oxidation of reduced leuco dyes. Dyeing under pressure is also possible using jigs that roll into an end-opening autoclave.

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

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

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

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

12.4.3 Beam dyeing machines

In principle, beam dyeing is similar to package dyeing but with a single large package. As mentioned above, beams of warp yarns can be dyed by circulating dye liquor through the bed of yarns laid down on a perforated roller. Beam dyeing of fabric involves winding it onto a perforated beam and pumping dye liquor through this (Figure 12.5). This dyeing method is widely practised for those fabrics that might crease, extend or abrade when dyed in machines where the fabric is in motion. Obviously, it is not appropriate for compact fabrics that severely limit the flow of dye liquor through the many layers on the roll. Some early machines had an open bath with a vertical beam placed in it. The autoclave type with a horizontal beam is now more common. The autoclave allows higher dyeing temperatures and, if required, two-way flow through the roll of fabric. Beam dyeing under pressure is easier than jig pressure dyeing.
The winding of the fabric onto the beam is a critical step. The beam is usually first wrapped with a few layers of cotton fabric. This provides a soft bed for the material, allows dispersion of the solution, and filters out any particles. The fabric is then wound onto the beam at constant speed with a uniform but not excessive tension. It is essential to avoid creases and to have evenly aligned selvages without any curling. A piece of polypropylene or calico is stitched to the end of the fabric, rolled around a few times and re-stitched. This prevents the centre of the roll from ballooning and keeps it clean. Tubular knit fabrics are usually slit along one crease before beaming. Although successive lengths of fabric can be joined and dyed on the beam, the number of seams should be kept to a minimum. As in jig dyeing, heavy seams tend to retain more dye solution and can cause deeper dyeing on adjacent layers in contact with the seam.

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

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

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

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

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

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

12.4.4 Jet dyeing machines [2]

The first jet dyeing machine, based on a design by Burlington Industries in the USA, was introduced by the Gaston Country company in 1961. Jet machines essentially all use the same principle (Figure 12.6). Dye liquor is injected at high speed from an annular orifice around a rope of fabric as it passes through a venturi tube. This is a tube with a constriction. The high linear velocity of the jet of liquid, and its flow around the fabric rope in the venturi, pull the fabric along towards the back of the machine. Fabric speeds are usually about 200–250 m min⁻¹ but can be much higher. The fabric then falls into the back of the machine and slowly moves to the front where it rises to the jet again. A typical cycle takes about 1 min.
The lifting of the fabric is mainly by the action of the jet. A non-driven lifter roller, or a small driven winch, in front of the jet, guides the fabric into the venturi tube. In large machines, several jets arranged side by side with one rope in each tube, share a common bath. Dye liquor that collects in the bottom of the vessel is pumped through a heat exchanger and back into the jet. Solutions of dyes and chemicals are added from a tank using a secondary pump.

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

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

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

Because the interior of most jet machines is not easily accessible, they are difficult to clean. In particular, polyester oligomer deposits may develop on the hot surfaces and later dislodge. Cleaning with circulating NaOH and Na$_2$S$_2$O$_4$ solution is common. The inside surfaces must be smooth to avoid snags.

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

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

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

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

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

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

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

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

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

Rotating drum machines are also useful for dyeing hose and garments. These have an inner perforated drum that rotates in either direction inside a sealed drum of slightly greater size. Baffles divide the inner drum into quadrants to ensure that the goods move as it rotates. The rate of rotation is quite low, about 3–4 rev min\(^{-1}\), with frequent reversals of direction. Again, the goods are preferably bagged. As for all dyeing machines, a smooth interior is essential to avoid snagging. A variety of tumbling machines have higher rotation speeds and can spin dry at the end of the cycle. These are similar to dry-cleaning machines.

Rotating drum machines are more efficient and cleaner to operate than paddle machines. The more vigorous mechanical action often promotes more shrinkage and bulking, which may be desirable for some articles.
Nylon hose can be mounted on appropriately shaped boards that are placed in a type of autoclave that allows dyeing, drying and heat setting to be carried out in sequence. Garment dyeing machines are also available that allow pressure dyeing of polyester articles.

12.6 CONTINUOUS DYEING EQUIPMENT

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

12.6.1 Padding mangles

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

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

The bath level must remain constant. A simple mass balance for the dye solution shows that the rate of flow of solution (kg soln min⁻¹) from a supply reservoir into the pad bath must equal the rate at which solution leaves the bath in the fabric. The latter is equal to the fabric pick-up (kg soln kg⁻¹ fabric) times the mass flow rate of fabric (kg fabric min⁻¹). At a typical running speed of 15 kg fabric min⁻¹ with 60% solution pick-up, 9.0 kg soln min⁻¹ must flow into the pad bath. Since the volume of solution in the bath is around 30–40 l, fresh solution completely replaces it in about 3–4 min. The dye solution from the supply reservoir feeds into a perforated pipe running along the bottom of the pad bath at the back of the fabric, the holes pointing away from the fabric. A controller maintains a fixed bath level or depth and activates the feed from the dye solution supply reservoir.
The pad rollers are called bowls and may be horizontally or vertically opposed. The region where they are in contact and exert pressure on the wet fabric is called the nip. On leaving the bath, the fabric passes vertically into the nip of horizontally opposed bowls, or over a small free-running smooth roller in front of the nip of vertically opposed bowls (Figure 10.7). After the nip, the fabric should leave both bowl surfaces at the same time to avoid back-to-face colour differences. In fact, after leaving the nip, contact of the wet fabric with any roller or guide should be minimal. The heavy padder must be on a firm floor with the fabric accurately centred.

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

The two pad rollers are called bowls and their axes may be horizontally or vertically opposed. They are typically about 2 m long and 35–40 cm in diameter. The roller axes are usually exactly aligned. A pneumatic system applies a pressure of up to about 50 kg cm\(^{-1}\) of bowl length at both ends of one of the mandrels, the upper one when they are vertically opposed. This gives a contact width of about 1 cm where the rubber flattens. The higher the applied pressure, the greater the degree of deformation of the rubber surface, the lower the solution pick-up, but the greater the extent of wear over time. The rubber surface should be treated with great care. Any surface damage holding dye solution may transmit repeating colour spots onto the padded fabric. The bowls should be hosed down immediately after use and the pressure released. The pressure should only be applied when the rollers are rotating to avoid forming a permanent flattened zone that can cause an irregularly coloured stripe on the fabric.
The pressure at the ends of the mandrel causes some bending. This gives higher pressures towards the fabric selvages and a higher solution pick-up in the centre. To counteract this, the surface camber of one or both bowls can be modified to give even pick-up across the nip width under pressure. The rubber surface is ground so that it tapers slightly towards each end. The camber introduced will only give a uniform pressure across the width of the nip for one application pressure. Alternatively, the axes of the two bowls can be skewed slightly so the applied pressure is greater in the middle and less at the ends. The degree of skew can be varied for different applied pressures.

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

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

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

12.6.2 The Thermosol process

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

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

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

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

12.6.3 Roller steamers [3]
Steamers are used for the continuous fixation of vat, sulphur, reactive and direct
dyes on cotton, particularly in blends with polyester. The padded fabric passes through a zone filled with saturated air-free steam for about 20–60 s. If the polyester component has already been dyed by the Thermosol process, the dry fabric already contains the dyes for the cotton. Before entering the steamer, it is padded with chemicals for assisting the dyeing of the cotton. The steamer usually has a bank of driven rollers at the top and a set of free rollers at the bottom, the fabric being interlaced up and down through the two sets. A steamer typically holds about 30–60 m of fabric. Again, good roller alignment is necessary to avoid lengthways creases.

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

12.6.4 Continuous washing units [4]

Continuous washing units are used both for washing after continuous scouring and bleaching of grey cotton, and also for removing unfixed dye and chemicals after continuous dyeing. The vertical types have horizontal banks of rollers along the top and bottom. The upper rollers are driven and are not in the wash liquor. The lower set are free-running and immersed. The fabric being washed therefore undergoes a series of dips into the washing liquor. This flows countercurrent from one washing box to the previous one, often by overflow of the compartment wall, provided that the water is not overly contaminated. They usually operate at temperatures up to around 95 °C. Direct steam injection into the in-coming water is used to heat the washing solution. A number of devices are used to increase the efficiency of such units to minimise heat and water consumption. The dirty hot water discharged to the drain may pass through a heat exchanger to heat up the in-coming water. Carry-over of dirty liquor between compartments, or between adjacent washing units, can be minimised using a squeeze roller in contact with the last top roller.
The horizontal types of wash box have vertical banks of rollers at each end and the fabric passes up through the unit moving horizontally from one side to the other. Water enters at the top and flows downwards over the layers of fabric so the flow is again countercurrent. Horizontal washers work better with more open fabrics. Compact fabrics give too much water dropping off the sides of the fabric into the machine bottom. This type of washer contains a smaller amount of water but the fabric is under greater tension than in a vertical type washing unit.

REFERENCES
CHAPTER 13

Acid, pre-metallised and mordant dyes

13.1 GENERAL DESCRIPTION OF ACID DYES

This chapter deals with acid, mordant and pre-metallised dyes. Despite their different names, these three types of dye have many features in common. They dye both protein and polyamide fibres using similar dyeing methods. In the Colour Index, they are classified as 'acid dyes' or 'mordant dyes'. The name 'acid dye' derives from the use of an acidic dyebath. Most pre-metallised and mordant dyes are acid dyes. In the case of mordant dyes, the dyeings are aftertreated with a suitable metal ion mordant, usually chromium. In fact, mordant dyes are often referred to as chrome dyes. The metal in pre-metallised dyes is incorporated into the dye molecule during the manufacturing process.

The dyeing properties of acid dyes vary widely (Section 13.2.2). The acids used in the dyebath range from sulphuric acid (dyebath pH < 2.0) to ammonium acetate (dyebath pH > 6.5). Acid dyes are usually sodium salts of sulphonic acids, or less frequently of carboxylic acids, and are therefore anionic in aqueous solution. They will dye fibres with cationic sites. These are usually substituted ammonium ion groups in fibres such as wool, silk and nylon. These fibres absorb acids. The acid protonates the fibre's amino groups, so they become cationic. Dyeing involves exchange of the anion associated with an ammonium ion in the fibre with a dye anion in the bath (Scheme 13.1).

Acid dyes have molecular weights in the range 300–1000 g mol⁻¹. The dyes with larger molecules have higher substantivity for wool or nylon. Such dyes have slower diffusion in the fibre and therefore less ability to migrate and dye level. The more hydrophobic, high molecular weight dyes therefore have better fastness to wet processes. Their absorption by wool and nylon also involves the interaction of

\[
\text{Fibre} - \text{NH}_2 \text{(s)} + \text{H}^+ \text{(aq)} + \text{HSO}_4^- \text{(aq)} \rightarrow \text{Fibre} - \text{NH}_2^+ \text{HSO}_4^- \text{(s)}
\]

\[
\text{Fibre} - \text{NH}_3^- \text{HSO}_4^- \text{(aq)} + \text{Dye} - \text{SO}_4^- \text{(aq)} \rightarrow \text{Fibre} - \text{NH}_2^+ \text{Dye} - \text{SO}_4^- \text{(s)} + \text{HSO}_4^- \text{(aq)}
\]

Scheme 13.1
the dye with hydrophobic groups in the fibre. Dyeing is therefore not solely a consequence of simple ionic attraction.

The colour gamut of acid dyes is complete, including greens and blacks. The dyes are available as powders, grains and liquids for continuous dyeing, and as fine dispersions of the less soluble types. The selection of acid dyes for dyeing a particular material is not an easy matter, given the wide range of textile products and fastness properties demanded. Manufacturers recommend groups of selected acid dyes for each type of application. Compatible dyes are selected to have similar rates of dyebath exhaustion, when applied together by the recommended procedure, and similar fastness properties.

13.2 CLASSIFICATION OF ACID DYES

13.2.1 Classification according to chemical structure

Acid dyes are of many different chemical types. Sulphonated azo dyes constitute the major group and are mainly mono- and bis-azo compounds ranging in colour from yellow, through red to violet and brown. There are some navy blue bis-azo dyes that can build up to give blacks. The substantivity of azo dyes for polyamide and protein fibres is greater the higher their molecular weight and the lower the number of sulphonate groups per dye molecule. Many mordant and metal-complex dyes are also azo compounds. Their molecular structures are discussed later in this chapter (Sections 13.7.2 and 13.8).

Acid dyes usually have low substantivity for cellulosic fibres and do not give appreciable exhaustion onto them. Some of the higher molecular weight azo acid dyes, however, are difficult to distinguish from direct dyes for cotton (Chapter 14). The latter are often sulphonated bis-azo and polyazo dyes. There are therefore a number of acid and direct dyes with similar structural features that could be classified in either group. These dyes will dye wool, nylon and cotton. One feature that distinguishes acid dyes from direct cotton dyes, apart from their lower molecular weights, is that molecular planarity is not essential for acid dyes, but is for direct cotton dyes.

Anthraquinone acid dyes complement the azo dyes, ranging in colour from violet through blue to green. These dyes often have very good light fastness. Acid dyes with triphenylmerthene (blues and greens) and xanthene (reds and violets) chromophores are less important types noted for their brilliant colours. These
often have only poor light fastness. Sulphonated copper phthalocyanine dyes provide bright turquoise dyes of very good light fastness.

13.2.2 Classification according to dyeing characteristics

Acid dyes are commonly classified according to their dyeing behaviour, especially in relation to the dyeing pH, their migration ability during dyeing and their washing fastness. The molecular weight and the degree of sulphonation of the dye molecule determine these dyeing characteristics. The original classification of this type, based on their behaviour in wool dyeing, is as follows:

(1) level dyeing or equalising acid dyes;
(2) fast acid dyes;
(3) milling acid dyes;
(4) super-milling acid dyes.

Milling is the process in which a woollen material is treated, in weakly alkaline solution, with considerable mechanical action to promote felting. Dyes of good fastness to milling are essential to avoid colour bleeding during the process.

| Table 13.1 Characteristics of the various types of acid dyes |
|-------------------|----------------|-----------------|-----------------|----------------|
|                   | Levelling dyes | Fast acid dyes  | Milling dyes    | Super-milling dyes |
| Acid used         | Sulphuric      | Acetic         | Acetic or NH₄⁺ | NH₄⁺           |
| Dyebath pH        | 2–4           | 4–6            | 5–7             | 6–7            |
| Migration ability | High          | Moderate       | Low             | Very low       |
| Washing fastness  | Poor–fair     | Good           | Very good       | Very good      |
| Molecular weight  | Low           | Moderate       | High            | Very high      |
| Dye solubility    | High          | Moderate       | Low             | Low            |
| State in solution | Molecular     | Aggregated     | Aggregated      | Aggregated     |
| Substantivity (pH 6) | Very low      | Moderate       | High            | High           |

In the progression from levelling to super-milling dyes, the washing fastness improves gradually as the dye molecular weight increases and the number of sulphonate groups per dye molecule decreases. Larger molecules, with fewer sulphonate groups, have lower water solubility, migrate least during dyeing, and give dyeings of better washing fastness. They exhaust well on wool when dyeing in
weakly acidic baths with a pH above 5. On the other hand, small dye molecules with many sulphonate groups migrate very well during dyeing and have poor wet fastness. For low molecular weight acid dyes the dyebath exhaustion is low when dyeing at a pH greater than 4. Acid dyes therefore show the usual inverse relationship of migration ability to wet fastness. Table 13.1 summarises the dyeing properties of the various types of acid dye. Note the difference in molecular structure between the levelling dye CI Acid Red 1 and the milling dye CI Acid Red 138 in Figure 13.1.

![Chemical constitutions of some typical acid dyes](image)

**Figure 13.1** Chemical constitutions of some typical acid dyes

### 13.3 THE APPLICATION OF ACID DYES IN DYEING WOOL [1]

#### 13.3.1 Levelling acid dyes

Dyeing wool with levelling acid dye requires sulphuric or formic acid in the dyebath, along with Glauber’s salt, Na₂SO₄.10H₂O (5–10% owf). Considerable amounts of a strong acid are needed to achieve good exhaustion, typically 2–4% owf of sulphuric acid. Under such acidic dyeing conditions, levelling acid dyes have rapid strike for the wool because of the high concentration of cationic
ammonium ion groups in the wool. The dye molecules are not, however, firmly bound to these sites. Their good migration at the boil overcomes any initial colour unlevelness, provided sufficient time is allowed. If the initial dyeing is not quite on shade, the bath can be cooled somewhat, appropriate dyes added, and dyeing continued at the boil.

Because of the ease of migration of levelling acid dyes during dyeing, the fastness to washing of their dyeings is only from poor to moderate. Their light fastness, however, ranges from fair to good. These dyes are therefore used for pale to medium depths on wool fabric and yarn where a high degree of levelness is essential and good fastness to washing is not critical. In general, they produce much brighter shades than mordant or metal-complex dyes. Their relatively small molecular size provides high water solubility and good penetration into the individual fibres of tightly woven fabrics and high twist yarns. If the dye molecules do aggregate in solution at the maximum dyeing temperature, the aggregates are quite small, or there are enough individual molecules present in the solution for good penetration into the pores of the wool. Figure 13.2 illustrates a typical dyeing method.

Figure 13.2 A typical dyeing procedure with level dyeing acid dyes
Wool contains about 820 mmol kg\(^{-1}\) of amino groups, some of which convert into ammonium ions in the presence of sulphuric acid, with a bound bisulphate anion. During dyeing, a dye anion displaces the bisulphate ion associated with an ammonium ion site (Scheme 13.1). In typical dyeings, only a very small fraction of the available cationic sites have associated dye anions. The wool is far from being saturated with dye anions. The displacement of simple anions in the wool by dye anions is a consequence of the dye's greater substantivity for the wool. Other possible types of dye–fibre interaction, besides ionic forces, will be discussed later (Section 13.4.2).

The added Glauber's salt acts as a retarding and levelling agent. Sulphate and bisulphate ions inhibit the initial rapid strike of the dye by occupying and thus blocking ammonium ion sites in the wool. Dye anions of higher substantivity then gradually displace the sulphate and bisulphate ions. These anions, however, do have slight substantivity for the wool and will displace some absorbed dye in acidic solution. The presence of Glauber's salt thus promotes levelling and reduces the dyebath exhaustion. Partial stripping of faulty dyeings is possible using 15–20% owf of Glauber's salt in an acidic bath at the boil. Level dyeing can also be controlled by using less sulphuric or formic acid in the initial bath. This gives fewer cationic sites in the wool. As dyeing proceeds, more acid is then gradually added to decrease the bath pH.

Levelling dyes give decreasing exhaustion on increasing the dyebath pH to values above 4, and with increasing temperature. These effects are consistent with a simple ion exchange process that is exothermic. Above the isoelectric point of wool around pH 5, the fibres become more anionic as the ammonium ions are then present in smaller numbers than carboxylate ion groups (Scheme 13.2). In weakly alkaline dyebaths, for example in the presence of dilute ammonia solution, levelling acid dyes readily desorb from wool fibres. This provides another method for stripping the colour from faulty dyeings.

\[
\begin{align*}
\text{pH} &< 5 & \text{HO}_2\text{C} \rightarrow \text{Wool} \rightarrow \text{NH}^+ \\
\text{pH} &= 5 & \text{O}_2\text{C} \rightarrow \text{Wool} \rightarrow \text{NH}_3 \\
\text{pH} &> 5 & \text{O}_2\text{C} \rightarrow \text{Wool} \rightarrow \text{NH}_2
\end{align*}
\]

Scheme 13.2
13.3.2 Fast acid dyes

These are usually monosulphonated acid dyes of somewhat higher molecular weight than typical levelling dyes. They dye wool by essentially the same dyeing method (Figure 13.2) using acetic acid (1–3% owf) and Glauber’s salt (5–10% owf). They have reasonable migration at the boil. In some cases, a levelling agent may be recommended. These dyes are used where level dyeing is necessary but when the washing and perspiration fastness of levelling acid dyes are inadequate.

13.3.3 Milling acid dyes

These anionic dyes have higher molecular weights and greater substantivity for wool than levelling or fast acid dyes. They usually only have one sulphonate group per dye molecule and therefore have lower water solubility. They aggregate strongly, possibly even in boiling water, and give colloidal solutions. Dyeing with milling dyes is carried out in the pH range from 5 to 7, usually starting in the presence of sodium acetate or ammonium sulphate. Acetic acid may be added later in the process to promote exhaustion by increasing the number of ammonium ion groups in the wool. At best, milling dyes have low rates of diffusion in wool and poor levelling ability. Besides simple anion–cation attraction, other types of intermolecular forces bind the dye molecules to the wool. Milling acid dyes give dyeings with moderate to good washing fastness, better than for levelling acid dyes. In particular, they give dyeings that are reasonably fast to alkaline milling and with fair to good light fastness.

When dyeing with milling acid dyes, Glauber’s salt is never added. Under typical dyeing conditions, at pH 6, it increases the exhaustion of such dyes and hinders levelling. The high concentration of sodium ions from the Glauber’s salt helps to suppress the natural negative surface charge of the wool so that the dye anions are not repelled to the same extent and therefore have higher substantivity. The fibre’s negative surface charge is much less evident in acidic solution when the wool has an excess of cationic ammonium ion groups. This effect of Glauber’s salt is exactly the same as that of added salts in cotton dyeing and is discussed more fully in Section 14.4.1.

Because of the poor migration of milling acid dyes, level dyeing initially depends upon gradually increasing the dyeing temperature, and then possibly decreasing the dyebath pH by addition of a small amount of acetic acid. Some of these dyes have a tendency to stain cotton. They often have poor dyeing compatibility in mixtures and are preferred for self-shades (shades determined by the colour of a single dye).
13.3.4 Super-milling acid dyes

The super-milling acid dyes have much the same properties as milling dyes but are even more hydrophobic. They often have long alkyl chains in the dye molecule, give very good washing fastness, and good to very good light fastness. Super-milling acid dyes are widely used for yarn dyeing when the final fabric will be scoured and milled.

Dyeing wool with both types of milling dye in the presence of sulphuric acid at pH 3 results in very rapid absorption and unlevel dyeing, with no chance of levelling by migration. Dyeing is therefore started at about pH 6.5–7.0. The rate of dye absorption is controlled by the gradual temperature increase of the dyebath, and later by a gradual decrease in dyebath pH to complete exhaustion, if required. The initial pH of the dyebath must be even higher for dyeing pale shades to mitigate the initial strike. The pH can be lower for dyeing loose fibre and tops where levelness is less critical since the fibres will be blended together during spinning. Dyeing is slow below 60 °C. It may, however, increase rapidly above 70 °C, once the dye aggregates in solution begin to break up with increasing temperature. In the critical temperature range a decreased rate of temperature increase avoids uneven dyeing.

A typical wool dyeing procedure using super-milling dyes follows the scheme shown in Figure 13.2 except that the initial bath contains 2–3% owf of a weak acid such as ammonium acetate. The use of ammonium acetate or sulphate as the dyeing assistant gives a gradual decrease in the pH value as dyeing proceeds. It has been proposed that heating such ammonium salts in solution liberates ammonia, which escapes from the dyebath, thus giving a decrease in pH (Scheme 13.3). In fact, the pH of ammonium acetate or sulphate solution decreases slightly as the temperature rises even without ammonia loss. In some cases, ammonium phosphate provides some neutralising and buffering action if there is any residual alkali in the wool from scouring.

\[
\text{CH}_3\text{CO}_2^- + \text{NH}_4^+ \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{NH}_3
\]

Scheme 13.3

Many milling and super-milling acid dyes give ‘skittery’ dyeings on wool despite using a gradual temperature increase to control the dyeing rate and the colour uniformity. Dyes penetrate more readily into the wool fibre in regions where
weathering of the fibre tips or mechanical stress during processing has damaged the epicuticle (Section 7.2.2). If the dye is unable to migrate, the result is an uneven skittery dyeing. Skitteriness is the perceived uneven colour effect from pale and dark fibres in proximity. Goodall’s dyeing method overcomes this. Dyeing is commenced at the boil, at relatively high pH in the presence of ammonia and its acetate. Under these conditions, the dye molecules readily penetrate into the swollen wool fibres. The pH gradually falls during dyeing as ammonia escapes and the dyeing rate slowly increases giving more uniform dyeings. Alternatively, proprietary levelling agents may be used (Section 13.5.3).

Colour stripping is difficult with higher molecular weight dyes of greater substantivity. Hot ammonia solution will remove some dye. This simply decreases the number of ammonium ion groups in the fibre so that anionic dye molecules held by ionic attraction are released. This may be assisted by a cationic/non-ionic auxiliary product that holds the anionic dye in the bath by complex formation and prevents its re-absorption by the fibres (Section 13.5.3). The non-ionic component keeps the dye–auxiliary complex in suspension and avoids its precipitation. Complete stripping of azo dyes is possible with reducing agents such as zinc sulphoxylate-formaldehyde, which split azo dyes into amines, thus destroying the chromophore. The stripping conditions should be as mild as possible because of the tendency of wool to felt. Long, vigorous stripping increases the risk of fibre damage and the development of a harsh handle, especially under alkaline conditions.

Under neutral conditions, wool is slightly anionic, with more carboxylate than ammonium ion groups. Even so, super-milling dyes exhibit high substantivity. The desorption of super-milling dyes from dyed wool is only slight in solutions with a pH value of up to 9.5. This shows that the dye binds to the fibre by forces other than the electrostatic attraction between ions of opposite charge. Desorption only becomes significant above pH 9.5 as the wool fibres begin to swell more. A dyeing mechanism based on simple ion exchange does not explain the high fastness to washing of these dyes. Other intermolecular forces are obviously involved, including dipole, dispersion and hydrophobic interactions (Section 13.4.2).

13.4 MECHANISM OF WOOL DYEING [2]

13.4.1 Absorption of acids by wool
Wool contains about 820 mmol kg⁻¹ of amino groups. Under acidic conditions,
some of these will accept protons to form ammonium ions. These cationic groups are capable of binding dye anions by ionic attraction. Practical dyeing with acid dyes, even in the presence of sulphuric acid, only involves a very small fraction of the available cationic sites. Saturation of all such potential sites in acidic wool with a simple acid dye such as Orange II (Figure 1.1, molecular weight 350 g mol\(^{-1}\)) corresponds to almost a 30% owf dyeing.

Figure 13.3 shows the molar amount of acid combined with wool at equilibrium as a function of the pH of the solution, as well as some similar data for dyes in the form of their free sulphonic acids. Each dye has a limiting pH above which the dye does not absorb. This pH is higher the greater the substantivity of the dye. Thus, the curves in Figure 13.3 shift to higher pH as the dye substantivity increases because of dye-fibre interactions other than those involved in ion exchange.

In wool, the numbers of amino and carboxylic acid groups are almost equal (820 and 770 mmol kg\(^{-1}\), respectively). Because these belong to different amino acid units, wool only absorbs small amounts of acid or alkali in the pH range from about 4 to 9 (Figure 13.3). The isoelectric point, where the wool contains equal numbers of cationic and anionic groups, occurs at about pH 5–6.
13.4.2 Ion exchange and hydrophobic bonding

Wool strongly absorbs milling and super-milling dyes even under weakly alkaline conditions when the fibre has more anionic carboxylate groups than ammonium ion groups. These dyes give high dyebath exhaustion under these conditions. The ion exchange mechanism is clearly an oversimplification and other modes of dye–fibre interaction must operate in these cases.

The substantivity of acid dyes for wool generally increases with increase in the dye molecule surface area but decreases when the dye has additional sulphonate groups in the molecule. For large hydrophobic dye molecules, other types of dye–fibre interactions become important besides the coulombic attraction between ammonium ion groups in the wool and dye anions. These additional dye–fibre forces may involve dipole interactions, hydrogen bonding, and dispersion forces operating between groups in the dye molecule and appropriate groups in the protein. Wool, silk and nylon all have regions along the polymer chains that are quite hydrophobic, being void of ionic and polar groups. Dye–dye and dye–fibre hydrophobic interactions might be expected in such regions.

Hydrophobic bonding is simply the term used to describe the tendency of hydrophobic groups to associate together to avoid interaction with water, as in the formation of soap micelles and dye aggregates. The driving force in hydrophobic bonding is the collapse of the hydrocarbon–water interface that occurs when the hydrophobic groups in the dye molecule interact with hydrophobic groups in the wool. Water molecules tend to become more highly hydrogen bonded together, and therefore more highly structured, at an interface with a hydrophobic group.

When the hydrophobic group is surrounded by other hydrophobic groups rather than water, the water molecules liberated give a significant increase in entropy. This explanation of the substantivity of the more hydrophobic acid dyes has considerable merit.

Evidence for the importance of hydrophobic interactions comes from dyeing experiments on chemically modified wool. Wool in which all the free amino groups have been benzoylated by treatment with benzoic anhydride, shows enhanced absorption of typical milling dyes, but reduced absorption of low molecular weight levelling acid dyes that have several sulphonate groups per dye molecule. In wool dyeing, dye–fibre interactions therefore range from purely ionic interactions between dye anions and ammonium ion sites in the wool to purely hydrophobic interactions between non-polar groups in the fibre and in the dye molecule. The consensus seems to be that the extent of absorption of acid dyes depends on the hydrophobic interactions between the dye and the wool, which also determine the
washing fastness. The coulombic attractions between wool ammonium ions and dye anions, however, determine the rate of dyeing.

13.4.3 Kinetics of wool dyeing

Above about 40 °C, increasing temperature increases the dyeing rate with acid dyes but decreases the overall degree of exhaustion, in agreement with Le Chatelier’s principle for an exothermic dyeing process. The rate of dyeing increases by decreasing the dyebath pH, even though the diffusion coefficients for acid dyes in wool are independent of pH. A lower pH increases the dye concentration on the available wool fibre surfaces by increasing the number of ammonium ion sites. This increases the concentration gradient for diffusion of the dye into the fibres. Diffusion into the fibre is usually considered to control the rate of dyeing. Because of this, wool fibres may be ring dyed at low dyeing temperatures. This implies rapid mass transfer of dye to the fibre surface and rapid adsorption, but slow diffusion into the fibre. At higher temperatures, when diffusion is faster, rate-controlling mass transfer of dye to the fibre surfaces can occur at low dye concentrations and when the relative movement of the goods and dye liquor is inadequate.

The kinetics of wool dyeing is quite complex. The penetration of dye molecules into wool fibres was discussed in Section 7.2.2. What is important from the practical viewpoint is to control the dyeing rate so that dye is absorbed neither too rapidly in the early stages of dyeing, giving unlevel coloration, nor so slowly that the process is uneconomic. The objective is to produce a level, well-penetrated dyeing in as short a time as possible. Some of the means of achieving this are discussed in the following section.

13.5 PROBLEMS OF DYEING WOOL LEVEL

13.5.1 Temperature and pH control

One of the major objectives of dyeing is to produce goods with an even colour. This is usually more of a problem when using rapid dyeing dyes that have little migrating capability. Unlevelness of a dyeing arises from:

1. unequal access of the fibres to the dye solution, resulting from densely packed fibres or yarns and from poor agitation of the dyebath;
2. variation of the temperature throughout the dyebath and the goods;
3. uneven pH in the bath and the material.
Wool dyeing starts under conditions of low substantivity, at low temperatures and at higher pH. After alkaline scouring of undyed wool, the goods should be run in the dyeing machine in the presence of a buffer or weak acid to ensure complete and uniform neutralisation of any residual alkali in the wool. A high initial pH minimises the number of excess ammonium ion groups in the wool and avoids rapid initial dye adsorption. The rate of dyeing is controlled by slowly increasing the temperature of the bath, and possibly also by gradually decreasing the bath pH using additions of a weak acid, or by using a substance that releases a weak acid on hydrolysis, such as chloral hydrate or ethyl lactate (Scheme 13.4).

\[
\text{CH}_2\text{Cl(OH)}_2 \rightarrow \text{HCHO} + \text{HCO}_2\text{H} \\
\text{CH}_3\text{CH(OH)}\text{CO}_2\text{H}_2 \rightarrow \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH(OH)}\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH}
\]

Scheme 13.4

Milling and super-milling dyes give a substantial increase in the dyeing rate at a critical temperature around 70 °C. This is probably because these dyes begin to de-aggregate extensively above this temperature. If temperature and pH control do not give adequate levelness, then proprietary levelling agents may be used. These are discussed in Section 13.5.3.

13.5.2 Dyeing damaged wool fibres

Both the thin epicuticle and the scales covering a wool fibre offer considerable resistance to dye penetration. Damage to these surface layers enhances the local dyeing rate compared to that of undamaged fibres. The damage may be of natural origin or a result of the severity of chemical processes during manufacture. Wool is a sensitive natural fibre. Fibres from different locations on a sheep have different dyeing properties because of differences in fineness (fine fibres dye more rapidly than course ones) and different degrees of weathering and abrasion. A wool fabric may also contain fibres damaged during setting, crabbing, decatising, scouring (alkaline), bleaching with hydrogen peroxide (alkaline), chlorination or carbonisation (acidic). Uniform treatment in these processes is essential. The kinetics of wool dyeing therefore depends upon the extent of fibre damage and the levelness of dyeing upon the uniformity of the distribution of damaged fibres.
Damaged wool fibres give two main types of unlevel dyeing:

1. dyeings with coloured patches of different depths caused largely by uneven treatment with chemicals during processes such as scouring, bleaching or chlorination, or incomplete and non-uniform removal of the residual chemicals;

2. skitteriness – the uneven dyeing of individual wool fibres whose tips have degraded more from the greater exposure to the elements during the growth of the wool fleece.

Wool fibres with damaged scales absorb dye more rapidly than undamaged fibres. Weathered tips of wool fibres tend to give skittery or so-called 'tippy' dyeings. The fibre tips may have surface damage and have undergone chemical modifications. They may dye lighter or darker in depth. In the more usual case, the damaged tips absorb more dye than the rest of the fibre and are darker. If the underlying protein is chemically changed because of weathering, lighter dyed tips sometimes arise because of their lower dye absorption at equilibrium compared to the undamaged fibre root. When dyeing with mixtures of dyes containing different numbers of sulphonate groups per dye molecule, the wool fibre tip may even dye a different shade than the root.

Skitteriness is much easier to see in dyed loose fibre. The colour of skittery dyeings is often weak. This is because a mixture of undyed and dyed fibres always gives a paler shade than the same total mass of evenly dyed fibre containing the same amount of dye. The colour strength of a skittery dyeing therefore improves if the dyes can migrate and the colour becomes more level. When dyeing with non-migrating dyes, the use of specific cationic or amphoteric auxiliary levelling agents avoids 'tippy' dyeings (Section 13.5.3).

Wool is a sensitive protein. Even dyeing with acid dyes at the boil causes some degradation, particularly on prolonged boiling to promote dye migration. This causes hydrolysis of various wool proteins. This is slowest around the isoelectric point at about pH 5. It is particularly rapid with alkaline solutions. Hydrolysis impairs the mechanical properties of the wool, giving more brittle fibres with decreased resistance to abrasion. If the goods are in the form of loose fibre, fibre brittleness can complicate carding and spinning. Hydrolytic damage of wood fibres also produces unacceptable yellowing. Certain protective auxiliary products are used to minimise degradation and yellowing of the wool. These protective agents are most useful for high temperature dyeing processes, such as the dyeing of wool/polyester blends at 120 °C, or when dyeing has to be extended or repeated. In
wool dyeing, the conditions should always be as mild as possible, at as low a temperature as possible, and in weakly acidic solution.

Chlorination is one process deliberately used to modify the scale structure of wool fibres to prevent felting and shrinkage of woollen goods on washing (Section 7.4.2). The dyeing of chlorinated wool poses several problems. Acid dyes have increased initial substantivity for chlorinated wool because of the severely damaged scales. The rapidity of the reaction of chlorine with wool increases the risk of uneven chlorination resulting in subsequent unlevel dyeings, even when using levelling acid dyes. The dyeings also have lower washing fastness because of the increased ease of desorption of dyes from chlorinated wool. The difference in the dyeing behaviour of untreated and chlorinated wool appears to be entirely a consequence of dyeing rates since the two fibres give the same equilibrium dye absorption.

13.5.3 Use of wool dyeing assistants [3]

A wide variety of auxiliary products are used in wool dyeing to promote dye levelling. Levelling agents function by retarding dye absorption. They are of two main types: anionic and cationic/non-ionic. Wool absorbs anionic levelling agents and they retard dye absorption by initially blocking the cationic ammonium ion sites. The more substantive dye anions eventually displace the anionic product. Anionic surfactants with long alkyl chains have higher fibre substantivity and are more effective, but they decrease the equilibrium uptake of the dye. Although the ion exchange explanation may be an oversimplification of the action of anionic levelling agents in wool dyeing, it adequately explains their retarding effect. Typical products are the sulphate esters of fatty alcohols, R–OSO$_3$Na.

The action of cationic/non-ionic levelling agents is quite different. Cationic agents form a complex with the anionic dye in the dyebath and prevent its uptake by the wool. The non-ionic portion of this type of product keeps the auxiliary–dye complex (Dye–Aux$^+$) dispersed in solution. This is important to avoid its precipitation in the bath or on the material surface. Free dye molecules are liberated as the dyeing temperature increases since the complex is less stable at higher temperatures (Scheme 13.3). Strong levelling action can be achieved using a cationic polyethoxylated amine (such as I, Figure 13.4) with a short chain (n = 5–20), mixed with a purely non-ionic product to keep the complex in dispersion. The greater cationic character of products with short polyethoxylated chains gives strong complex formation, pronounced retardation of dyeing and a higher risk of
precipitation. When the polyethoxylated chain is longer (n > 50), the dye–auxiliary complex is dispersed by the cationic auxiliary product alone.

Some levelling agents are amphoteric, with both anionic and cationic groups present in the molecule. Their form in the dyebath depends upon the pH (Scheme 13.6). Amphoteric auxiliaries (such as 2, Figure 13.4) help to eliminate differences in dye uptake between the roots and tips of wool fibres by increasing the rate of dyeing of the undamaged portions. The cationic portion complexes the dye in solution, the non-ionic chain ensures dispersion and solubility, while the terminal anionic group promotes substantivity for the wool surface. This is assisted by the dye–auxiliary complex being more hydrophobic than the uncomplexed dye. On chlorinated wool with a Hercosett polymer, however, the wool surface is more hydrophilic and such amphoteric products may have no effect or even retard dye absorption. Clearly, the choice of auxiliary products in wool dyeing requires care and experience.

\[
\text{RN H}_2 \text{CO}_2^+ \quad \text{cationic in acidic solution} \\
\text{RN H}_2 \text{CO}_2^- \quad \text{amphoteric in neutral solution} \\
\text{RN H}^+ \text{CO}_2^- \quad \text{anionic in alkaline solution}
\]

Scheme 13.6

13.6 SPECIAL WOOL DYEING PROCESSES

High temperature wool dyeing, under pressure, decreases the dyeing time and is useful if additions are not required. At dyeing temperatures above 100 °C, the rate of levelling is higher but there is a risk of dye hydrolysis and chemical
reduction of azo dyes by wool degradation products. Addition of a small amount of a mild oxidising agent prevents such reduction. Dyeing at 110 °C, for not longer than 60 min, at a pH around 5, avoids damaging the wool fibres. Dyeing at 120 °C is possible for wool/polyester blends but the dyebath must contain fibre-protective agents. These are often products that slowly release formaldehyde, such as dimethylolethylene urea (3, Figure 13.5), that are much safer and easier to use than free formaldehyde. The released formaldehyde probably provides some fibre protection by crosslinking ruptured cystine links. Other types of protective agents form a hydrophobic coating on the fibre surface.

![Figure 13.5 Dimethylolethylene urea, a fibre-protective agent](image)

Low temperature dyeing methods greatly reduce wool damage. These methods involve pretreatments to modify the wool, the use of solvents to modify the non-keratinous regions, or the addition of surfactants. Auxiliary chemicals are needed to assist dye penetration, otherwise ring dyeings result with inferior rubbing fastness. Dyeing in the presence of benzyl alcohol in an aqueous dyebath greatly increases the rate of dyeing and dyeing at temperatures around 80 °C is possible, thus minimising any degradation of the wool surface. Benzyl alcohol breaks up dye aggregates in solution and forms a layer of solvent at the fibre surface in which acid dyes are very soluble. The concentrated layer of dye solution at the fibre surface promotes more rapid diffusion. Dyebath exhaustion is complete and the bath containing the benzyl alcohol can be re-used. The Inga-solvent process (Ciba) is one such solvent-assisted method. Most current low temperature methods depend upon the use of special auxiliary products such as polyethoxylated alcohols with short chains, in combination with non-ionic dispersants with longer chains. These allow dyeing at 80–85 °C, with minimal fibre damage, and probably function much like benzyl alcohol.

There are also a number of processes for the continuous dyeing of loose wool and sliver that involve padding or spraying, followed by fixation in steam or by radio frequency radiation. The dye solution contains a thickening agent to prevent drainage through the fibre mass and a variety of auxiliary products.
13.7 MORDANT DYES FOR WOOL

13.7.1 Introduction

In Chapter 1, we saw how metallic mordants improve the fixation and fastness properties of dyes lacking substantivity for natural fibres. Many of the natural dyes were polygenetic. They gave different colours with different metallic mordants such as salts of aluminium, tin, iron or copper. Today, almost all wool mordant dyes have a chromic ion mordant (Cr\(^{3+}\)) and are therefore often called chrome dyes. The chromic ion is invariably complexed with the dye after the initial dyeing with an acid dye, to produce dark, dull shades of excellent light and wet fastness. The final hue is usually quite different from that of the original non-metallised dye so that colour matching is more difficult than in direct dyeing. The presence of chromium in the dyehouse effluent poses a severe environmental problem, because of its toxicity, particularly in the form of dichromate ion (Cr\(_2\)O\(_7\)\(^{2–}\)). Improved mordanting processes must minimise loss of this metal in the dyehouse effluent.

13.7.2 Basic principles of metal-complex formation

Transition metal ions in aqueous solution can interact with anions to form simple salts such as FeCl\(_3\), which results from a combination of one Fe\(^{3+}\) and three Cl\(^{–}\) ions. They also combine with anions and neutral electron donors to form complexes involving coordinate covalent bonds. For example, potassium ferricyanide, K\(_3\)Fe(CN)\(_6\), consists of three K\(^+\) ions and one complex ion Fe(CN)\(_6\)\(^{3–}\) (Scheme 13.7). Coordinate bonds involve sharing of electron pairs that originate with the anion or electron donor (Lewis base). The species providing the electron pair is a ligand. The orbital containing the lone electron pair of the ligand donor overlaps with a vacant orbital of the transition metal ion acceptor (Lewis acid). For a transition metal, the lowest energy vacant orbitals available are d orbitals or their hybrids. The maximum number of ligands that can attach to the metal ion is the coordination number. The most common values of this are 4 and 6.

In aqueous solution, four water molecules acting as ligands surround and hydrate the cupric ion (Cu\(^{2+}\), coordination number = 4). Stronger ligands (stronger electron donors) such as ammonia can displace the water molecules to

\[
\text{Fe}^{2+} + 6\text{CN}^{–} \rightarrow \text{Fe(CN)}_6^{3–}
\]

(Scheme 13.7)
form other complex ions (Scheme 13.8). If anions act as ligands, then the charge on the complex ion will be less than that on the hydrated metal ion and can be negative, as in the case of ferricyanide (Scheme 13.7), or even zero.

\[
\text{Cu(H}_2\text{O)}_4^{2+} + 4\text{NH}_3 \rightarrow \text{Cu(NH}_3)_4^{2+} + 4\text{H}_2\text{O}
\]

Scheme 13.8

The bond between a ligand and the metal ion is a covalent bond and can be difficult to break if the ligand is a strong electron donor. For example, in a solution of the green complex salt CoCl}_3.4\text{NH}_3, only one third of the total available chlorine precipitates as silver chloride after addition of silver nitrate solution. Two of the chloride ions act as ligands bonded to the cobalt ion to give the stable complex ion Co(NH}_3)_4\text{Cl}_2^{+}. In this ion, the cobalt has a coordination number of 6 and the initial charge of the Co}^{3+} ion falls to +1 because of the two chloride ion ligands bonded to it. The third chloride ion is the counter-ion to the complex cation and it is this that precipitates as silver chloride (Scheme 13.9)

\[
\text{Co}^{3+} + 4\text{NH}_3 + 3\text{Cl} \rightarrow \text{Co(NH}_3)_4\text{Cl}_2^{+} + \text{Cl}^- \quad (\text{Co coordination number} = 6)
\]

Scheme 13.9

The formation of complex ions involves overlap of vacant orbitals of the acceptor metal ion with the orbitals containing lone pairs of electrons from the ligand donors. In Pauling’s valence-bond treatment, the type of vacant hybrid orbitals of the metal ion determines the coordination number and the stereochemistry. For example, chromium (electronic configuration [Ar]4s\text{1}3d\text{5}4p\text{0}) forms the chromic ion (Cr}^{3+}, electronic configuration [Ar]4s\text{0}3d\text{3}4p\text{0}). The hybridisation of the empty 4s, two empty 3d and three empty 4p orbitals gives six vacant d\text{2}sp\text{3} hybrid orbitals, each capable of accepting a lone pair of electrons from a ligand. On combination with six electron pairs from six ligands, all the orbitals are filled. They form an octahedral arrangement in the complex ion to minimise repulsions between the six bonds (Cr(NH}_3)_6^{3+}).

Copper (electronic configuration [Ar]4s\text{1}3d\text{9}4p\text{0}), on the other hand, forms cupric ion (Cu}^{2+}, electronic configuration [Ar]4s\text{0}3d\text{9}4p\text{0}), which promotes one
electron from a 3d to a vacant 4p orbital to give the electronic configuration \([\text{Ar}]4s^03d^84p^1\). This permits formation of four vacant dp^2 hybrid orbitals from the vacant 3d, 4s and 4p orbitals, which results in a square-planar arrangement of four ligand donors.

There are a number of aspects of coordination chemistry that Pauling’s theory fails to explain and the newer ligand field theory has been more successful. For our purposes, it suffices to recall that chromium has a coordination number of 6 and that the ligands in a chromium complex give an octahedral arrangement around the central chromium atom. Copper usually has a coordination number of 4 and the four ligands form a square around the central copper atom.

Many ligands have more than one electron donor site and are bi-, tri-, or even polydentate (Figure 13.6). For example, ethylene diamine (1,2-diaminoethane) has two amino groups and is bidentate, whereas EDTA (Figure 8.1) is hexadentate (hexa = six, Greek; dens, dent = tooth, Latin). Note the relation to the French word mordre (to bite), the origin of the word mordant.

The most important transition metal ions in metal-complex dyes are chromium (coordination number = 6) and copper (coordination number = 4) and, to a much lesser extent, cobalt (coordination number = 6) and nickel (coordination number = 4). Chromium and cobalt complexes are particularly stable and therefore resist de-metallisation during application and use. The majority of the

![Figure 13.6 Chemical structures of complexes from polydentate ligands](image-url)
dyes that act as ligands are tridentate. Examples include o,o′-dihydroxyazo, o-carboxy-o′-hydroxy-, and o-hydroxyarylazopyrazalone compounds (Figure 13.7). In some cases, the original ligand group in the dyestuff is a methoxy group, the methyl group being lost when the complex forms. Both salicylic acid or 1-hydroxyanthraquinone groups function as bidentate ligands and form chromium and copper complexes.

![Chemical structures](image)

Figure 13.7 Partial chemical structures of dye–metal complexes

The charge on the metal in a dye–metal complex is usually somewhat delocalised onto the electronegative atoms that surround it. The overall electric charge of a complex ion will depend on the charge of the original metal ion, the localised negative charge of sulphonate groups in the ligand dye molecule, and on any charge of additional monodentate ligands. Figure 13.8 gives some examples. It shows that complexes with chromium involve either one or two tridentate dye molecules and a single chromic ion. These are called 1:1 and 2:1 metal-complex dyes. In the latter, the two dye molecules may be identical or different.

13.7.3 Acid mordant dyes for wool [1]

The most common mordant dyeing process today is the after-chrome process in which mordanting takes place after first dyeing the wool with an acid dye. The
Figure 13.8 Chemical structures of dye–metal complex dyes

oldest method of mordant dyeing, in which the material is mordanted before dyeing, and the metachrome process, in which the dye and chromium mordant are applied simultaneously to the wool, are obsolete.

Mordanting with chromium involves treatment of the dyed wool with sodium dichromate solution in the presence of a strong acid. Wool adsorbs the dichromate anions (Cr_2O_7^{2–}) by interaction with ammonium ion sites. The dichromate is then reduced to chromic ion (Cr^{3+}) (Scheme 13.10), oxidising cystine and other amino acid residues in the protein fibre. This oxidation of the wool causes a decrease in wet strength. Dichromate is used for wool chroming because it has reasonable substantivity and migration under the acidic conditions. It is, however, the chromic ion that forms the dye–metal complex. This cation has little substantivity for wool under acidic conditions and does not migrate because it binds strongly to
carboxylate groups in the fibre. Dichromate adsorption increases with decreasing bath pH and its reduction to chromic ion consumes considerable amounts of acid (Scheme 13.10), increasing the pH of the bath, so there must be a high concentration of acid in the chroming bath.

\[ \text{Scheme 13.10} \]

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

The after-chrome procedure is the most important for dyeing wool with mordant acid dyes. It has the advantage of requiring only a single bath. Dyeing is carried out with an acid dye, capable of forming a chromium complex, in the presence of acetic acid (3.0% owf) at the boil. Addition of formic acid completes exhaustion, if necessary. The exhausted bath is cooled to 75–80 °C, sodium dichromate added, and the bath reheated to boiling. It is important that the initial dyeing is level because the metallised dye is incapable of migration. Complete exhaustion of the dye bath before mordanting avoids any complexation in the solution. The pH of the chroming bath is 3.5–3.8 during the entire mordanting operation. At this pH, chromium is present mainly as dichromate rather than as chromate ion (CrO$_4^{2-}$) (Scheme 13.11).

\[ \text{Scheme 13.11} \]

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}
\]

After-chroming usually gives a pronounced bathochromic shift in hue and the shades produced are usually dark and dull. A bathochromic shift involves an increase in the wavelength of maximum light absorption of the dye. This means that the colour shifts in the direction yellow–red–violet–blue–green (Chapter 1, Table 1.3). The final dyeing has very good washing and light fastness. Because of the pronounced change in hue on metal-complex formation, shading and colour matching are more difficult than in direct dyeing. Shading with small amounts of stable non-complexing dyes, such as mulling, super-milling or 2:1 metal-complex dyes, does not jeopardise the washing fastness and brightens the rather dull shades of chrome dyes.
The significant increase in fastness to wet treatments that occurs on after-chroming the initial acid dye may be a consequence of the dye being chemically bonded to the fibre. This would involve carboxylate and amino groups in the wool acting as ligands and forming coordinate bonds to the metal in a 1:1 dye–metal complex. This has never been confirmed and it could not occur with 2:1 dye–metal complexes since all the coordination sites are full. The improved fastness to washing is therefore most likely due to the reduced solubility and diffusion of the complex because of the increase in molecular size on complexation, particularly for the formation of 2:1 dye–metal complexes.

The major problems with chrome dyes for wool are the long treatment time at the boil, which results in damage to the wool fibres, and the residual chromium in the dyehouse effluent. Dyeing at 80–90 °C, with added acetic acid, and after-chroming with sodium dichromate at around 90 °C, in the presence of formic acid and sodium thiosulphate, avoids detrimental effects on the quality of the wool cloth. The thiosulphate assists reduction of dichromate to chromic ion (Scheme 13.12). Fibre protective agents may also be added to the chroming bath. A minimum amount of dichromate in the after-chroming bath avoids excessive chromium in the effluent. Addition of thiosulphate ensures complete reduction to the less toxic chromic ion. In the past, the % owf of sodium dichromate for after-chroming would be half of the % owf of the applied dye. It is now substantially less. This minimises wool damage by oxidation and the effluent problem.

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{Cr}^{3+} + 3\text{S}_4\text{O}_6^{2-} + 7\text{H}_2\text{O} \]

Scheme 13.12

Chroming is best carried out at pH 3.5–3.8, using the manufacturer’s recommended amount of sodium dichromate, and preferably in a fresh bath. Newer methods to reduce the chromium levels in the waste water include the use of chromic ion complexes with lactic acid. The proprietary chemical Lyocol CR (Clariant) contains a mild reducing agent and a complex chelating agent that binds chromic ion and exhausts it onto the wool. The newer methods for after-chroming, at low chromium levels, increase the risk of unlevel complexation and recommended procedures must be adhered to.

The tips of weathered wool fibres may have higher absorption of chromium than the roots and reduce dichromate to chromic ion more efficiently. Mordant
dyes may therefore give differences in colour depth, or even two different hues, on the roots and tips of ‘tippy’ wool.

In the metachrome method, dyeing and mordanting the wool occur simultaneously, dyeing in the presence of sodium dichromate, ammonium sulphate and sodium sulphate at a pH around 6–7. Only a limited number of dyes are stable in hot solutions of dichromate and have reasonable substantivity at pH 6–7. The procedure has the advantage of facilitating shading and requires less time than the after-chrome procedure. It gives higher levels of residual chromium in the effluent. Only a few dyes of this type are now used (CI Mordant Brown 48) and the method is almost obsolete.

13.8 PRE-METALLISED METAL-COMPLEX DYES [4]

13.8.1 Chemical structures
Pre-metallised dyes are anionic 1:1 or 2:1 dye–metal complexes (Figure 13.8) used for dyeing wool and nylon under conditions typical of acid dyes. The properties of 1:1 and 2:1 metal-complex dyes resemble those of levelling and milling acid dyes, respectively. The fastness properties of both types on wool approach those of chrome dyes. Complexing a dye with chromic ion produces a bathochromic shift and dulls the shade. The dyeings are, however, slightly brighter than those of after-chromed mordant dyes. The dye-metal complex is pre-formed and stable. Hence, these dyes do not need any aftertreatment and are therefore much easier to use in colour matching.

In dyeing with all types of metal-complex dyes, soft water is preferred. If it is necessary to counteract any hardness, a polyphosphate sequestering agent is used rather than an EDTA type. The latter are capable of removing the metal from the dye–metal complex, thus liberating a non-metallised acid dye of different hue.

The 2:1 metal-complex dyes for wool, along with fibre-reactive dyes, are gradually replacing the other types of acid dyes, because of their superior fastness properties. Pre-formed metal-complex dyes are gradually replacing after-chrome dyes whose lengthy dyeing procedure tender the wool, and which pose a serious environmental problem. With increasingly stringent surface water quality standards imposed by governments, there is now concern that dyeing with metal-complex dyes will have to be optimised to reduce chromium and cobalt levels in dyehouse waste water even further. If future water quality standards cannot be met, the use of metal-complex dyes will decline in favour of the metal-free fibre-reactive dyes for wool (Section 16.6).
13.8.2 Pre-metallised 1:1 dye–metal complex dyes

The Neolan dyes, originally introduced by Geigy in 1919, are 1:1 metal-complex dyes containing one atom of metal and one dye molecule with one or two sulphonate groups per dye molecule. Although the chromium complexes of those o,o'-dihydroxyazo dyes with only one sulphonate group would have no overall net electric charge, because the negative charges of two dissociated hydroxyl groups and one sulphonate group neutralise the positive charge on the original chromic ion, they behave as anionic dyes. This is because the residual positive charge on the chromium atom in the complex is somewhat delocalised while the sulphonate ion has a relatively localised negative charge. Alternatively, one of the non-dye ligands that completes the coordination of the central chromic ion may be a hydroxide ion rather than a water molecule or a neutral colourless ligand.

Dyeing wool with 1:1 metal-complex dyes involves a very acidic dyebath with sulphuric acid (pH 2) and possibly sodium sulphate. Without other dyeing assistants, the amount of concentrated sulphuric acid required is greater the higher the liquor ratio and the greater the amount of the dyes. It can easily reach 8% owf H₂SO₄. When dyeing with such high concentrations of sulphuric acid, there is a risk of hydrolytic damage to the wool fibres. Most manufacturers of these dyes now recommend dyeing methods with reduced amounts of sulphuric acid or the use of other acids such as formic acid. With lower concentrations of sulphuric acid (4–6% owf), a polyethyleneoxide levelling agent in the dyebath retards dyeing by complex formation with the dye. Alternatively, sulphamic acid can be used. At the boil, this hydrolysés to ammonium bisulphate and increases the bath pH from about 2.0 to 3.0–3.5, thus reducing fibre damage (Scheme 13.13). After dyeing, the residual acid in the goods must be neutralised or buffered using sodium acetate in the rinse.

\[
\text{NH}_2\text{SO}_3\text{H} + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{HSO}_4^-
\]

Scheme 13.13

The Neolan P dyes (Ciba) are 1:1 dye–chromium complexes in which the coordination of the chromic ion is completed with colourless hexafluorosilicate ligands (SiF₆²⁻). They only require 3–4% owf of concentrated formic acid at a pH of 3.5–4.0. This gives much less tendering of the wool compared to dyeing with high concentrations of sulphuric acid and eliminates the need for neutralising or buffering after dyeing.
A typical dyeing procedure for dyeing wool with 1:1 dye–metal complex dyes follows the scheme in Figure 13.2 but using 6% owf of sulphuric acid in the dyebath.

The fastness to washing of these dyes on wool is lower than for after-chrome dyes. It is comparable to that of fast acid dyes. Light fastness is usually good. These dyes are still important for dyeing loose wool, yarn for carpets, and for dyeing wool fabric after carbonising or acid milling, when the acid remaining in the goods serves directly for dyeing. It is unlikely that ligand groups in the wool bond to the 1:1 dye–metal complex since they have only moderate to good washing fastness and migrate readily under the acidic dyeing conditions. Because of this, the exhaustion is not optimal at pH 2. When applied at a higher pH of around 4, they give higher exhaustion, but produce skittery dyeings without a levelling agent. Their shades are often brighter than those of after-chrome dyes, but duller than those of non-metallised acid dyes. Shading and colour matching are relatively straightforward as there are no aftertreatments.

13.8.3 Pre-metallised 2:1 dye–metal complex dyes

These dyes have two dye molecules per metal atom and the molecular structures may be symmetrical, with two identical tridentate dye ligands, or unsymmetrical, with two different dyes. There are three types of 2:1 metal-complex dyes:

1. Weakly polar types that do not have sulphonate groups in the dye molecules. Their limited water solubility comes from polar methyl sulphone or alkylsulphonamide groups in the dye molecule. The complexes are anionic since the trivalent chromic ion reacts with four anionic ligand groups, such as the four hydroxyl groups from two o,o'-dihydroxyazo dyes;

2. Monosulphonated 2:1 dye–metal complexes that have an unsymmetrical structure since the two dye ligands are not identical and only one is monosulphonated;

3. Disulphonated 2:1 dye–metal complexes with symmetrical molecular structures since both identical dye ligands are monosulphonated.

The weakly polar 2:1 dye–metal complex dyes are applied to wool from a nearly neutral dyebath in the presence of ammonium acetate or sulphate. They require careful temperature and pH control since they have only limited levelling ability. In some cases, acetic acid may be added to the dyebath towards the end of dyeing. This decreases the pH to around 5.5 and promotes exhaustion. These dyes have
very good light fastness and good washing fastness, but, for deep shades, the latter is lower than for dyesing with after-chrome dyes. They are used mainly on loose wool, slubbing, yarn and knit goods because they tend to highlight irregularities in woven materials. The 2:1 dye–metal complex dyes have high substantivity for wool, even in neutral solution. Dye levelling and penetration are usually good, provided that proprietary levelling agents are present in the dyebath. Uniformity of the initial fabric pH is critical and the goods are carefully neutralised after carbonising or other acidic processes.

The polar types usually have improved wet fastness compared to the weakly polar dyes, and have good light fastness. They can replace mordant dyes where there is a risk of damage to the wool from the extended boiling required in the after-chrome process. All the 2:1 dye–metal complex dyes have large molecules that tend to aggregate in solution and have slow diffusion in the wool fibre. The presence of sulphonate groups in the dye molecules leads to decreased substantivity in neutral solution, an indication of the importance of hydrophobic interactions in dyeing with the non-polar types. With increase in the degree of sulphonation, the dyeing pH must be lower to increase ionic interaction with ammonium ion sites in the wool fibre. The weakly polar dyes dye wool at pH 6–7 using ammonium acetate or sulphate in the dyebath, the monosulphonated dyes at pH 5–6 with ammonium acetate plus acetic acid, and the more polar disulphonated dyes at pH 4–5 using acetic acid. Dyeing is usually carried out at temperatures close to the boil, with careful control of the temperature during the heating phase. Alternatively, both low (80 °C) and high temperature (110 °C) dyeing methods are possible.

The disulphonated dyes possess the highest all-round fastness. The levelling capability of the disulphonated 2:1 complexes is poor, somewhat better for the monosulphonated type, and better still for the weakly polar dyes. The ability to migrate during dyeing increases with increasing dyeing pH and thus decreasing interaction with the diminishing number of ammonium ion sites in the wool. The dyes of lower migration therefore tend to give skittery dyeings and are not suitable for piece dyeing because of this.

All types of 2:1 metal-complex dye are suitable for dyeing shrink-resist wool from the Hercosett process (Section 7.4.2). Because of the cationic nature of the polymer deposited on the fibre surface and residual acid from the required prechlorination, strict control of the initial fabric pH and temperature are necessary to obtain level dyeings because of the greater substantivity of the dyes for the treated wool. An ester that slowly liberates an acid on hydrolysis, such as ethyl
lactate, will gradually decrease the bath pH during dyeing (Scheme 13.4). To obtain optimum wet fastness in medium to heavy shades on shrink-resist wool, the dyeing may be aftertreated with a proprietary cationic agent. This presumably complexes with the anionic dye, reducing its solubility and diffusion capability.

Loose wool and slubbing can be dyed continuously by padding with metal-complex dyes, fixation usually being achieved by steaming. The pad bath contains wetting agents, a thickener to prevent drainage in the fibre mass since the solution pick-up is high (100–120%), as well as a variety of proprietary chemicals.

Coulombic interactions between dye anions and ammonium ion groups in the wool are important for determining the rate of dyeing and the degree of migration that is possible. As in the case of milling and super-milling acid dyes, the good washing fastness of metal-complex dyes, however, is more likely a consequence of hydrophobic interactions between the dye and the wool protein or between dye molecules themselves leading to aggregation of the dyes in the fibre.

13.8.4 Optimised acid dye ranges

A number of commercial dye ranges for wool are available in which the member dyes have a wide colour gamut and good compatibility. All the dyes have very similar dyeing and fastness properties. They have a common dyeing method despite being of several different types. The dyebath pH is around 4.5–5.0, close to the isoelectric region for wool. This minimises damage to the wool. Their high degree of exhaustion makes shade reproducibility much easier. Each range requires the use of a proprietary levelling agent that ensures good coverage of root and tip differences of the wool fibres. The dyes of the Sandolan MF (Clariant) range behave like fast acid dyes. For dyeings with good levelness, an acid release agent such as ethyl lactate is used in combination with a levelling agent. The Lanaset range (Ciba-Geigy) contains milling, reactive and 2:1 dye–metal complex dyes, whereas the Lanasan CF range (Clariant) has milling and 2:1 dye–metal complex dyes. The last two ranges give very good washing fastness.

13.9 DYEING NYLON WITH ACID DYES

13.9.1 Introduction

Nylon molecules have amino groups at the end of the polyamide chains. Nylon, like wool, can therefore be dyed with all types of acid dyes by an ion exchange process. Nylon filaments are sensitive to mechanical, thermal and chemical
stresses during filament production as well as during their assembly into fabric and its preparation for finishing. These stresses modify both the chemical and physical structure of the nylon filaments and result in changes in dyeing rate and dye uptake. If the modification of the nylon is not uniform along the length of the filament, the final colour will be uneven. Disperse dyes, which dye most synthetic fibres, migrate readily when dyeing nylon and cover such chemical and physical irregularities in the filaments (Section 15.6). Unfortunately, the washing fastness of disperse dyes on nylon is only poor to moderate, particularly in heavy shades. They are used mainly for ladies’ hosiery and lingerie. The washing fastness of non-metallised acid dyes on nylon is moderate to good and the light fastness is usually good. Milling or metal-complex dyes give dyeings of superior washing fastness on nylon. Their unlevel dyeing behaviour, however, results in poor coverage of filament irregularities. The 2:1 pre-metallised dyes, in particular, give dyeings of high light fastness, as required for example for nylon automotive fabrics. Besides hosiery and apparel, carpets are a major consumer of nylon, particularly in the USA, and are usually dyed with acid dyes.

13.9.2 Preparation of nylon before dyeing

Nylon filaments are relatively free from impurities. Scouring with a detergent and soda ash (Na₂CO₃) at 70 °C usually removes spin finishes and lubricants present on the filaments and any polyvinyl alcohol or other synthetic size on woven fabric. In some instances, where white nylon fabric has yellowed from overly severe heat setting (Section 13.9.3), bleaching with peracetic acid or sodium chlorite solution is possible. Compared to fabrics from natural fibres, the preparation of those from nylon is quite simple.

13.9.3 Heat setting

Nylon is a thermoplastic polymer. When treated in hot water, the temperature is well above the glass transition temperature (T_g) of nylon. Fabrics may give considerable changes in dimensions as filament tensions introduced during manufacture relax. Heat setting avoids fabric deformation and shrinkage provided that the temperature is higher than that to which the material will be subsequently exposed.

The full width fabric is heat set using a tenter frame. The separation of the chains holding the selvages, and the speed through the oven, define the final
fabric width and length, respectively. On heating, intermolecular hydrogen bonds between amide groups break (Scheme 4.3) so that the polymer chains can move and adopt the positions required by the newly imposed dimensions without stress. At the setting temperature, new hydrogen bonds then form that stabilise the polymer structure. These new bonds are stable at temperatures up to the heat setting temperature at which they formed. They impart the required dimensional stability to the material.

Open-width fabrics are dry heat set at 190–215 °C for nylon 6.6, and 175–190 °C for nylon 6. Temperatures are lower for steam setting: 115–130 °C for nylon 6.6 and 110–120 °C for nylon 6. Since dry heat setting in hot air involves much higher temperatures than setting in steam, it involves a greater risk of polymer degradation. Dry setting sometimes results in yellowing of the material. Nylon hose are placed on shaped forms and heat set in a steam autoclave.

After dry heat setting in hot air at temperatures up to about 200 °C, the rates of dyeing of nylon 6.6 and 6 with both acid and disperse dyes decrease. This is mainly because of increased polymer orientation and crystallinity, but the number of polymer amino groups also decreases. Because of the decrease in dyeing rate and the risk of unlevel dyeing from non-uniform heat setting, it is preferable to heat set after dyeing, if this is possible. This requires a minimum level of dimensional stability at the maximum temperature of the dyeing process. Steam setting, however, increases dyeing rates with acid and disperse dyes. This latter process opens up the polymer structure making it more accessible to dyes.

13.9.4 Adsorption of acid dyes by nylon

The dyeing of nylon with acid dyes differs in a number of respects from that of wool. A simple ion exchange process (Scheme 13.14), similar to that for dyeing wool, explains many practical dyeing observations. The limited number of amino groups in nylon and its more hydrophobic nature, however, have a profound influence on its dyeing behaviour.

The amino group content of nylon is usually around 45 mmol kg⁻¹ but can vary from about 15–20 up to 80–90 mmol kg⁻¹ for different types. These values are much lower than the 820 mmol kg⁻¹ for wool. In dyeing nylon at moderate acidity (pH 3–4), it is therefore relatively easy to saturate all the available ammonium ion sites with acid dye anions. The equilibrium molar adsorption of polysulphonated acid dyes is particularly low because of this. A simple acid dye with three sulphonate groups per molecule will neutralise the positive charge of all
the available ammonium ion sites in the nylon at one third the molar quantity of a
dye with a single sulphonate group. For a nylon with 45 mmol kg\(^{-1}\) of amino
groups, the maximum dye adsorption of a trisulphonate dye is 15 mmol kg\(^{-1}\).
This corresponds to less than a 0.9 % owf dyeing for an acid dye with a molecular
weight less than 600. The equilibrium molar dye adsorption at saturation of a
polysulphonated acid dye of known molecular weight and purity is, in fact, a good
method of determining the amino group content of the nylon. The limited number
of ammonium ion sites in nylon, when dyeing with acid dyes under weakly acidic
conditions, poses problems in dyeing deep shades. In particular, the production of
blacks and other deep shades is problematic, since the amount of dye that
saturates all the ammonium ion sites is insufficient to give the depth of colour
required.

The non-polar environment inside nylon filaments, and the large separation
between the amino and carboxyl groups, may not favour a zwitterionic form in
nylon, as in wool, and absorption of acid probably involves protonation of free
amino groups in a non-ionic polymer (Scheme 13.14).

\[
\text{HO}_2\text{C-Nylon-NH}_2 + \text{H}^+ \rightarrow \text{HO}_2\text{C-Nylon-NH}_3^+ X^-
\]

\[
\text{HO}_2\text{C-Nylon-NH}_3^+ X^- + \text{Dye}^- \rightarrow \text{HO}_2\text{C-Nylon-NH}_3^+ \text{Dye}^- + X^-
\]

Scheme 13.14

Isotherms of the equilibrium adsorption as a function of pH for acid dyes of low
substantivity (Figure 13.9) show that the dye initially interacts with ammonium
ion groups in the nylon until these are all occupied at around pH 3. The shape of
the isotherm resembles a titration curve. The amount of dye adsorbed depends on
the acidity of the dyebath, which determines the number of ammonium ion sites.
At low pH values, the nylon adsorbs additional dye beyond the saturation limit at
pH 3. Under such acidic conditions, protonation of the carbonyl group oxygen
atom of amide groups generates new cationic sites for dye adsorption. This also
renders the amide group susceptible to hydrolysis at the elevated temperatures
used in dyeing. Hydrolysis of an amide group forms a new amino group that, on
protonation, can bind an additional dye anion (Scheme 13.15). In practice, dyeing
below pH 2.5 is not possible because acid catalysed hydrolytic fibre degradation results in a loss of tensile strength.

Once a dye anion with moderate substantivity adsorbs onto an ammonium ion site in the nylon, it is quite resistant to displacement. A rapidly adsorbed dye anion can block a site and prevent adsorption of other dyes in the dyebath. The competition of acid dyes for the limited number of available dye sites can cause problems when dyeing with mixtures of incompatible dyes. Dyeing nylon with a mixture of the monosulphonated dye CI Acid Blue 47 and the disulphonated CI Acid Yellow 17 in acidic solution gives the expected green dyeing at low dye concentrations of 0.25% owf yellow and 0.17% owf blue, respectively. If dyeing is carried out using the same yellow to blue ratio but at higher dye concentrations of 1.5% owf yellow and 1.0% owf blue, however, the nylon is dyed yellow, most of the blue dye remaining in the bath. The yellow dye is more rapidly and more strongly adsorbed than the blue dye and is able to rapidly block the alkylammonium ion
sites in the nylon. It will even displace any blue dye already adsorbed by the nylon. Many pairs of dyes exhibit this type of competition behaviour.

For milling dyes, which have higher substantivity for nylon, the isotherms showing the amount of dye adsorbed at equilibrium as a function of pH are similar to those for simple acid dyes, but displaced to higher pH values and with considerable dye adsorption above pH 7. Figure 13.9 shows an example.

As in the case of wool dyeing, the ion exchange mechanism is simple and useful. It does not, however, explain the pronounced substantivity of milling and metal-complex acid dyes in neutral solution, under conditions where the nylon only has very few ammonium ion groups. In the case of these types of acid dye, the dye–fibre interaction must involve forces other than the attraction of oppositely charged ions. Obviously, dipole–dipole and hydrophobic interactions between the dye and nylon molecules play an important role in determining the high substantivity and good washing fastness of these types of dyes.

Many of the high substantivity acid dyes, particularly hydrophobic monosulphonated or non-polar pre-metallised dyes, often dye nylon in amounts well over the amino group content, even at pH values as high as 6–7. Build up of deep shades is not a problem with such dyes. This phenomenon is called over-dyeing. In some cases, it has been shown that dyeing isotherms, giving the dye on the fibre as a function of the dye remaining in solution at equilibrium, are a combination of the Langmuir and Nernst isotherms. This behaviour corresponds to ion exchange up to saturation of the available cationic sites plus over-dyeing by solution of the dye in the nylon (Figure 13.10).

![Combined isotherm](image)

Figure 13.10 Adsorption isotherm for a metal–complex acid dye on nylon
The influence of temperature on the rate of acid dye absorption by nylon is complex. The glass transition temperature (T_g) of water-saturated nylon is probably not much greater than about 40 °C. Once the temperature exceeds T_g, the movement of polymer chain segments that is then possible should increase the rate of dye absorption as diffusion of dye molecules into the polymer matrix becomes easier. The temperature at which the initial rate of dyeing begins to significantly increase is called the dyeing transition temperature (T_D). This temperature, however, is often 20–30 °C higher than T_g under the given dyeing conditions. At temperatures somewhat higher than T_g, the voids between the chains in the amorphous polymer are too small to accommodate large dye molecules. Therefore, in spite of the increased mobility at temperatures above T_g resulting from easier polymer chain rotation, there is little dye absorption. Once the temperature exceeds the value of T_D, however, the greater ease of chain mobility creates voids whose average volume has increased to the point that allows dye molecules to enter them. The increasing size and mobility of these voids, now containing dye molecules, allows a significant increase in the rate of diffusion of dye into the polymer matrix.

13.9.5 Practical application of acid dyes to nylon

Many of the acid dyes used for dyeing nylon were first developed for dyeing wool and, like wool acid dyes, they are also classified according to their substantivity for nylon at a given dyeing pH. There are three main groups:

1. low molecular weight dyes of low substantivity for nylon at pH 6–7. Although these dyes have good migration during dyeing, they require an acidic dyebath containing acetic or formic acid for good exhaustion;
2. dyes that have moderate substantivity for nylon and good exhaustion when applied at pH 3–5 in the presence of acetic acid. These dyes have good fastness to washing on nylon;
3. higher molecular weight dyes of high substantivity for nylon even in neutral solution. Dyeing is usually at pH 6.5–7.0 in the presence of ammonium acetate.

The substantivity of a given acid dye for nylon is invariably higher than for wool. Even when dyeing at the boil, the extent of dye migration when dyeing nylon will be less than for wool, but the dyed nylon will have better washing fastness. Monosulphonated acid dyes are preferred for dyeing nylon since their fibre
saturation concentration is equal to the amino group content of the nylon and they build up to deeper shades better than polysulphonated dyes.

Dyeing of nylon with acid dyes starts at 40–50 °C in the presence of an appropriate acid, such as acetic acid or ammonium acetate depending on the substantivity. The temperature then gradually increases to the boil. Dyeing with weak acids is essential to avoid acid-catalysed hydrolysis and tendering of the nylon. The initial dyeing pH and the temperature gradient during the heating phase control the rate of exhaustion. The paler the shade being dyed, the higher the initial pH must be. At low concentrations of dye in the dyebath, a greater percentage of the total amount of dye present transfers to the fibre per unit time and the risk of unlevel dyeing is greater unless the bath circulation is very efficient. Many of the higher molecular weight dyes tend to exhaust very rapidly above a critical bath temperature (65–75 °C). This corresponds to the dyeing transition temperature, $T_D$. For this reason, the rate of heating is decreased in this temperature range. The dyebath may even be held at constant temperature for a while, around this critical value, before continued heating to the final dyeing temperature. For deep shades, addition of acetic acid, to decrease the bath pH, promotes better exhaustion as dyeing proceeds.

Despite the uniform appearance of continuous nylon filaments, they are often difficult to dye level. It is common to see paler filaments on a fabric surface where they have absorbed less dye than their neighbours. This effect is called barré. It arises from physical and chemical differences along the polymer filament, which influence both the dyeing rate and the total amount of absorbed dye. Unfortunately, many higher molecular weight acid dyes, which do not readily migrate, emphasise these irregularities giving filaments with different depths, and even hues. Uniform coverage of barré in nylon is just as difficult a problem as the level dyeing of ‘tippy’ wool. It is discussed in more detail in Section 13.9.6.

Auxiliary chemicals in the dyebath assist level dyeing, particularly for dyes of higher substantivity and poor migration. An anionic levelling agent present in the dyebath will block a number of ammonium ion sites in the fibres. This decreases the initial rate of dye adsorption and thus promotes level dyeing. If barré is likely to be a problem, the goods are run for some time in a heated bath with the required acid and anionic levelling agent before dye addition. The levelling agent anions exhaust onto the nylon, the bath is cooled and the dyes are then added to start the dyeing cycle. Too much anionic levelling agent causes excessive blocking and lowers dyebath exhaustion. Some levelling agents are cationic compounds, containing a non-ionic dispersant to prevent precipitation of the dye–auxiliary
anion–cation complex. The formation of such a complex in solution retards exhaustion at low temperatures. The complex gradually dissociates as the temperature increases, liberating dye molecules that are then available for adsorption by the nylon (Scheme 13.5).

When dyeing nylon, acid dyes are often incompatible in mixtures. The dyes in a mixture must all have similar solubility and fastness properties. They will usually have the same number of sulphonate groups per dye molecule and give about the same rate of exhaustion. The dyeing will then always be on tone and there will be no hue change on repeated washing or light fading. The dyestuffs’ suppliers recommend suitable trichromatic combinations.

Compatible dyes have about the same rate of exhaustion under the given conditions. Rates of exhaustion of individual dyes, however, may not always be a reliable guide to their dyeing behaviour in a mixture with other dyes. If a supplier’s recommendations are not followed, selection of compatible dyes requires careful testing. The dyeing rate of a given acid dye often tends to be lower in the presence of other dyes. For example, CI Acid Violet 5 alone dyes nylon less rapidly than CI Acid Yellow 23 although both dyes are disulphonated. When dyeing with a mixture of these two dyes, under the same conditions, both dyes exhaust less rapidly, but now the violet dye adsorbs faster than the yellow. This may be related to the violet dye having a more extensive surface adsorption but a slower diffusion rate into the polymer than the yellow dye. Dyeing is never simple.

A number of direct cotton dyes are useful for dyeing nylon, particularly for deep shades. These are applied as acid dyes. They do not cover yarn irregularities well in pale shades but give reasonable fastness to light and washing.

The addition of benzyl alcohol to the dyebath (Irga-Solvent process, Ciba-Geigy) improves the coverage of barré and the washing fastness of the resulting dyeing. This process gives almost 100% exhaustion at lower temperatures (80–90 °C), in a shorter dyeing time. Re-use of the exhausted dyebath minimises the cost of the benzyl alcohol. Better levelling during nylon dyeing is also possible at temperatures above 100 °C using pressurised dyeing machines. Under these conditions, mild reducing agents such as thiourea in the dyebath scavenge oxygen that can oxidise amino groups in the nylon.

In most respects, the dyeing of nylon 6 with acid dyes resembles that of nylon 6.6. The washing out of the unreacted caprolactam monomer after filament spinning gives a more porous fibre that is easier to dye than nylon 6.6. Nylon 6 is more amorphous and has a lower melting point than nylon 6.6. It can be heat set at lower temperatures. The more open fibre structure and higher amino group
content result in greater dye exhaustion rates, better dye build-up and better migration during dyeing with acid dyes. Dyeings of nylon 6, however, have somewhat lower washing fastness than those on nylon 6.6 when compared at the same depth of shade. When dyeing nylon 6 fabric at the boil, using a winch machine, permanent stretching of the fabric can occur. It may be necessary to use a lower dyeing temperature so the goods are less plastic.

To correct unlevel dyeings on nylon, the goods are treated at pH 8.0–8.5 at the boil. At this pH, there are few ammonium ion groups and some of the dye desorbs. The bath can then be acidified and the desorbed dye re-exhausted onto the nylon. This is less successful with high substantivity acid dyes. Chemical stripping requires the use of reducing agents such as sodium sulphoxylate-formaldehyde (NaSO₂.CH₂OH) but complete stripping may be difficult.

13.9.6 Barré

Barré is the visual difference in colour depth, and possibly of hue, along the length of dyed nylon filaments in a fabric caused by physical and chemical variations in the polymer. This gives a continuous pattern of colour stripes seen in the course direction in circular knits, as warp streaks in warp knits, or as weft or warp streaks in woven materials. Unfortunately, many acid dyes tend to accentuate barré, some dyes being more sensitive to chemical variations in the polymer filaments and others to physical variations. Filaments with chemical variations are more difficult to dye level.

Chemical irregularities in nylon filaments are mainly from a non-uniform distribution of the polymer amino groups, which causes variations in the rate of dye uptake and particularly the equilibrium dye content of the filaments. Polyamide formation is reversible and the amino group content may change as additional polycondensation or hydrolysis occur when the nylon is at high temperatures during processes such as heat setting or texturing. The number and distribution of amino groups may also vary because of their oxidation during processing.

Similar differences in dyeing rate along filaments come from variations in the degree of polymer orientation and crystallinity. These physical variations can arise from uneven treatment in processes such as filament drawing and texturing, fabric heat setting, and from uneven filament tensions during fabric construction and processing. Barré from physical variations in filaments can be minimised by using levelling acid dyes, or by promoting dye migration by dyeing above 100 °C,
using an anti-oxidant such as thiourea to protect the amino end groups. Pretreating the goods with an anionic blocking agent before the acid dyes are in the dyebath is also a common method of promoting level dyeing. Lustre variations, arising from the effects of both filament surface and internal structure on light reflection and refraction, may also give a barré effect.

There are several dyeing tests for evaluating barré on nylon. Physical variations in the filaments influence the rate of dyeing, and chemical variations affect the extent of dyeing at equilibrium. Both types of barré may even be present in the same fabric, the rate of dyeing barré being more easily detected. Because of their good migration properties on nylon, disperse dyes, such as CI Disperse Blue 3, will uniformly cover most barré except that from gross physical variations in the filaments. When using acid dyes on nylon, those capable of migration will cover barré more uniformly. Unfortunately, these are the acid dyes of lower substantivity and lower fastness to washing. When deep shades are dyed to equilibrium, the amount of this type of adsorbed dye depends upon the number of ammonium ion sites. A trisulphonated acid dye such as CI Acid Red 18, applied to nylon at the boil in weakly acidic conditions, in sufficient concentration to saturate the fibre, will readily show if any variations in amino group content are present in the filaments. CI Acid Blue 45 (disulphonated), dyed to equilibrium under similar conditions, is also widely used for this purpose. Acid dyes of higher substantivity, such as CI Acid Blue 80 (disulphonated), will dye the more accessible filaments more rapidly and are useful for detecting physical variations in the filaments because of the poor migration under the dyeing conditions.

Pressure dyeing, dyeing with added benzyl alcohol, and dyeing with additions of levelling agents, all minimise barré. Pretreatment of the nylon material in a blank dyebath at a temperature around 85–90 °C, above the prevailing dyeing transition temperature, is also beneficial. Under these conditions, the movement of polymer chain segments allows the relaxation of tensions. This gives filaments with different chemical, thermal and mechanical histories time to equilibrate before dyeing takes place. A new dyeing process for nylon, developed by Du Pont and called the "Infinity" process, uses this principle. The process involves running the goods in a blank bath containing the appropriate weak acid, at a constant temperature above the prevailing dyeing transition temperature, usually in the range 75–90 °C. The dye solution slowly runs into the bath over about 45 min using a metering pump. The conditions are such that the dye strike is so rapid that the actual concentration of dye in the bath is essentially zero during the entire dyeing operation. The name of the process comes from the condition of infinite
exhaustion that prevails throughout dyeing. The rapid strike and poor dye migration result in yarns whose filaments are unevenly ring dyed on their exposed surfaces. This gives a higher colour yield than a well-penetrated dyeing. These ring dyeings show no decrease in washing, light and abrasion fastness when compared with well-penetrated dyeings at the same depth. By allowing the filaments to equilibrate by dyeing in a hot isothermal bath, barré is much less of a problem using this dyeing method.

13.9.7 Back-tanning

Many of the simple but brightly coloured acid dyes give dyeings on nylon of only moderate fastness to washing, particularly for deep shades. The washing fastness of such dyeings improves on aftertreatment of the dyed nylon with a solution of tannic acid containing formic acid at 90 °C (70 °C for nylon 6). This is done using a fresh bath. The anionic tannic acid is adsorbed onto the nylon surface by attraction to the cationic ammonium ion groups at the ends of the polymer chains. Subsequent treatment with a solution of tannic acid (potassium antimonyl tartrate, K\textsubscript{2}SbOC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}) produces a film of the insoluble antimony salt of tannic acid all around the filament surface. It is this film that limits desorption of the dyes during subsequent washing. When using low liquor ratio dyeing machines, a fresh bath for the tannic acid solution avoids precipitation of the antimony salt of tannic acid in the liquor.

This so-called full back-tanning aftertreatment gives a somewhat stiffer, slightly yellower fabric but with improved colour fastness to washing. The process has, however, a number of disadvantages:

1. Antimony salts are poisonous and pose an environmental threat;
2. The process is time-consuming, since ideally two separate baths are required after dyeing;
3. Yellow-brown impurities in commercial grade tannic acid dull the shade;
4. Tannic acid tends to discolour under alkaline washing conditions.

Because of the dulling and yellowing effect on the hue, back-tanning is limited to deep dyeings that tend to have poor washing fastness without this aftertreatment. The improvement in washing fastness obtained by back-tanning is lost if the fabric is heat set after dyeing, using either hot air or steam, as these processes rupture or even remove the surface film.

Because the back-tanning process is expensive and environmentally unsound,
cheaper synthetic chemicals for this purpose were developed [5]. They are called synthetic tanning agents or syntans. These are colourless, anionic, water-soluble polymers formed by condensation of formaldehyde with phenol, naphthol, or hydroxybiphenylsulphone sulphonic acids or their mixtures. Commercial syntans are complex polymeric mixtures. The average molecular weight must be as high as possible while still allowing solubility in water. Syntans are applied to dyed nylon at 80 °C at around pH 4 using acetic or formic acid in the bath. Although direct syntan aftertreatment in the exhausted dyebath is possible, a fresh bath is desirable.

The anionic syntans do not form a skin like the tannic acid/tartar emetic combination. In acidic solution, the syntan is substantive to nylon. The molecules adsorb on the filament surface by interaction with ammonium ion sites in the nylon but, because of their molecular size, they cannot penetrate far into the polymer. The layer of adsorbed syntan polymer molecules on the nylon surface presents a considerable barrier to dye transfer in either direction. They therefore improve the washing fastness of the dyeing but their presence also prevents dye penetration. Syntans are therefore useful for preventing absorption of direct dyes by nylon when dyeing cotton/nylon blends with direct cotton dyes. The improvement of the washing fastness of nylon fabrics dyed with acid dyes obtained by syntan aftertreatment is somewhat less than that of the full back-tanning process. Syntans, however, have little or no influence on the hue of the dyeing although they may slightly reduce the light fastness.

13.10 DYEING NYLON WITH METALLISED DYES

13.10.1 Mordant dyes

Nylon can be dyed with acid dyes suitable for after-chroming. Dyeing is usually at the boil using ammonium acetate or small amounts of acetic acid. After-chroming in the exhausted dyebath reduces water and steam consumption. If complexation of the dye occurs in the solution, there is a risk of deposition of the less soluble metallised dye on the nylon surface. This deposit decreases the fastness to perspiration and rubbing. To complete exhaustion, some additional acid may therefore be needed towards the end of the dyeing process. This generates more ammonium ion sites in the nylon and promotes further dye adsorption. If the extent of dyebath exhaustion is not adequate, a fresh bath is necessary for after-chroming.
Nylon, unlike wool, contains few groups capable of reducing sodium dichromate to chromic ion, the form required for complex formation with the dye. A reducing agent such as sodium thiosulphate is effective (Scheme 3.12). After-chroming is carried out at the boil using sodium dichromate and formic acid. The sodium thiosulphate is added once most of the dichromate anions have adsorbed onto the nylon. The reduction process is much slower than for wool. Efficient after-chroming of dyed nylon at 130 °C is possible without added thiosulphate. It is likely that formic acid reduces the dichromate under these conditions. Residual dichromate, left in the nylon, promotes tendering on exposure to light. Therefore, complete reduction of dichromate to chromic ion and effective complexation with the dye are essential. Despite the good fastness to washing and light of the after-chromed dyeings on nylon, this dyeing process is now restricted mainly to blacks. The after-chrome process makes shade correction and colour matching much more difficult because of the pronounced change in hue that occurs.

13.10.2 Metal-complex dyes

The dyeing characteristics of pre-metallised dyes vary widely depending on the type of metal-complex dye and on the molecular complexity and degree of sulphonation. Like all acid dyes, their application to nylon involves the usual problems:

1. competition for the available ammonium ion sites in the nylon and exclusion of the less substantive dyes;
2. difficulties in producing deep shades because of the limited number of available ammonium ion sites in nylon;
3. poor migration and levelling during dyeing, which accentuate barré.

The 2:1 metal-complex dyes have very good light fastness in pale shades and good washing fastness, even in deep shades. Many weakly polar 2:1 dye-metal complex dyes, particularly those without sulphonate groups in the dye ligands, have good build-up properties on nylon, because of over-dyeing (Section 13.9.4). In deep shades, they absorb in amounts exceeding the amino group content of the nylon and therefore must interact with the fibre by forces other than ionic forces. They do not therefore give blocking effects. Most 2:1 dye–metal complexes, however, accentuate physical irregularities in the nylon filaments and cause barré. Dyeing with either a weakly dye-complexing (cationic) or site-blocking (anionic) auxiliary levelling agent in the dyebath overcomes this problem. Alternatively, dyeing at
120 °C (110 °C for nylon 6), in the presence of an anti-oxidant to avoid amino group oxidation, promotes better levelling.

The 2:1 pre-metallised dyes have poor migration during dyeing of nylon, and level dyeing requires good control of the dyeing process. Dyeing is usually started at pH 7. The goods are pretreated with a suitable levelling agent and ammonium sulphate. The dyes are added and the temperature raised to the boil. Some dyes may have very rapid strike at 60–70 °C. A decreased rate of heating in this temperature range lowers the risk of unlevel dyeing.

The very acidic dyebaths used in wool dyeing with 1:1 dye–metal complex dyes will cause hydrolysis of the nylon. Some dyes of this type will dye nylon using acetic acid at pH 4–6 with a weakly cationic levelling agent. They give dyeings of good washing and light fastness.

13.11 LIGHT AND OZONE FADING OF ACID DYED NYLON

Nylon fabrics dyed with acid dyes generally have moderate to good light fastness. All auxiliary chemicals used in dyeing or for aftertreatments should be tested to ensure that any residue left in the fabric does not decrease the fastness to light. This also applies to ozone fastness. Ozone is a major constituent of polluted urban air and is a powerful oxidising agent capable of rapidly destroying the colour of many types of dyes.

Nylon is a major fibre for production of automotive fabrics and carpets because of its superior properties. It is, however, becoming increasingly difficult to meet the car manufacturers’ demands for light fastness ratings of 6 (Section 24.3.4) or even higher. Some nylon fabrics are aftertreated with copper derivatives (1–2% owf) to improve their fading resistance but with the increased risk of environmental contamination by copper. Automotive carpets and fabrics are often aftertreated with colourless ultraviolet photostabilisers. These strongly absorb ultraviolet light on the nylon surface and protect both the fibre and the dyes in it from photodegradation. The light fastness is therefore better. These chemicals function like sun screen products, the absorbed ultraviolet light being converted into heat. For automotive interior fabrics and carpets, the UV stabilisers do not need to have any significant degree of washing fastness but they must be colourless, odourless and non allergenic.

The fading of the colour of dyed nylon by ozone in industrial environments is a surface phenomenon. The fastness to ozone is therefore lower for dyeings that have poor dye penetration into the filaments. The ozone fastness, however,
increases with increase in the extent of dye-fibre interaction. For dyes with the same chromophore, the ozone fastness on nylon increases in the following order: disperse dye, disulphonated acid dye, monosulphonated acid dye, and reactive dye. Unfortunately, even reactive dyes (Chapter 16) cannot meet the ozone fastness demanded for automotive carpeting. Testing of ozone fading is not easy but is necessary because there is no relation between colour fading by ozone and by light.

13.12 NYLON CARPET DYEING

Manufacture of tufted carpets consumes large quantities of nylon multi-filament yarn. Modern filaments often have unusual properties compared to the original cylindrical nylon filaments. They may have trilobal cross-sections that hide dirt more effectively, and even conductive surfaces or cores that effectively dissipate static electricity. In addition, fluorocarbon finishes reduce soiling, stain blockers hinder penetration of anionic colorants in spilled food and drink, while ultraviolet photostabilisers improve the stability of the both the nylon and the dyes present towards light.

Considerable quantities of wide, tufted nylon carpeting are dyed continuously, particularly in the USA. The nylon filament yarn is textured to give it bulk, and heat set before tufting using dry heat or steam. Tufting involves punching of the multi-filament yarn through the primary backing and forming and tying of the filament loops. These may or may not be cut to form the pile.

13.12.1 Continuous dyeing of nylon carpets with acid dyes

For large quantities of carpet in a single colour, continuous dyeing is by far the most economic method of coloration. Great lengths of evenly dyed carpet, up to 12 m wide, require even dye application and fixation. Before application of the dye solution, the carpet is often well wetted with a solution of a wetting agent such as disodium di-octylsulphosuccinate. Steam set yarns are much easier to dye than dry set yarns. Addition of gum to the wetting agent solution promotes uniform wetting and helps to eliminate ‘frostiness’ at the pile surface caused by the migration of the dye away from the fibre tips during steaming. The pre-wetted carpet may be vacuum extracted before dye application. A high pick-up (300–400%) of thickened dye solution is run onto the pile surface across the full carpet width. A variety of systems are available for this step. Pre-wetting avoids pools of dye solution on the pile surface that run into pools on the carpet backing. A carpet of
weight 1.0 kg m$^{-2}$, 12 m wide, moving at 20 m min$^{-1}$ with a 300% pick-up of dye solution, requires 720 kg min$^{-1}$ of dye solution. Liquid acid dyes are necessary for rapid preparation of solutions by simple dilution. Dye solution may also be applied continuously to dry carpet, in which case wetting agents are in the dye solution. By using separated streams of different dye solutions, various multi-colour effects are possible (Section 23.9).

The wet carpet is then steamed for 3–5 min, preferably in dry saturated steam at 100 °C. If dye penetration into the fibres during steaming is not adequate, the colour fastness properties may be inferior, particularly the ozone fastness. The latter can increase from 2–3 up to 4–5 as the steaming time increases and the dyes penetrate deeper into the filament interior. Finally, washing the carpet removes unfixed dyes, residual gum and auxiliary chemicals. When only small lots of carpet are involved, dyeing is carried out using winch machines.

Stain blockers improve the stain resistance of nylon carpets towards anionic dyes in spilled food and drink. The original stain blockers were of low substantivity and the appreciable amounts remaining in the bath increased the BOD problems of the effluent (Section 8.5.1). They also turned yellowish on light exposure. A pale blue carpet would therefore become greener in the exposed areas. Current formulations include the stain blocker and fluorocarbon polymers, and are more stable. The fluorocarbon polymer forms a film on the nylon surface that resists the spreading of both oil and water and to which particles of dirt do not adhere readily. The build-up of static electricity is also reduced. Stain blockers are anionic polymers similar to the syntans used for the aftertreatment of nylon dyed with acid dyes (Figure 13.11). Because of their anionic nature, they repel the anionic colorants in spilled foods and the polymer film on the surface of the nylon fibres provides a physical barrier to the penetration of non-ionic materials.

The fluorocarbon polymer and stain blocker are usually applied after dyeing since they interfere with dye fixation. Application procedures and conditions depend upon the particular products selected. Continuous application of the stain blocker by spray, foam, or liquid jet, to the wet carpet after continuous dyeing is common. The lack of colour of these products requires extra care to ensure their uniform application for the best performance in use. The dispersion contains stain blocker, magnesium sulphate and fluorocarbon polymer. Acids such as acetic, formic, citric, or sulphamic acid will give a pH of 2.2–4.5, depending upon the
product selected, the nylon type and heat setting method used. The carpet is then steamed. The magnesium ions lower the aqueous solubility of the anionic stain blocker thus favouring transfer to the filament and the formation of an insoluble polymer film on the surface. Hydrogen bonds between the hydroxyl groups of the stain blocker molecules and amide groups in the nylon hold it onto the fibre surface. This is augmented by coulombic attraction between the blocker’s sulphonate groups and ammonium ion groups in the nylon surface. This promotes substantivity of the stain blocker for the nylon but its molecular size prevents penetration into the polymer.

Treated carpets have good water resistance, in the absence of surfactants. If water penetrates into the nylon fibres, coloured anions will not. The anionic layer of polymer blocker on and just inside the nylon surface repels them. Excessive steaming may cause a loss of the stain blocking effect if the polymer diffuses too far into the nylon. The degree of penetration is clearly less, the higher the molecular weight of the polymer. Stain blockers offer no resistance to non-ionic stains such as those from coffee and mustard. They also interact strongly with cationic chemicals found in some cleaners and creams. The use of anionic stain blockers on nylon carpets has increased dramatically despite their far from ideal performance. Some would claim that their market success involves more consumer persuasion than consumer demand.

13.13 DYEING MODIFIED NYLONS

There are a number of modified nylon polymers available having different substantivities for both acid and basic dyes (Section 4.2.4). Light dyeing, normal dyeing, deep dyeing and ultra deep dyeing types are available for dyeing with acid
dyes. These have increasing amino group contents, respectively, but all dye to the same depth with disperse dyes. In addition, there are also basic dyeing varieties of nylon, containing anionic groups capable of binding cationic dyes (Section 4.2.4). Mixtures of different nylon types in a carpet give attractive tone-in-tone and multi-colour effects because of their differential dyeing behaviour.

REFERENCES
CHAPTER 14

Dyeing cellulosic fibres with direct dyes

14.1 INTRODUCTION

Direct cotton dyes have inherent substantivity for cotton, and for other cellulosic fibres. Their aqueous solutions dye cotton usually in the presence of an electrolyte such as NaCl or Na₂SO₄. Direct dyes do not require the use of a mordant and, as their name implies, the dyeing procedure is quite simple. The goods go into the bath followed by the dissolved dyes. The bath is then gradually heated, usually to the boil, and additions of salt promote dyeing.

Many direct dyes are relatively inexpensive. They are available in a full range of hues but are not noted for their colour brilliance. Their major drawback is their poor to moderate fastness to washing. This limits their use to materials where good washing fastness is not critical. The light fastness of dyeings with direct dyes on cellulosic fibres varies from poor to fairly good, although some copper complex direct dyes have very good light fastness. As usual, the deeper the colour of the dyeing, the lower the fastness to wet treatments, and the higher the fastness to light. Various aftertreatments of the dyeings improve the fastness to washing. In some cases, however, such aftertreatments decrease the light fastness. They also invariably cause a change in hue that makes shade correction and colour matching more difficult.

Cotton, and other cellulosic fibres, are dyed with direct, sulphur, vat, reactive or azoic dyes – more types than for any other fibre. Each of these classes of dye has its own application methods, dyeing characteristics, cost, fastness properties and colour range, and therefore its own particular advantages and disadvantages. Within each group, application and performance properties vary considerably so the choice of which dyes to use is often not easy. Direct dyes generally cannot meet today’s more stringent washing fastness requirements for apparel and linens. In recent years, their share of the market has gradually declined in favour of reactive dyes. The latter have very good washing fastness on cellulosic materials and often have bright colours.
14.2 CHEMICAL CONSTITUTIONS OF DIRECT DYES

Sulphonated azo dyes constitute the predominant group of direct dyes (1, in Figure 14.1). These are usually bis-, tris-, or tetra-azo compounds, the latter type often being brown and black. Direct dyes usually have long, coplanar molecular...
structures. In general, the greater the extent of conjugation, the longer the wavelength of maximum light absorption. Green dyes must have two absorption bands in the red and violet regions of the visible spectrum. Green polyazo direct dyes, however, tend to be dull and bluish in hue. Bright green direct dyes have blue and yellow dye structures bonded together by a linking group that prevents their mutual conjugation (3, in Figure 14.1).

There are some yellow and orange stilbene direct dyes obtained from condensation reactions of 4-nitrotoluene-2-sulphonic acid. These are often of unknown constitution but have stilbene, azo and azoxy groups. Sulphonated copper phthalocyanines give turquoise direct dyes. These have good light fastness, but low wet fastness and poor colour build-up. A number of blue dyes based on the triphenodioxaizine structure (4, in Figure 14.1) have good fastness to light. There are also some pre-metallised azo copper complexes that give dyeings of very good light fastness (2, in Figure 14.1).

Many of the older azo direct dyes based on benzidine and its derivatives, such as Congo Red (Figure 1.3), and some made from 2-naphthylamine, are no longer manufactured in many countries. Benzidine and 2-naphthylamine are proven carcinogens.

Although direct dyes often have similar structures to acid dyes, they generally have higher molecular weights and extended coplanar molecular structures. There is, however, no clear demarcation between acid and direct dyes. Some direct dyes dye protein and nylon fibres just as a few acid dyes will also dye cotton.

14.3 DYEING PROPERTIES OF DIRECT DYES

14.3.1 Classification according to dyeing characteristics

Classification of direct dyes according to their chemical structures is not of much use to the dyer since dyes with similar chemical constitutions can have quite different application and fastness properties. Direct dyes vary widely in their dyeing behaviour giving compatibility problems. Grouping of direct dyes according to their dyeing properties is therefore more useful. The most common classification of direct dyes is that of the Society of Dyers and Colourists (SDC), based on their levelling ability and their response to increase in the dyeing temperature and to added salt during exhaust dyeing.
SDC Class A direct dyes. These are self-levelling dyes with good migration, even in the presence of salt. They usually require considerable amounts of salt for good exhaustion because of their lower substantivity. These dyes are relatively low molecular weight mono- and bis-azo dyes with several anionic sulphonate groups per molecule. They therefore have good water-solubility and do not aggregate to a significant degree in solution. Dyeing is started at 50 °C in the presence of added salt, the bath heated to the boil over 30–40 min, and dyeing continued at the boil for up to an hour. Several further salt additions, of increasing size, are required to promote exhaustion, the total amount of salt (5–20% owf NaCl) depending upon the depth of shade and the liquor ratio. Although these dyes would give greater exhaustion by dyeing at lower temperatures, dyeing at the boil allows good levelling and adequate penetration of the dyes into the fibre.

SDC Class B direct dyes. These are salt-sensitive or salt-controllable dyes, with poor levelling characteristics. They are of higher molecular weight than Class A dyes, often bis- and tris-azo dyes with just a few sulphonate groups per molecule. They have low to moderate substantivity in the absence of salt but give much increased exhaustion on addition of small amounts of salt to the dyebath. The dyeing method is the same as for Class A dyes but the initial salt is omitted. Gradual addition of dissolved salt, at the boil, controls the exhaustion.

SDC Class C direct dyes. These very salt-sensitive dyes exhibit poor migration. Level dyeing depends on the gradual increase of the dyeing temperature and subsequent additions of limited amounts of salt. Levelling agents may be required. These dyes are temperature-controllable. Dyeing is started at low temperature without added salt. The bath is slowly heated, with particular care in the temperature region where exhaustion is most rapid. Some salt may be added during further dyeing at the boil. These dyes are often polyazo dyes with few sulphonate groups and of high substantivity for cellulose. At lower dyeing temperatures, they are very prone to aggregation in solution and sensitive to salt addition. Salt in the dyebath impedes exhaustion at low temperatures because it promotes even more aggregation. The higher the degree of aggregation of the dye, the lower the concentration of individual dye molecules in the solution that can diffuse into the fibre, and therefore the lower the rate of dyeing. Dye aggregates are too large to penetrate into the pores of cellulosic fibres.
The SDC classification tests involve dyeing trials using a 30:1 liquor ratio. A migration test and a salt sensitivity test are carried out using the dyes under examination along with standard dyes for comparison [1,2]. The migration test (Section 10.4.5) is conducted at the boil in the presence of 10% owf salt using a dyeing of the test dye along with an equal weight of undyed cotton. Dyes that exhibit good migration, comparable to that of the standard dyes, belong to Class A. For the other dyes showing poor migration ability, a salt sensitivity test is carried out. Dyeings are prepared at the boil in the presence of 0.6, 0.8 and 1.0% owf salt for 30 min. The dyed samples are removed and replaced with the same weight of undyed material, further salt is added to give a total of 20% owf NaCl and dyeing continued for another 30 min. For Class B dyes, the initially removed samples, dyed at low salt concentrations, are lighter or the same as the second samples dyed in the presence of additional salt. For Class C dyes, the initial dyeings are darker than the later ones.

An examination of the molecular structures of direct dyes from the three groups, shows that in passing from Group A to Group C, dye substantivity generally increases because of increased molecular weight and a lower number of sulphonate groups per dye molecule. Class C dyes therefore generally have better washing fastness than Class B dyes, with Class A dyes having even lower fastness. Despite its value, the SDC classification is not readily applicable to dyeing at low liquor ratios as in jet, jig or pad dyeing. In these cases, a strike test may be a more useful indicator for selecting compatible dyes (Section 14.3.4). At low liquor ratios, dye aggregation is more pronounced since the dye solution is more concentrated for a given % dye owf. SDC Class B direct dyes may then require temperature control as well as salt control to obtain level dyeings.

14.3.2 Introduction to dyeing methods

The selection of specific direct dyes for dyeing cellulosic fibres depends on their dyeing properties, the particular fastness requirements, any aftertreatments used to improve the washing fastness, and on the particular finishing processes involved. Possible staining of other fibres present in the material by the direct dyes is another consideration. Dyeing with direct dyes is carried out in neutral solution. The dyebath is gradually heated to promote diffusion and levelling of the dyes, usually with gradual salt addition to exhaust the dyebath. Figure 14.2 illustrates a typical dyeing procedure.
Dyeing liquor ratios range from about 30:1 for open loose fibre machines, through 20:1 for winch dyeing, 5:1 for jet and package machines, to less than 1:1 in jig dyeing and padding. Direct dyes usually have good water solubility but the solubility is lower in the presence of salt. At low liquor ratios and temperatures, limited dye solubility may become critical when dyeing deep shades. Any undissolved particles of dye that touch the fabric surface will usually give a dark coloured spot. The dye solution is prepared by pouring boiling water onto an aqueous paste of the dye, prepared with some wetting agent if the powder is difficult to wet. Some dyes require soft water to avoid precipitation of the calcium and magnesium salts of the sulphonated dyes. Others give salts or complexes of different hue with metals such as iron and copper that are sometimes present in the water supply. A sequestering agent such as EDTA (Section 8.3.3) will bind unwanted metal ions and prevent the above problems. Sodium hexametaphosphate is the preferred sequestrant when using copper complex dyes. Agents such as EDTA remove the copper ion from the metal-complex dye giving the very stable EDTA–copper complex and freeing the non-metallised dye that usually has a different hue.

Levelling agents are useful when using dyes that do not easily migrate. These
are surfactants, or mixtures of surfactants, based on non-ionic polyethylene oxides and may also contain cationic agents. These chemicals form complexes with many types of anionic dyes, including direct dyes. Complex formation at relatively low temperatures reduces the concentration of the free dye in the bath so that the rate of dyeing is reduced. The dye–auxiliary complex molecule is too large to penetrate into the fibres’ pores. The surfactants in these products disperse the dye–auxiliary complex and prevent its precipitation. As the dyeing temperature increases, the dye–auxiliary complex gradually breaks up, liberating more free dye, which is then available for dying. In this way, the rate of temperature increase controls the rate of exhaustion, giving dyeing with improved levelness.

High dyeing temperatures for cellulosic fibres give much better dye migration, smaller risk of unlevelness and better fibre penetration. The SDC Class B and C dyes migrate better at 120 °C, although the dyebath exhaustion is usually lower at this temperature. Decreasing the dyeing temperature towards the end of the process, once the dyeing is level, will then improve the exhaustion. At 120 °C, however, there is a greater risk of dye decomposition or azo dye reduction by the cellulose. Dyes must therefore be selected with care.

Scouring and bleaching of cotton consume large amounts of steam and hot water. Because of increasing energy costs, many dyehouses dye grey cotton and cotton/polyester fabric in a combined scouring and dyeing process, provided this gives satisfactory results. This is possible for dull and deep shades on some knitted materials, where the major contaminant to be removed is the lubricating oil used in knitting. For a brighter hue, it is usual to simultaneously scour and dye the goods, and then to add hydrogen peroxide and alkali to the exhausted dyebath and bleach at 80–90 °C. This is called post-bleaching. In this way, the bath is heated only once, minimising steam consumption. Dye suppliers recommend dyes for these types of combined processes that are stable to alkali and resist fading during post-bleaching.

Problems with tailing arise in padding with solutions of direct dyes because of the inherent substantivity of these dyes for cellulose (Section 10.5.2). To minimise this, the selected dyes should have low, comparable strike rates. Padding may be carried out at higher temperatures in the range 50–90 °C, with dye solution containing a minimum of salt, to reduce the substantivity. SDC Class A direct dyes tend to migrate during drying and steaming and Class C dyes have rapid strike and give most tailing. Class B dyes are therefore often the best choice for continuous dyeing. Dyes of widely differing substantivity obviously cannot be applied together by padding.
The major pad dyeing processes are:
1. Pad with dye solution, dry, pad with salt solution, steam;
2. Pad with dye solution, steam;
3. Pad with salt solution, pad wet-on-wet with dye solution, steam.

Cotton/polyester materials can be continuously dyed by padding with combinations of direct and disperse dyes.

Stripping of dyeings with direct dyes is possible by hypochlorite (NaOCl) or dithionite (Na₂S₂O₄) bleaching, which destroys the dye on the fibre by oxidation or reduction, respectively. This is more difficult with aftertreated dyeings. Cationic aftertreatment agents must be removed from the stripped goods with formic acid since they influence re-dyeing. Copper complexes can be demetallised by treatment with EDTA, usually giving a paler shade, and then stripped or re-dyed.

14.3.4 Rates of dyeing with direct dyes and compatibility
The rate of dyeing cotton with direct dyes can vary widely from dye to dye. Times
of half dyeing of viscose with direct dyes varied by 2–3 orders of magnitude, when determined for dyeings in which the final exhaustion was limited to 50% by changing the concentration of added salt in each case (Section 11.2). Fortunately, under practical dyeing conditions, giving economic exhaustion, dyeing rates do not vary by more than ten-fold.

Rates of dyeing with single direct dyes are very dependent on the actual dyeing conditions and may not be a good guide to their properties in the typical dye mixtures used in most commercial dyeings. Ideally the dye mixture should behave as a homogeneous dye. As dyeing proceeds, the colour of the goods will gradually become deeper but will then always be of the same hue. For this, the dyes in the mixture must have similar rates of exhaustion and are said to be compatible. The compatibility of direct dyes depends on the rates of dyeing and migration, and the salt sensitivity of the dyes. Hue differences as dyeing proceeds are much more apparent than depth differences. Incompatible dyes also tend to give unlevel dyeings. They have different rates of migration, different degrees of fibre penetration because of dissimilar diffusion rates, and give a change of fabric hue during dyeing because of differences in their overall rates of absorption.

It is preferable to select compatible dye combinations from within each SDC classification group. Combination of some Group A and B, or Group B and C dyes, is possible, however, because of similarities in their properties. Ideally, all the selected dyes should have similar rates of exhaustion and often have the same molecular ionic charge. Dyes with low rates of exhaustion but good migration (SDC Class A dyes) are useful for shading towards the end of the dyeing process.

A dip test is useful for establishing dye compatibility. Small pieces of cotton of equal weight are dyed in the same bath with a mixture of direct dyes. At various intervals, a small dyed sample is removed from the bath and replaced by an identical piece of undyed fabric. A series of dyed samples arranged in order of increasing dyeing time will have gradually decreasing colour depth, but invariant hue, when the dyes used are compatible. When this is so, the series of samples that were added to the dyebath during dyeing will be of increasing colour depth, but also with the same constant hue, when arranged in order of their dyeing times.

The results of compatibility tests for direct dyes are only valid under the given dyeing conditions. Rates of exhaustion are very dependent upon the dyeing temperature and salt concentration. For example, for a mixture of CI Direct Blue 1 (5, Figure 14.3) and Direct Yellow 12 (6) at 60 °C, the yellow dye dyes cotton more rapidly than the blue dye in 0.01 M NaCl, but less rapidly in 0.10 M NaCl.

For some mixtures of two direct dyes, the presence of the second dye reduces
the equilibrium exhaustion of the other component. The formation of a complex of the two dyes in the dyebath would explain this. Spectrophotometry of the dye solutions sometimes confirms such complex formation. The spectrum of a solution of the two dyes at room temperature is not the simple sum of the two individual spectra of the separate dye solutions, indicating some interaction between them. Whether this is significant at higher dyeing temperatures is debatable. CI Direct Blue 1 and Yellow 12 show this behaviour and give some unusual dyeing results. For example, the series of dyeings obtained with a mixture of these two dyes, carried out at increasing constant temperatures, becomes paler and bluer. As the dyeing temperature increases, the amount of the yellow dye on the cotton decreases significantly. Surprisingly, the amount of the blue dye increases slightly, contrary to its behaviour when dyed alone at the same temperatures. In dyeing with direct dyes, there are many unexplained phenomena. Obviously, the selection of direct dyes for application in combination requires care, advice from the dye supplier and some preliminary dyeing trials.

### 14.4 THE EFFECTS OF VARIATIONS IN DYEING CONDITIONS

#### 14.4.1 The influence of added salt

Gradual addition of salt to the dyebath assists direct dye exhaustion onto cellulosic fibres. The actual effects of this on the rate of dyeing vary considerably from dye to
dye. The salt provides sodium ions to counteract the negative surface potential of the wet cotton. All fibres immersed in water develop a negative surface potential. This is a characteristic of any two different phases in contact – one will develop a small, electric charge at its surface, opposite in sign to the charge of the other phase. This occurs because one surface is a better electron acceptor than the other. In the case of cellulose at pH 7, water is a better electron donor than the cellulose. Negatively charged carboxylate groups, from oxidation of the primary alcohol group on carbon-6 in some glucose units, also augment the surface charge.

The negative charge of the cellulose surface repels anionic dye molecules. A high concentration of surrounding sodium ions counteracts this. Rapid solution flow also helps to break down the surface layer in which this charge is effective. Direct measurement of the potential difference between the inside of the fibre, where the dye is adsorbed, and the external solution is impossible. Streaming or zeta potentials, which develop when aqueous solutions flow across a fibre plug held between electrodes, can be measured. The values are probably lower than the total potential difference between the inside of the fibre and the external solution. As expected, the negative zeta potential of cotton is reduced by salt solutions, particularly those containing polyvalent metal ions, and increased by adsorption of anionic direct dyes.

The influence of added salt is the most important factor in the dyeing of cellulosic fibres with direct dyes. In dyeing, there are two objectives: good exhaustion and good colour uniformity. Both depend on the salt-controllability of the dyes, or how the gradual salt additions during dyeing influence the rate of exhaustion. Unfortunately salt-controllability is very dependent on the dyeing temperature. For practical purposes, it is useful to have some idea of the degree of exhaustion at different salt concentrations for each dye, possibly at different dyeing temperatures. For two dyes having about the same substantivity, salt should have a greater influence on the exhaustion of the one with the larger number of sulphonate groups, and therefore the larger negative molecular charge. The fibre’s negative surface potential repels the more highly charged dye molecules to a greater extent so this dye will respond more to salt additions. This conclusion, however, is not necessarily of great practical value because commercial direct dyes already contain much electrolyte.

The nature of the anion of the added electrolyte has little influence on the amount of adsorbed dye. Therefore, NaCl and Na₂SO₄, at the same total sodium ion concentration, have about the same influence. A higher positive charge on the cation promotes increased adsorption because polyvalent metal ions counteract
the negative surface potential more effectively, thus decreasing the repulsion of approaching dye anions. Polyvalent metal salts are, however, much more expensive than sodium chloride, the usual choice of the dyer.

14.4.2 The effect of temperature

Increasing temperature increases the rate of dyeing and of dye migration. From Le Chatelier’s principle for an exothermic dyeing equilibrium, the exhaustion will decrease as the dyeing temperature increases, as for some direct dyes on cellulosic fibres ((a) in Figure 14.4). Despite this, higher dyeing temperatures ensure good levelling and better penetration of the dye into the fibres in tightly packed yarns. In practice, such direct dyes are often allowed to finally exhaust in a cooling bath. For isothermal dyeings at increasing temperatures, some dyes, however, show an initial increase in equilibrium exhaustion, up to a temperature of maximum exhaustion, after which the exhaustion then decreases again as the dyeing temperature increases more ((b) in Figure 14.4). Still others, exhibit only increasing exhaustion at temperatures up to the boil ((c) in Figure 14.4).

These diverse variations of direct dye exhaustion depend on two opposing influences of the increasing dyeing temperature. These are the usual effect of

![Figure 14.4 Direct dye exhaustion as a function of the dyeing temperature](image-url)
increasing temperature decreasing the dyebath exhaustion because dyeing is exothermic, and its enhancement of the dyeing rate particularly at lower temperatures. Increasing temperature also promotes dye de-aggregation in the dyeing solution liberating more individual dye molecules to enter the fibre.

Manufacturers often cite a temperature of maximum exhaustion and provide optimum dyeing temperature profiles. The dyes CI Direct Yellow 12, Direct Red 81 and Direct Yellow 28 have maximum exhaustion at 30 °C, 60 °C and 100 °C, respectively, corresponding approximately to the behaviour of dyes (a), (b) and (c) in Figure 14.4. Despite this, the actual dyeing temperature may often depend on machinery limitations. For example, open jig dyeing machines cannot achieve dyeing temperatures much above 85 °C.

14.4.3 The influence of dyeing pH

Dyeing with direct dyes is usually carried out in neutral solution. Under alkaline conditions, cellulose fibres have an even greater negative potential, partly because of increasing dissociation of a number of cellulose hydroxyl groups, and exhaustion is lower. Oxycellulose, present in cotton that has been over-bleached, has a higher proportion of carboxyl groups, and is dyed much paler than undamaged cellulose because carboxylate ions repel the dye anions of like charge. Dyeing in the presence of formic acid suppresses ionisation of the carboxyl groups and the oxycellulose is then dyed to about the same depth of shade as regular cellulose. Under alkaline conditions, reducing end groups, particularly prominent in low molecular weight cellulosics such as viscose, reduce some azo direct dyes, decreasing the colour yield. In general, however, if dyeing of cellulosic fibres is in acidic solution, only weak acids are used and the residual acid in the goods is thoroughly rinsed out before drying. Strongly acidic dyeing conditions favour the acid-catalysed hydrolysis of cellulose. Any traces of residual mineral acid dried into the material can cause considerable damage.

14.4.4 The effect of liquor ratio

As we saw in Section 10.4.3, dyebath exhaustion should increase with decrease in the dyeing liquor ratio. This is certainly the case for direct dyes. This means that dyeing at low liquor ratio decreases the amount of waste dye in the effluent. It also consumes less water and steam, and allows a given salt concentration with less added salt. There has been a strong trend towards dyeing at as low a liquor ratio as is practicable. It should always be remembered, however, that the required amount
of dye must then be dissolved in a bath of reduced volume. It is important to ensure that the dye is, in fact, in solution at the beginning of dyeing when the temperature is relatively low and after addition of salt.

14.5 THE AFTERTREATMENT OF DYEINGS WITH DIRECT DYES

Aftertreatment of dyeings of direct dyes on cellulosic materials aims to improve the washing fastness by increasing the dye’s molecular weight. This makes it less soluble and of slower diffusion. Some of these processes decrease the light fastness of the dyeing. Aftertreatments are difficult and costly to carry out, and often give changes in hue that greatly impede shade correction and colour matching. Many of the direct dye aftertreatments now have limited use because reactive dyes give dyeings of much better washing fastness.

14.5.1 Diazotisation and development

Diazotisation of direct dyes with primary aromatic amino groups, followed by coupling of the diazonium ion with an appropriate developer, can be a very effective aftertreatment. Primuline, CI Direct Yellow 59 (7, in Figure 14.5), is a classic example of such a dye. Diazotisation involves treating the yellow dyeing with an acidic solution of sodium nitrite at room temperature or lower. Both amine and phenol developers can be used. The diazotised dye in the material is sensitive to light and heat so immediate coupling in a second bath containing the developer is necessary. A final wash removes any dye deposited on the fabric surface to ensure good fastness to washing and rubbing. Although the washing fastness improves by about one grade, there is often a considerable change in hue. For example, a dyeing with Primuline, diazotised and developed with 2-naphthol (8), turns from yellow to red. This technique is useful for cheap navies and blacks with a washing fastness of 3–4 but is little used today.

14.5.2 Coupling with diazonium salts

Direct dyes with free positions ortho and para to hydroxyl or amino groups react with an appropriate diazonium ion to introduce one or two additional azo groups. \( p \)-Nitroaniline, diazotised in a freshly precipitated suspension of its hydrochloride, has been widely used for this purpose.
14.5.3 Aftertreatment with formaldehyde
This type of aftertreatment is applicable to a few mostly black dyes. Dye molecules are linked by methylene groups, usually in ortho positions to hydroxyl or amino groups. The dyeing is treated with acetic acid and formaldehyde in solution at 70–80 °C. This aftertreatment may result in decreased light fastness.

14.5.4 Metal complex formation
In this type of aftertreatment, cupric or chromic ions convert the dye into a metal complex. The most common ligand structure is a o,o'-dihydroxyazo compound, or its dimethyl ether. In the latter case, the methyl groups are displaced and the dye forms the complex of a dihydroxyazo compound (9 and 10, in Figure 14.6). Coppering involves treating the dyeing with acetic acid and copper sulphate solution and heating to 70–80 °C. Complexation usually increases the light fastness. The process results in a change in hue and may be reversible on repeated washing due to de-metallisation. This results in a gradual decrease in washing fastness. Both copper and chromium are environmentally undesirable. Copper aftertreatment is still used for a few brown, navy and black shades, taking care that
there is a minimum of copper ion in the effluent. Because of this problem, most dye-copper complex dyes are pre-metallised by the dye manufacturers. Even the release in the effluent of the small amounts of copper in unexhausted pre-metallised direct dyes is now reaching the point of exceeding allowable limits.

14.5.5 Cationic fixatives
This aftertreatment involves precipitation of anionic dyes in the cotton with a cationic surfactant or polymer in warm water. It tends to reduce the fastness to light of the dyeing. The change in hue is only slight.

14.5.6 Resin and crosslinking agents
Amino resins and crosslinking agents impart dimensional stability to cotton and viscose fabrics and provide crease resistance and easy care properties. These finishes also improve the wet fastness of direct dyes but again may decrease the light fastness and give a hue change.

The Indosol SF range of dyes (Clariant) are SDC Class B and C copper complex direct dyes. After dyeing, the cotton fabric can be finished by padding with Indosol CR liquid, followed by drying and curing. This imparts dimensional stability and crease recovery as well as good washing fastness and moderate to good light fastness.
14.6 DYEING DIFFERENT TYPES OF CELLULOSIC FIBRES

Cellulosic fibres include cotton, mercerised cotton, linen and the various forms of viscose, each with their own particular dyeing characteristics. Because of the differences in molecular weight and morphology between native and regenerated cellulose fibres, there are large differences in their physical properties. Wet cotton is a strong, rigid fibre and most woven cotton fabrics will withstand considerable stress. This is not true of fabrics made from regular viscose. Their wet strength is only moderate and they require careful handling during dyeing. Viscose also swells much more than cotton when wetted. This can lead to limited solution flow and dye penetration problems in dyeing packages or packed loose fibre.

The different types of cellulosic fibre are all dyed by direct dyes using essentially the same dyeing method. The temperature increase of the dyebath, and the amount of salt added to it, control the rate of exhaustion and levelling. In the dyeing of blends of these cellulose fibres with direct dyes, they do not absorb dyes at the same rate or to the same extent because of the differences in their morphology. Even the extent and conditions of drying after preparation can influence the dyeing of a fabric of cellulose fibres. Despite these differences, the standard affinity of a given direct dye is remarkably constant for the different cellulose fibres.

The effects of carboxylate groups are important at low salt concentrations where there is little effective shielding of their negative charge by sodium ions. The higher negative surface charge of viscose compared with cotton is partly because of its additional carboxylate groups. In general, with more than 2 g l⁻¹ NaCl, the extent of dye absorption increases in the order cotton, mercerised cotton, regular viscose; in the same order as increasing fibre accessibility. Even different grades of cotton fibre have different dye absorption characteristics. This is one reason why intimate blending of cotton fibres before spinning is so important.

The rate of dyeing increases as the diameter of a fibre decreases, even though the equilibrium exhaustion for chemically identical fibres with different diameters hardly vary. This is readily demonstrated for viscose filaments of different denier. The internal volume of the pores is different for the various cellulosic fibres. These internal volumes have been estimated to be 0.30, 0.50 and 0.45 l kg⁻¹ for cotton, mercerised cotton and regular viscose. A value of 0.22 l kg⁻¹ is widely used for cotton in estimating dye affinities (Section 11.1.2). In dyeing, these fibres are far
from being saturated with dye, so the dye only adsorbs onto a very small part of the internal surface.

Covering neps of immature cotton fibres (Section 5.2.3) is always a concern in cotton dyeing. With dyes of low substantivity, neps usually absorb less dye and appear as paler spots on the fabric. Since immature fibres give much greater rates of dye desorption, the paler dyed neps may not appear until after washing. Better coverage can be achieved using dyes of high substantivity and can be much improved by mercerisation before dyeing, since this swells the immature fibres (Section 5.4.6).

Mercerised cotton will absorb more dye and be darker in colour than normal cotton dyed in the same bath. It is more accessible than regular cotton and its lower negative surface potential decreases repulsion of dye anions. It will appear darker in colour even for the same amount of dye in the fibre because of a higher degree of internal light scattering that results in greater light absorption. This effect is, however, dependent on the dye being used and the conditions of mercerisation.

Viscose fibres and filaments are available in a number of variants with different dyeing characteristics. They have different internal structures, skin-to-core ratios, porosities and degrees of fibrillation. These different forms therefore have different dyeing rates, equilibrium dye absorptions and colour yields. Direct dyes have higher substantivity for regular viscose than for cotton because viscose is less crystalline and oriented so it has a much greater internal surface. The fastness to light of dyeings of direct dyes on viscose is up to one fastness grade better than on cotton. The fastness to washing on viscose, however, is often less than on cotton because of its higher accessibility. The more highly oriented viscose types give better wet fastness.

The physical and chemical properties and the dyeing behaviour of the various cellulosic fibres are therefore quite different. About all they have in common, is the cellulose that constitutes them.

14.7 THE ORIGINS OF SUBSTANTIVITY FOR CELLULOSE

The dyeing of cotton with direct dyes is completely reversible. For dyeings at equilibrium, the Freundlich isotherm usually applies (Section 11.1.1) but some dyeings with direct dyes give a better correlation with the Langmuir isotherm. The former isotherm usually indicates that adsorption is non-specific and the latter
that the dye adsorbs on specific fibre sites. This dichotomy of behaviour is typical of the poor understanding of dyeing cellulose fibres.

Direct dyes invariably have extended, conjugated, coplanar molecules, with widely spaced hydrogen bonding groups and some sulphonate groups to provide solubility in water. The greater the number of sulphonate groups in the dye molecule, the higher the water solubility but the lower the fastness to wet treatments, and the lower the dye substantivity. Molecular coplanarity is, however, a specific requirement for substantivity. Whereas the dye Benzopurpurine 4B (11, in Figure 14.7) has good substantivity for cotton, its isomer meta-Benzopurpurine (12), which cannot be coplanar, does not. While most dyes substantive to cellulose fibres are coplanar, they are not always long and linear (see Chapter 17 on vat dyes).

Long, coplanar dye molecules can sit on top of a cellulose polymer chain with the aromatic rings parallel to the glucose rings. This would allow short range intermolecular attractive forces to operate. This interaction has long been considered to involve hydrogen bonding. Cellulose has an abundance of hydroxyl groups and direct cotton dyes often have hydroxyl, amino or amide groups capable of hydrogen bonding. This interpretation of the origin of the substantivity of direct dyes is prevalent in the dyeing literature. It is by no means proven. The cellulose hydroxyl groups are in the equatorial positions around the glucose units and do

![Figure 14.7 Benzopurpurine 4B (11); meta-Benzopurpurine (12)](image-url)
not necessarily present an appropriate angle to the hydrogen bonding groups in the
dye molecule when the latter is sitting above or below the glucose ring. Cellulose
hydroxyl groups are usually hydrogen bonded together or to water during dyeing.
Many leuco vat dyes, derived from polycyclic quinones and leuco sulphur dyes
(Chapter 17) have high substantivity for cellulose fibres, yet they have neither
linear structures nor many hydrogen bonding groups. Substantivity may therefore
depend more on van der Waals and dispersion forces between the dye and fibre
molecules.
Substantivity may also involve the surface active properties of direct dyes. The
more hydrophobic sections of the dye molecule would prefer to approach the
relatively hydrophobic axially oriented carbon–hydrogen bonds of the glucose rings
in cellulose to avoid interaction with surrounding water molecules. This is the
driving force of surface activity. Since cellulotic fibres are extremely porous, they
have an extended internal surface and surface activity effects could account for a
considerable degree of dye adsorption.
Direct dyes aggregate in solution and in the fibre, another facet of their surface
activity. There is circumstantial evidence that aggregation of the dye molecules in
the cellulose fibre is the cause of the dye’s substantivity. Dye aggregation increases
with increasing dye and salt concentration, and decreases with increasing
temperature. Most evidence suggests that aggregation is not significant in boiling
solutions but the inability of the limited experimental techniques to detect small
aggregates in solution, or in the fibre, could give misleading conclusions. Some
dyes do not appear to aggregate, but are substantive (CI Direct Yellow 12). Others
are so highly aggregated that dyeing is almost impossible at low temperatures
(copper phthalocyanine direct dyes), and others appear to have no substantivity
unless salt is present (CI Direct Blue 1).

Despite the considerable literature on the effects of varying molecular structure
on the substantivity of dyes for cotton, the origins of such substantivity are poorly
understood. Are both dye–fibre and dye–dye interactions as well as surface activity
involved in promoting substantivity of direct dyes for cellulotic fibres? The best
answer one can give is – possibly. How little we understand of this technology.

REFERENCES
2. SDC Committee on Direct Dyes, J.S.D.C., 62 (1946) 280; 64 (1948) 145.
CHAPTER 15
Disperse dyes

15.1 INTRODUCTION TO DISPERSE DYES
Cotton can be dyed with anionic direct, sulphur vat, reactive and azoic dyes. These types of dyes, however, are of little use for the dyeing of synthetic fibres. Disperse dyes, on the other hand, are non-ionic. They dye all the synthetic and cellulose acetate fibres using a direct dyeing technique. Only the dyeing temperature varies from one fibre to another. They are thus one of the major classes of dyestuff. The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough. Their major use today is for the colouration of polyesters, the most important group of synthetic fibres.

What is a disperse dye? These non-ionic dyes are relatively insoluble in water at room temperature and have only limited solubility at higher temperatures. They do, however, possess substantivity for hydrophobic fibres such as nylon and polyester, in which they are quite soluble. As their name implies, these dyes are present in the dyebath as a fine aqueous suspension in the presence of a dispersing agent. The water dissolves a small amount of the dye in monomolecular form. The hydrophobic fibres then absorb the dye from the solution. Because these dyes are non-ionic organic compounds of relatively low molecular weight, many sublime on heating and dyeing by absorption of the dye vapour is also possible.

When cellulose diacetate fibres first appeared in 1921, few of the available ionic dyes were able to successfully colour them. Secondary acetate fibres absorb little water, do not swell and have only small pores. In addition, their surface potential is much more negative than that of cotton and therefore they repel anionic dyes. Although cellulose diacetate fibres will absorb some cationic dyes, and a few acid dyes, there is little or no penetration of the dye unless the fibre is pre-swollen. The dyeings produced using ionic dyes also have poor fastness properties.

The first dyes for cellulose acetate fibres were water-soluble. The dye molecules

\[
\text{Dye} = \text{NH} - \text{CH}_2\text{SO}_2\text{Na}(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{Dye} = \text{NH}_2(\text{s}) + \text{CH}_2\text{O}(\text{aq}) + \text{NaHSO}_3(\text{aq})
\]

Scheme 15.1
Disperse dyes contained a methylamino sulphonate group (–NHCH₂SO₃Na) introduced by reaction of a primary amino group with formaldehyde and sodium bisulphite (Ionamine dyes, 1922). During dyeing, this group hydrolysed to the less soluble parent amine (Scheme 15.1). It was soon recognised that it was this compound that the cellulose acetate absorbed. The first true disperse dyes were simple, relatively insoluble azo and anthraquinone compounds dispersed in water using the sodium salt of sulphated ricinoleic acid (1, in Figure 15.2). Many of these dyes are obsolete but their development provided the technology for preparing fine aqueous dispersions by grinding the dye with dispersing agents. A fine dispersion is essential for rapid dyeing and avoids deposition of larger dye particles on the material.

Disperse dyes have slight water solubility because of the presence of polar substituents in their molecular structures. During dyeing, a small quantity of dye is present in true aqueous solution in a monomolecular form. These dye molecules are able to penetrate into hydrophobic artificially-made fibres such as those of cellulose acetate, nylon or polyester. The dye is much more soluble in the fibre than in water so deep dyeings are possible. The dye particles in dispersion are very small. Their large specific surface area ensures rapid solution to maintain saturation of the aqueous solution as the soluble dye transfers to the fibre. Dyeing consists of a solubility equilibrium coupled to a solid solvent extraction equilibrium (Scheme 15.2).

Dyeing isotherms, graphs of \( C_f \) (concentration of dye in the fibre) as a function of \( C_s \) (concentration of dye in solution) at a given constant temperature, are of the linear Nernst type (Figure 11.1). This is true whether the equilibrium is established starting with undyed fibres and an aqueous dispersion of the dye, or with the dyed fibre and water. The final point on the linear portion of the isotherm gives the solubilities of the dye in the fibre and in water. Beyond this point, the dye saturated fibre is in equilibrium with the saturated aqueous solution, which is in equilibrium with solid dye particles. The slope of the isotherm gives the value of the partition coefficient \( (C_f/C_s) \). This dyeing equilibrium constant decreases with increasing temperature since dyeing is exothermic.
CHEMICAL CONSTITUTIONS OF DISPERSE DYES

15.2 CHEMICAL CONSTITUTIONS OF DISPERSE DYES

The majority of disperse dyes are low molecular weight, non-ionic mono-azo and anthraquinone derivatives. Polar substituents are usually present in the dye molecule so that the dye has the slight solubility in water required for dyeing. Hydroxyethylamino groups (NHCH₂CH₂OH) are typical of such substituents. The interaction of such polar groups with the water, by dipole interactions and hydrogen bonds, is crucial for water solubility. Dipole forces and hydrogen bonds, as well as dispersion forces, also bind the dye molecules to polar groups in the fibres.

There are many thousands of azo disperse dye structures because of the numerous substitution patterns possible in the diverse diazonium ion and coupling components. Colours that are less typical of simple azo compounds, such as greenish-yellow and blue, are also possible using more specialised components. These may have heterocyclic units or cyano substituents. There is also a limited number of other chromophores providing disperse dyes with particular properties. Figure 15.1 gives some typical disperse dye structures.

Anthraquinone disperse dyes are usually 1-hydroxy or 1-amino derivatives. These have bright colours ranging from red through to blue. Simple anthraquinone dyes have low molar absorptivities (Section 24.1) compared to azo compounds and therefore give dyeings of lower colour yield. Apart from a few
DISPERSE DYES

Bright pinks and blues, anthraquinone disperse dyes are gradually being replaced. In their manufacture, the production of the required intermediate chemicals, and of the dyes themselves, often involves complex reactions under pressure. The reaction equipment is more sophisticated than that used for the simpler azo coupling reaction. In addition, anthraquinone-1-sulphonic acids are key intermediates and the sulphonation reactions for their preparation use a mercuric ion catalyst. The environmental threat of mercury in the chemical plant effluent has led to increasingly stringent regulations for its containment and therefore increased production costs.

There are no true green or black disperse dyes. Dyes with both red and blue light absorption bands for greens, or with several overlapping absorption bands for blacks, are difficult to prepare. A major constraint for disperse dye structures is the relatively low molecular weight that the dye must have to be slightly water-soluble and to be able penetrate into hydrophobic synthetic fibres. A combination of blue and yellow dyes gives green dyeings. Blacks require an aftertreatment of the dyeing involving diazotisation of the absorbed dye containing a free primary amino group followed by reaction with a coupling component. Black disperse dyes may also be mixtures of dull orange, rubine and navy dyes. Many disperse dyes are mixtures generated by the reactions used in their synthesis. Techniques such as thin layer chromatography are useful for establishing the number of components (Section 24.5.3).

15.3 DISPERSE DYE DISPERSIONS

Disperse dyes are available as powders, grains, pastes or aqueous dispersions. These all contain micro-fine dye particles, many with diameters below 1 μm, as well as varying amounts of dispersing agents. Powders may cause dusting but this is not as bad as with some ionic dye powders. Granular forms pour easily, dust less and facilitate weighing. Solid forms of the dyes contain much more dispersant than pastes and liquid forms to prevent particle aggregation during drying. Liquid disperse dyes are useful for continuous dyeing. Settling and aggregation of dye particles in pastes and liquids can lead to coloured specks on the dyed fabric. Powdered or granular disperse dyes rarely contain more than 50% dye, the rest being dispersant plus smaller amounts of diluents, oils and shading colours.

The role of the dispersing agent is to coat the surface of each dye particle with a monomolecular layer of adsorbed dispersant. Since these chemicals are invariably anionic polymers, the more hydrophobic sections of the polymer chain adsorb onto...
the hydrophobic dye particle surface with the anionic groups of the polymer exposed to the surrounding water. The overall negative charge on the surface of each particle prevents their coalescence and aggregation. The original dispersant was sulphated ricinoleic acid (1, in Figure 15.2). Modern dispersants are often either lignosulphonates from paper pulping, sulphonates of alkylarylpolyformaldehyde condensates (Figure 15.3), or sodium oleyl-p-anisidide sulphonate (2). Many commercial dispersants for dyeing are mixtures of non-ionic and anionic compounds. The dye particles dissolve in the micelles of the non-ionic surfactant and the anionic component raises the cloud point of the former (Section 9.3.3) to values above the dyeing temperature so that the dispersion is stable.

The presence of a dispersing agent in the dyebath increases the apparent water solubility of the dye and therefore decreases the dyeing exhaustion. This is because dispersant micelles in solution dissolve an appreciable number of dye molecules. The number of dye molecules per solid particle is much larger than the number per surfactant micelle. The number present as single soluble molecules in true solution is even less. All these dye species appear to be in rapid equilibrium in the dyebath. Therefore, dye transferred from the aqueous solution to the fibre is rapidly replenished by dye from a micelle or from a particle surface.

To ensure that the rate of solution of the dye does not control the overall rate of dyeing, the dyes consist of very small particles to give the maximum specific surface area. Therefore, during dyeing the average particle size will gradually increase because the smaller particles dissolve more rapidly. The very fine state of division avoids dye specks on the goods. In fact, the quality of the fine dispersion is often evaluated by running it through coarse filter paper and examining for any coloured residue. Dispersions may not always be stable under the dyeing conditions, particularly those involving high temperatures and high shear forces as
in jet and package machines. The dyebath usually contains additional dispersant to maintain the dispersion of the dye and to promote levelling. This is more important for pale shades when the amount of dispersant added from the dye powder or liquid is low. No electrolyte is added to the dyebath since it will not influence the dyebath exhaustion. Disperse dyes are non-ionic and the negative water–fibre boundary charge does not influence adsorption. Salt addition often affects the layer of anionic dispersant on the surface of the dye particles, resulting in undesirable particle aggregation.

As always in dyeing, good quality water is essential. Some dyes react with traces
metal ions such as iron or copper and give shade changes. Calcium and magnesium ions may react with anionic dispersants and wetting agents rendering them much less effective. Addition of a sequestering agent is valuable, especially with metal-sensitive dyes.

15.4 FASTNESS PROPERTIES OF DISPERSE DYES

The fastness to washing and light of dyeings with disperse dyes on synthetic and acetate fibres is usually moderate to good (Table 15.1). The washing fastness on nylon, however, is only fair, particularly for deep shades. The results of washing fastness tests on deep polyester dyeings often depend upon how well residual disperse dye particles on the fibre surface have been cleared after dyeing. When disperse dyes have migrated from inside the polyester fibre to the surface during thermal treatments such as heat setting or drying, the dyeings may have reduced fastness to washing, dry cleaning and rubbing (crocking). This effect is enhanced when the dyes are soluble in hydrophobic surface finishes such as softeners. The fastness to wet treatments of dyeings on secondary cellulose diacetate is inferior to that on the more hydrophobic triacetate. The summary in Table 15.1 shows that dyeings of artificially-made fibres with disperse dyes generally have good fastness properties. For any fibre, however, a particular fastness property will vary considerably from dye to dye.

<table>
<thead>
<tr>
<th>Fastness property</th>
<th>Acetate</th>
<th>Triacetate</th>
<th>Nylon</th>
<th>Polyester</th>
<th>Acrylic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing</td>
<td>Moderate</td>
<td>Good</td>
<td>Poor to fair</td>
<td>Good</td>
<td>Very good</td>
</tr>
<tr>
<td>Light</td>
<td>Good</td>
<td>Good</td>
<td>Moderate to good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Crocking</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Moderate to good</td>
<td>Moderate</td>
</tr>
<tr>
<td>Gas fume fading</td>
<td>Fair</td>
<td>Moderate</td>
<td>Fair</td>
<td>Moderate to good</td>
<td>Good</td>
</tr>
</tbody>
</table>

The light fastness of disperse dyes may be very good in standard shades but is less so for pale shades, and lower still for tests conducted using a carbon arc light source. Non-ionic UV absorbers increase the light fastness for dyed fabrics such as those used for automobile upholstery.
DISPERSE DYES

Certain blue and violet anthraquinone disperse dyes with basic amino groups are very sensitive to fading by nitrogen dioxide in polluted air. High temperature combustion processes produce low concentrations of nitrogen oxides. They are most abundant in industrial or city environments. Their effect on dyeings is called gas fume fading. This type of fading is usually worst for dyeings with sensitive dyes on cellulose acetate fibres. It is less severe on nylon and polyester fibres, but still poses a problem when the highest fastness is required. Nitrogen dioxide will nitrosate a relatively nucleophilic primary amino group of the dye, converting it into a hydroxyl group. This reaction usually reddens the shade. Colourless fading inhibitors protect sensitive dyes. These are readily nitrosated amines that preferentially react with the nitrogen dioxide and thus protect the dye. The fading inhibitor is added to the dyebath towards the end of dyeing, or is applied in an aftertreatment. Dyes that are more resistant to nitrogen dioxide fading have less nucleophilic phenylamino groups.

Ozone is a major air pollutant in metropolitan centres. It causes oxidation of many types of dyes, close to the fibre surface. Ozone fading of dyed nylon carpets and fabrics in automobile interiors is particularly serious for pale shades when the dye has not adequately penetrated into the fibres (Section 13.12). Aftertreatment of the dyeing with amine or phenol anti-oxidants, similar to gas fume fading inhibitors, improves the fastness to ozone fading of sensitive blue anthraquinone disperse dyes [1].

15.5 DYEING CELLULOSE ACETATE FIBRES

The dyeing of cellulose acetate materials is a simple direct dyeing process. The dispersion of dyes in warm water is sieved into the bath, possibly already containing additional dispersant. Boiling water and concentrated solutions of dispersing agents must be avoided as they can adversely affect the dye particle dispersion. Cellulose diacetate is dyed at temperatures not exceeding 85 °C, because of the risk of acetyl group hydrolysis on the fibre surface, which causes considerable dulling of the attractive lustre of the bright filaments. Because this thermoplastic material readily forms permanent creases at the usual dyeing temperature of 80–85 °C, dyeing of the full width fabric on a roller is necessary. A typical jig dyeing procedure involves two ends at 40–50 °C, followed by two ends at each higher bath temperature, up to the final dyeing temperature of 80–85 °C. At the higher temperatures, the lengthways tension must be as low as possible, to avoid elongation of the fabric. Beam dyeing is possible provided that the material
allows good liquor flow through the roll at a pressure low enough to avoid deforming the plastic filaments.

Disperse dyes for cellulose acetate vary widely in their rates of exhaustion and levelling ability. Dyeing with mixtures of compatible dyes is essential. The SDC gives testing procedures for dyeing cellulose diacetate with disperse dyes [2]. These tests establish the migration ability of the dye, the influence of temperature on dye uptake (temperature range test), the rate of dyeing and the colour build-up with increasing dye concentration relative to standard dyes of known properties.

The results of the temperature range test provide classic examples of the influence of temperature on dyeing kinetics and equilibrium. For dyes that adsorb rapidly at 50–60 °C, the amount of dye absorbed after dyeing for an hour will decrease as the dyeing temperature increases. This is the expected effect of temperature on an exothermic dyeing process that has reached or come close to equilibrium. The exhaustion (equilibrium constant) decreases with increasing temperature. For slow dyeing dyes, the amount of dye absorbed in one hour increases steadily with increasing dyeing temperature because this increases the rate of diffusion of dye into the fibre. After dyeing for one hour, the dyeing may be sufficiently far from equilibrium that the expected decrease of the exhaustion with increasing temperature does not occur. Some dyes may show a temperature of maximum dye exhaustion, showing the effects of temperature on dyeing rate at lower temperatures and on exhaustion at higher values. Slow dyeing dyes with poor temperature range properties will likely cause ending and listing when dyeing on a jig (Section 12.4.2) because the fabric ends and selvages tend to be cooler than the bulk of the material.

Blacks can be obtained in one of two ways. The simplest involves the use of a mixture of dull red, blue and yellow or orange disperse dyes at relatively high total concentrations. With appropriate combinations, this is quite successful. The second method is by a diazotisation and coupling aftertreatment. This involves diazotisation of a primary aromatic amino group in the disperse dye in the fibre and subsequent reaction of the diazonium ion with a suitable coupling component such as 3-hydroxy-2-naphthoic acid (BON acid after beta-oxy-naphthoic acid). Coupling in alkaline solution, as in the aftertreatment of direct dyes on cotton (Section 14.5.1), is less suitable for cellulose acetate because of the risk of surface hydrolysis of acetate groups. The amino disperse dye, for example CI Disperse Black 1 (3, in Figure 15.4), is applied by conventional dyeing at 80 °C. After rinsing the orange fabric, the amino groups of the dye in the cellulose acetate are diazotised by reaction with a solution of sodium nitrite and hydrochloric acid at
room temperature. After rinsing again, the fabric is treated with a dispersion of BON acid. This is prepared by precipitation of the free acid from a solution of its sodium salt in the presence of a dispersing agent. It is absorbed by the fibres at pH 4.5 exactly like a disperse dye. It reacts with the diazonium ion to form the dark navy pigment (4).

Other sequences for dye application, diazotisation and coupling, are possible. The coupling component can be applied to the fibre after dyeing, as above, or even concurrently along with the amino disperse dye followed by its diazotisation. Once the colour has fully developed, scouring the material in soap or detergent solution at relatively low temperature removes pigment from the fibre surface and biproducts from the diazotisation and coupling sequence. If this is not done, inferior fastness properties result, particularly poor fastness to washing and rubbing.

Cellulose diacetate fabrics must be handled and dyed with care to avoid forming crease marks and stretching. Even at a dyeing temperature of 85 °C, the material is quite plastic and easily deformed. It is therefore preferable to dye such fabrics in open width using a jig machine. This is, however, not as simple as it might seem. Section 12.4.2 outlines some of the problems inherent in jig dyeing. With many disperse dyes, ending and listing effects are all too common, and are particularly noticeable when using less compatible combinations of dyes.
Cellulose triacetate is considerably more hydrophobic than diacetate and dyeing it with disperse dyes requires higher temperatures, but carries less risk of surface hydrolysis. The more compact internal structure gives lower dye diffusion rates in this fibre. It is normally dyed with disperse dyes at the boil. Dyeing temperatures up to 130 °C are possible and give improved washing and crocking fastness because of the better penetration of the dyes into the fibres. This is beneficial when dyeing heavy shades. It also allows use of dyes that are absorbed too slowly at 100 °C, thus increasing the range of available dyes. For dyeing deep shades, dyeing at the boil using a carrier such as diethyl phthalate is possible. This acts as a fibre swelling agent and thus accelerates dye absorption by increasing the diffusion rate (Section 15.7.3). For a typical black, the amino disperse dye and coupling component are applied sequentially, or simultaneously. The black is developed by aftertreatment with a solution of sodium nitrite and hydrochloric acid that causes diazotisation of the dye and immediate coupling of the generated diazonium ion. Soaping removes surface colour, but usually a process called reduction clearing is preferred. In this, the dyed material is treated with a weakly alkaline solution of sodium hydrosulphite (hydros, Na₂S₂O₄·2H₂O), which reduces and eliminates the azo pigment on the fibre surface. Each combination of dye and coupling component requires its own particular dyeing and aftertreatment conditions so the dye supplier’s recommendations should be consulted.

As for nylon, dry heat setting of cellulose triacetate fabrics improves their dimensional stability but reduces the dyeing rate. If heat setting or texturising has not been uniform, barré effects may be evident on fabrics made of filament yarns. Dyeing under pressure at above 100 °C increases the rate of dye migration and minimises barré effects. For heat pleating of cellulose triacetate materials after dyeing, it is essential to use disperse dyes that do not readily sublime from the heated fibre.

15.6 DYEING NYLON WITH DISPERSE DYES

The use of acid dyes on nylon to produce dyeings of good washing fastness invariably involves the risk of barré because dyes of poor migration do not evenly dye filaments with chemical and physical variations. This risk is almost absent when using disperse dyes. The consequence of their good migration during dyeing, however, is poor to moderate wet fastness, especially in heavy shades. The dyeing of nylon with disperse dyes is therefore limited mainly to pale shades for lingerie fabrics and sheer hose that do not require repeated or severe washing. Disperse
DISPERSE DYES

dyes on nylon are also more sensitive to fading by ozone and nitrogen dioxide. They are, however, economical and easy to apply.

Most nylon filaments are oriented by drawing but both undrawn and partially oriented yarns can be dyed with disperse dyes. With increasing draw ratio, the increased polymer chain orientation decreases the rate of dyeing (decreased fibre accessibility) but not the extent of dye absorption at equilibrium (unchanged fibre availability). It is only at the very high draw ratios typical of strong industrial yarns that the equilibrium dye absorption decreases. Uniform drawing of filaments is essential. Accessibility differences in dyeing can be minimised provided that the selected dyes and conditions are conducive to levelling. Disperse dyes on nylon are much better in this respect than acid dyes.

15.6.1 Preparation of nylon for dyeing

The preparation of nylon goods for dyeing usually involves scouring with a detergent and soda ash (sodium carbonate) solution at 70 °C. This removes any soluble sizing material, lubricants, and spin finishes that might hinder access of the dye solution to the fibre surface.

Heat setting of nylon fabrics has already been discussed (Section 13.9.3). This process may be performed before or after dyeing, preferably the latter. It causes variations in dye substantivity and may be non-uniform, leading to unlevel dyeings. Dry heat setting in hot air decreases the rate of dyeing of nylon 6.6 and 6 with both acid and disperse dyes, but setting in steam increases their dyeing rates. Steam setting, however, decreases the wet fastness of dyeings with disperse dyes, particularly if setting is carried out after dyeing. The more open fibre structure resulting from heat setting in steam allows easier dye desorption during washing of the dyed material. If it is necessary to bleach nylon that has become yellow from over-vigorous heat setting in dry air, peracetic acid or sodium chlorite solution can be used.

15.6.2 Application of disperse dyes to nylon

The disperse dye is pasted in warm water and the dispersion slowly diluted. Hot water and concentrated dispersant favour the formation of large dye particles. The concentrated dispersion is then strained into the dyebath that usually also contains additional dispersing agent. The bath is gradually heated and dyeing continued at the boil. The disperse dyes used for nylon are usually level dying.
The exhaustion rates of individual disperse dyes on nylon are not overly high. They do vary from dye to dye so that selection of compatible dyes is necessary.

Although some dyes have good migration and build up well, deep shades are rarely dyed with disperse dyes because of their inferior washing fastness. Many of the simple disperse dyes developed for dyeing acetate at 85 °C are not particularly fast to heat and can sublime from the nylon during processes such as boarding. This is a form of heat setting used to stabilise the shape of ladies' hosiery after dyeing. Dyes of higher fastness to sublimation are invariably of greater molecular size and therefore have lower rates of dyeing. The usual temperature for rapid dyeing disperse dyes on nylon is 85–100 °C. If slow dyeing heat fast dyes are used, dyeing under pressure at up to 120 °C may be useful. The disperse dyes used for dyeing nylon will also colour spandex (segmented polyurethane) filaments in stretch hose but the washing fastness is only fair. As for cellulose acetates, blacks are produced by diazotisation of a disperse dye containing a primary amino group and coupling of the generated diazonium ion with a suitable coupling component.

Simple dyeing tests evaluate the migration, temperature range characteristics and dyeing rates of disperse dyes on nylon [3]. With rapid dyeing dyes, the dyeing rate increases with increasing temperature but the equilibrium exhaustion decreases. The more rapid dyeing dyes also migrate better and tend to be less temperature sensitive so that dyeings at different temperatures are close in shade.

Nylon 6 is more amorphous and has a lower melting point than nylon 6.6. Disperse dyes dye nylon 6 using the same method as for nylon 6.6. Dyeing is usually faster than for nylon 6.6 under the same conditions and the dyes will usually show better migration. This usually means that the washing fastness is somewhat lower on nylon 6. One advantage of nylon 6 is that heat setting using hot air or steam is at lower temperatures than for nylon 6.6.

15.7 DYEING POLYESTER WITH DISPERSE DYES

15.7.1 The problem of dyeing polyester
Polyester fibres are essentially undyeable below 70–80 °C, leaving only a 20–30 °C range for increasing the dyeing rate before reaching the boiling temperature. At any temperature, the rate of dyeing of polyester with a given disperse dye is very much lower than for cellulose acetate or nylon fibres. The rate of diffusion of disperse dyes into the polyester below 100 °C is so low that dyeing at the boil does not give reasonable exhaustion. The rate of dyeing is higher for


dyes of small molecular size that have higher diffusion coefficients. Dyeing is faster when using fibre swelling agents called carriers to improve the fibre accessibility, or when dyeing at higher temperatures above 100 °C to increase the dye diffusion rate.

Fibres of the most common polyester, polyethylene terephthalate (PET or PES), are quite crystalline and very hydrophobic. Hot water does not swell them and large dye molecules do not easily penetrate into the fibre interior. Polyesters have no ionic groups and are dyed almost exclusively with disperse dyes. The better diffusion at the boil of low molecular weight dyes results in moderate migration during dyeing but then the washing fastness is only fair. Many of the more recent disperse dyes are specifically for dyeing polyester. These are of higher molecular weight to provide adequate fastness to sublimation during heat treatments. Some of these produce a reasonable depth of shade by dyeing at the boil. Most, however, require higher dyeing temperatures or carriers for satisfactory results. Dyeings of polyester with disperse dyes have good light fastness. This does not always correlate with the light fastness on other fibres such as cellulose diacetate.

The disperse dyes provide a full range of colours with adequate to good build-up on PET fibres. Uneven filament texturising or heat setting can lead to barré but higher dyeing temperatures, or addition of some carrier, will promote migration to minimise this. Again, a full black requires aftertreatment of the dyeing by diazotisation of an amino disperse dye and coupling with a suitable component, often BON acid. Concurrent dyeing with a mixture of the amino disperse dye and dispersed BON acid, followed by treatment with sodium nitrite and hydrochloric acid, is a common procedure. Some blacks are mixtures of dull yellow, red and blue dyes.

15.7.2 Preparation for batch dyeing of polyester

Loose PET fibre is usually dyed directly without pretreatment because emulsification of the small amount of superficial processing chemicals is easy. This is not the case for knitted goods, that may contain additional oil or wax, or for woven goods with sized warp yarns. Typical preparation involves scouring with 2 g l⁻¹ each of soda ash (sodium carbonate) and an anionic detergent at 50 °C. Addition of an organic solvent may be useful if wax or much knitting oil is present. Because the dispersants present in the dyes or added to the dyebath are usually anionic, removal of any cationic auxiliary chemicals in the spin finish is necessary before dyeing.
When fabrics of PET are heated in water at the boil there is often considerable shrinkage as the tensions in the filaments relax. The shrinkage may be even greater at higher temperatures. Fabrics of PET can be dry heat set at 200–225 °C for 30–60 s. Alternatively, steam heat setting at 130–140 °C for several minutes is also possible but can cause a loss of strength due to some hydrolysis of the polyester. Steam setting provides dimensional stability in boiling water but, for stability to ironing, higher setting temperatures must be used.

After heat setting in air under conditions of free shrinkage, the dye exhaustion first decreases and then increases with increasing setting temperature. The minimum exhaustion occurs after setting at around 160–190 °C (Figure 15.5). If applied tension prevents fabric shrinkage during heat setting, the dye uptake/temperature profile is similar to that under conditions of free shrinkage, but with higher uptake values. Heat setting changes the morphology of the polyester fibres. The effects on the dyeing rate and the extent of dyeing are variable depending upon the particular dye, the setting temperature and heating time, and the tension imposed.

![Figure 15.5 Influence of hot air setting temperature on dye uptake of polyester at dyeing temperatures of 100 and 130 °C](image)

**15.7.3 Carrier dyeing**

There are obvious advantages to dyeing polyester fibres with disperse dyes at the boil, within a reasonable time, particularly for medium to deep shades. Unfortunately, this is only feasible with the most simple disperse dyes of low molecular weight. The more complex disperse dyes, which have the required
fastness to heat setting and hot pressing and pleating, only diffuse extremely slowly into polyester fibres at 100 °C. One solution to this problem that avoids dyeing under pressure at temperatures above 100 °C is dyeing in the presence of a carrier.

A carrier is an organic compound, dissolved or emulsified in the dyebath, which increases the rate of dyeing. Carriers allow dyeing of even deep shades at the boil within a reasonable dyeing time. Common polyester dyeing carriers include butyl benzate, methyl naphthalene, dichlorobenzene, diphenyl and o-phenylphenol, the latter two being the most popular. These are all aromatic compounds of low water solubility, so they are present in the dyebath as an emulsion. Typical commercial carriers therefore usually already contain anionic emulsifying agents.

A typical carrier dyeing procedure involves running the goods in the bath 60 °C and adding dilute dispersing agent, emulsified carrier and lastly the dispersed dyes. The temperature is then gradually raised to the boil and dyeing continued at this temperature. The sodium salt of o-phenylphenol is soluble in water and acidification liberates the insoluble phenol once dyeing has started. This ensures a fine emulsion. The usual effect of the carrier is to increase both the rate of dyeing and the dyebath exhaustion, but not in all cases. Benzoic acid, for example, decreases the exhaustion at equilibrium but increases the dyeing rate. Its effect is probably simply to increase the water solubility of the dye in the bath. Methylene biphthalene gives the best colour yield with many dyes at the lowest cost.

During dyeing in certain machines, such as winches and jigs, a steam-volatile carrier may condense as a concentrated emulsion on colder internal surfaces. Drops of this condensed emulsion that fall onto the goods produce darker dyed spots. This can also occur if the carrier emulsion is not stable during dyeing and drops deposit on the fabric.

The actual mechanism by which a carrier accelerates dyeing has been widely debated and probably depends upon the carrier used. The polyester fibres absorb the carrier and swell. This swelling can impede liquor flow in packages causing unevenness. The overall effect seems to be a lowering of the polymer glass transition temperature (Tg), thus promoting polymer chain movements and creating free volume. This speeds up the diffusion of the dye into the fibres. Alternatively, the carrier may form a liquid film around the surface of the fibre in which the dye is very soluble, thus increasing the rate of transfer into the fibre.

Incorporation of other monomers into the polyester also decreases the Tg value. Comonomers such as suberic acid (1,8-octanedioic acid) increase the polymer chain flexibility and give polyester fibres that can be dyed at 100 °C without a carrier. However, a polyester fibre, dyeable at the boil with disperse dyes of good
heat fastness, without use of a carrier, and without any modification of the properties of regular PET, remains somewhat elusive. The new polytrimethylene terephthalate fibre (Corterra) is a step in response to this problem. After dyeing, scouring of the goods removes most of the carrier. Any carrier remaining in the fibres invariably decreases the light fastness of the dyeing. Residual amounts of carrier vaporise during subsequent drying of the scoured fabric. Some carriers are quite volatile, have unpleasant odours and are toxic. Polyester dyeing carriers pose a serious environmental threat if present in the effluent or exhausted air. One of the easiest ways to eliminate o-phenylphenol is by mild alkaline washing, which dissolves this weakly acidic phenol.

Carrier dyeing has steadily declined since the development of suitable machines for dyeing polyester under pressure at temperatures around 130 °C. Carriers are still used in some garment and small commission dyehouses where high temperature pressurised dyeing machines are not available. The quantity of carrier required in dyeing decreases with increase in the dyeing temperature. The use of a small amount of carrier is useful for dyeing at 110–120 °C. Dyeing at this lower temperature leaches less oligomer from the polymer and better preserves the fibre bulk and elasticity. Carriers are also useful for dyeing wool/polyester blends when there is a risk of damaging the wool at dyeing temperatures above 100 °C. In this case, the carrier also helps to prevent cross-staining of the wool by the disperse dye.

Partial stripping of the colour of PET materials dyed with disperse dyes is usually possible by treatment with a solution of dyeing carrier or retarding agent at high temperature under pressure. Oxidative and reductive stripping are also possible but are likely to involve some undesirable effects upon the fabric handle or appearance. Prolonged treatment of polyester materials with alkaline solutions causes surface hydrolysis of ester groups and loss of weight. Once the surface has been degraded it is difficult to obtain the originally anticipated appearance.

15.7.4 High temperature pressure dyeing of polyester

As we have seen, the dyeing of polyester with disperse dyes at the boil is slow because of the low rate of diffusion of the dyes into the fibre. The activation energy for diffusion is quite high and raising the dyeing temperature from 100 to 130 °C considerably increases the rate of dye diffusion. Dyeing at this higher temperature under pressure, without a carrier, considerably increases the rate of dyeing and gives better coverage of filament irregularities because of the improved
migration of the dyes. Dyeing is then also possible using higher molecular weight
dyes, whose rates of diffusion at 100 °C are unacceptable. This permits
production of dyeings with better fastness to light and to sublimation during
permanent pleating. For those fabrics and yarns that lose bulk when dyed at
130 °C, dyeing at a lower temperature (110—120 °C) in the presence of some
carrier is preferred.

The dyebath is usually set at pH 4.5—5.5 using either ammonium sulphate plus
formic or acetic acid, or acetic acid alone. The weakly acidic dyebath ensures
neutralisation of any residual alkali from scouring, which readily catalyses
hydrolysis of the polyester, decreasing its strength. Reduction of some azo disperse
dyes can occur during dyeing at high temperatures, while others undergo
hydrolysis. These effects are minimal when dyeing in weakly acidic solution.

The concentrated dye dispersion is added to the bath at 50—60 °C. The bath
may already contain a small amount of dispersant (0.5 g l⁻¹), if required.
Lubricants in the dyebath avoid possible crack and crease marks in dyeing fabric in
jet machines. The temperature of the bath is then slowly raised to 130 °C. A
typical heating rate is about at 1.5 °C min⁻¹. Dyeing continues at the maximum
temperature for about 60 min.

Each particular dyeing will have an optimum temperature/time profile, depending
upon the type of goods, the machine being used and the dyes in the formula. A set
of generalised dyeing conditions is used, however, provided that the dyebath
exhaustion, the colour uniformity, and the shade reproducibility from batch to batch
are acceptable. Dyeing times can be kept to a minimum by temperature control of
the rate of exhaustion that gives uniform dye absorption. In this way, long levelling
times at the maximum dyeing temperature are not needed. The dyeing time should
be long enough for the dyes with the lowest dyeing rate to approach equilibrium.
Disperse dyes do not generally interfere with each other and prevent their mutual
absorption but they do have different dyeing rates. The dyeing rate is always higher
at low dye concentrations in the bath. Some disperse dyes are deliberate mixtures of
dyes of the same or different hue and about the same dyeing rate. They give fairly
rapid dyeing because each dye is only present at low concentration.

PET fibre contains 1—4% of oligomers, mainly a cyclic trimer of ethylene
terephthalate. It has a high melting point and is soluble enough in hot water
during pressure dyeing to be extracted from the fibre. The oligomers also migrate
to the PET fibre surface during steam heat setting, and to a lesser extent on dry
setting. The oligomer can often be seen as a white dusty powder on the surface of
the goods, or on the dyeing machine walls. Hydrolysis of oligomer deposits on machine surfaces by heating with an alkaline solution under pressure provides effective cleaning. Precipitated oligomer can cause nucleation of disperse dye crystal formation leading to coloured specks on the goods. In addition, oligomer particles reduce the rate of liquor flow through yarn packages and cause filament friction in spinning. The oligomer is much less soluble at temperatures below the boil. To avoid its precipitation once dyeing is concluded, the dyebath is drained at as high a temperature as possible, even above 100 °C. This can lead to problems in dyeing woven goods in rope form in jet machines since creases and crack marks can form while the polymer is still somewhat plastic. In these cases, draining at a lower temperature is necessary and the dyer must depend to a greater extent upon the subsequent rinsing and reduction clearing process to remove oligomer residues.

During dyeing, particularly of deep shades, there will invariably be some dye particles that adhere to the fibre surfaces, or are retained by yarns without penetration into the fibre. These mechanically held particles result in decreased fastness to washing, rubbing, sublimation and dry cleaning. Their presence also tends to dull the shade. Superficial dye particles can be detected by rinsing a dyed sample with a little cold acetone. This will dissolve the surface particles and produces a coloured solution but it does not remove any dye from within the PET fibres. For pale shades, scouring removes deposits of surface dye. Deep dyeings with disperse dyes on PET fibres will invariably require treatment by reduction clearing to give satisfactory crocking fastness. This process involves treatment with alkaline hydros (2 g l⁻¹ NaOH, 2 g l⁻¹ Na₂S₂O₄·2H₂O) and a surfactant (1 g l⁻¹) for 20 min at 70 °C. The reduction clearing temperature is well below the glass transition temperature of the polyester. The ionic compounds do not therefore penetrate into the fibres and only reduce the dye on the fibre surface. The reduction of azo disperse dyes is relatively easy but anthraquinone derivatives are more difficult to remove. The latter must be reduced and washed off the surface before re-oxidation occurs. The less soluble oxidised form is then held in suspension by the surfactant in the bath.

Some disperse dyes, originally from ICI (now available through DyStar), allow easy clearing of surface deposits. These are methyl esters of carboxylic acids that readily hydrolyse under alkaline conditions. The free carboxylic acids formed by hydrolysis are soluble in alkaline solution (Scheme 15.3). This allows clearing without a reducing agent. Since the alkali does not penetrate into the PET fibre at the clearing temperature, the dye within the fibres is unaffected.
Microfibres of PET for production of fabrics with a lush handle are a fairly recent development. Microfibres have a fineness of less than 1.0 dtex per filament, an arbitrarily chosen value. Normal PET filaments are in the range 2–5 dtex. The introduction of microfibres has created a number of dyeing problems. Firstly, microfibres require more dye than regular denier fibres to achieve the same depth of shade (Section 10.4.4). The concentration of dye (% owf) required to achieve a given depth of shade is usually assumed to be inversely proportional to the square root of the filament fineness:

\[ \frac{C_M}{C_R} = \frac{r_R}{r_M} \frac{\sqrt{dtx_R}}{\sqrt{dtx_M}} \]  

In this equation, \( C_M \) and \( C_R \) are the required concentrations of dye in the microfibre and regular denier fibre respectively, \( r_M \) and \( r_R \) the respective filament radii, and \( dtx_M \) and \( dtx_R \) the respective filament fineness. This approximate relationship predicts that a 0.5 dtex microfibre will require \((2.5/0.5)^{1/2}\) or about 2.2 times as much dye in the fibre to give the same depth of shade as a 2.5 dtex filament. It only applies, however, when the regular and microfibres being considered are identical in all other properties. In fact, it is the dyeing rate that should be proportional to the available filament specific surface area \((m^2 \text{ g}^{-1})\) and therefore inversely proportional to the filament radius and to the square root of the filament decitex. The value of the diffusion coefficient of the dye in the fibre does not change when the filaments are finer.

Secondly, because of the more rapid uptake of dye by microfibres, level dyeing requires greater control. The greater specific surface area of microfibres also means...
that dye desorption during washing is more rapid and the washing fastness is less than for fabrics made of conventional filaments. Dyed microfibre fabrics also have lower fastness to light at equal apparent depth. In addition, the closeness of microfibre packing in yarns makes wetting and yarn penetration difficult. Nevertheless, the lush handle and special surface effects that are possible for fabrics made of microfibres have ensured their success.

15.7.6 The Thermosol process

The Thermosol process is a continuous dyeing process introduced by Du Pont in 1949. A dispersion of the disperse dyes is padded onto the polyester fabric. The material is then dried using a hot flue air dryer or by infrared radiation, the latter usually giving much less migration of the dye. The use of a migration inhibitor in the pad bath is usually recommended. Even then, dye migration during drying of materials of 100% polyester is difficult to eliminate and such materials tend to dye more deeply on the yarn surface. Final drying of the padded material takes place using heated cylinders. Section 10.5 discusses padding and migration in continuous dyeing.

The dry fabric is then heated in air, or by contact with a hot metal surface, to a temperature in the range of 190–220°C for 1–2 min. In hot air, at least 50% of the time is for heating the polyester to the maximum temperature. The specific conditions depend on the type of equipment, the dyes and the fabric. As the fabric approaches the maximum temperature, the disperse dyes begin to sublime and the polyester fibres absorb their vapours. (Sublimation is the transformation of a solid directly into a gas without forming the liquid phase. A common example is the evaporation of ice on a cold day.)

At about 200°C, sublimation of the solid dye, transfer of its vapour into the fibres, and penetration into the fibres by diffusion are all quite rapid. Commercial disperse dyes for the Thermosol process are usually classified according to their ease of transfer by sublimation. This is related to the their fastness to heat in hot pressing and pleating. It is imperative that as much of the vaporised dye as possible be absorbed by the polyester fibres. If the rate of sublimation is too low, dye particles will remain in the fibre matrix and the colour yield will be low. When the rate of sublimation is too high, the dye vapour builds up faster than it can be absorbed by the polyester and escapes from the proximity of the fibres, usually depositing on the machine walls. The temperature and time of heating must
therefore be carefully controlled to provide the appropriate rate of sublimation and the optimum colour yield.

Despite the simple dyeing mechanism, there are a number of technical problems that can result in inferior dyeings. The fabric must initially contain a uniform distribution of dye particles if the final dyeing is to be level. Therefore, uniform dispersion and padding are crucial. Migration must be minimised, particularly if it leads to more dye on one face of the fabric than the other. During the sublimation stage, it is essential to provide conditions that allow a balance between the rate of dye vaporisation and absorption of the vapour by the fibres. The Thermosol process is widely used for narrow fabrics of 100% PET such as ribbons and belts. The vapour dyeing technique also applies to transfer printing, discussed in Section 23.8.

The Thermosol method is popular for dyeing the polyester component in cotton/polyester fabrics [5]. In this case, the absorbent cotton fibres in the fabric hold almost all the initial dye dispersion padded onto the material. This helps to reduce dye migration during drying. During subsequent heating, the dye vapours and transfers from the cotton into the polyester fibres. Since two types of fibres are being continuously dyed, each with a separate fixation step, the dyeing ranges for cotton/polyester materials tend to be very complex (Figure 10.7). Both the dyes for the polyester and for the cotton are initially padded onto the fabric. The polyester is dyed in the Thermosol unit. After additional padding of the cooled fabric with a solution of the other required chemicals for dyeing the cotton, it passes through a steamer. This promotes diffusion and fixation of dyes on the cotton. The second pad contains NaOH and salt solution for dyeing with reactive dyes (Chapter 16), NaOH and Na2S2O4 for vat dyes, NaS or NaSH for sulphur dyes (Chapter 17), and simply salt solution for direct dyes (Chapter 14). A thorough washing of the dyed fabric completes the process. This includes rinsing, an oxidation step in the case of vat and sulphur dyes, soaping to remove surface colour and final rinsing.

15.7.7 Classification of disperse dyes for polyester

Disperse dyes for a compound shade on polyester can have quite incompatible dyeing properties. The SDC classification of disperse dyes is based on migration ability during exhaust dyeing, colour build-up, sensitivity to changes in temperature and the rate of dyeing [2]. This type of dye is often classified on the basis of dyeing rate and sublimation fastness, particularly for polyester dyeing. These two properties are a function of
molecular weight and the number of polar groups in the dye molecule. Table 15.2 shows the most common classification. It applies to the dyeing of acetate, of polyester with or without carrier, and of polyester/cotton, but is somewhat arbitrary.

Most dyeing and fastness properties change gradually with increase in molecular size. Small dye molecules with low polarity are levelling, rapid dyeing dyes with poor heat resistance. These are called low energy disperse dyes. More polar, higher molecular weight dyes have low dyeing rates, poor migration during dyeing but good heat and sublimation fastness. These constitute the high energy disperse dyes. The development of disperse dyes of improved sublimation fastness required dye molecules with relatively polar and hydrophilic substituents to reduce their vapour pressure at high temperatures. This promotes somewhat higher solubility in water but the increase in molecular size reduces the dyeing rate at a given temperature. The high energy disperse dyes are those requiring a higher Thermosol temperature. The light fastness does not depend on the molecular size.

Dyes in a mixture are usually selected from the same energy class. Build-up of the colour on shade requires that the dyes all have about the same dyeing rate. Testing of dye recipes is essential because many disperse dyes, even dyes of the same dyeing group, are incompatible in mixtures. This is true even though they may have the same dyeing rates and build-up properties when tested separately. The dye manufacturers provide considerable information assisting the dyer to select appropriate dyes for a given application.

### Table 15.2 Classification of disperse dyes for polyester

<table>
<thead>
<tr>
<th>Classification</th>
<th>Molecular weight</th>
<th>Polarity</th>
<th>Dyeing rate</th>
<th>Sublimation fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low energy</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Medium energy</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Moderate</td>
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<tr>
<td>High energy</td>
<td>High</td>
<td>High</td>
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<td>High</td>
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15.7.8 Dyeing modified polyesters

A variety of modified polyester fibres are available that can be dyed with disperse dyes, and other types of dyes, at temperatures not exceeding 100 °C. The so-
called non-carrier types can be dyed with disperse dyes at the boil, although very deep shades may require a small amount of carrier. The basic polymer is PET but contains a comonomer with a more flexible molecular chain such as suberic acid (1,8-octanedicarboxylic acid). The polymer has a more open molecular structure, a lower \( T_g \) and dye penetration is therefore easier. The new polytrimethylene terephthalate fibre (Corterra) also has a lower \( T_g \) than PET and can be dyed with disperse dyes in a bath at the boil under normal pressure.

Polyester modified to have anionic sites contains comonomers such as 5-sulpho-isophthalic acid (Section 4.3.3). It is readily dyed with disperse dyes, and with cationic dyes. These types of modified polymer are also more easily hydrolysed. Therefore, during processing, the pH of solutions must not be excessive and the maximum pressure dyeing temperature should not be above 120 °C. Additions of Glauber’s salt to the dyebath protect basic dyeable polyester fibres from hydrolysis. Modified polyester fibres are also more sensitive to heat setting before dyeing, the maximum setting temperature being around 180 °C.

Cationic dyes require some acetic acid in the dyebath and dyeing at pH of 4-5 at 100–120 °C is typical. The brightly coloured dyeings with cationic dyes have good fastness to washing and light. Combinations of regular and basic dyeable polyester fibres can be dyed with mixtures of cationic and disperse dyes to produce two colour effects. The carpet industry is a major outlet for this type of fibre. The new polyester fibre poly(trimethylene terephthalate) produced from terephthalic acid and 1,3-propanediol, rather than the usual 1,2-ethanediol, is also initially intended for use in carpets.

15.8 DYEING OF OTHER SYNTHETIC FIBRES

Acrylic fibres can be dyed with disperse dyes but the extent of dye absorption is limited and the colour build-up is poor. Dyeing at temperatures above 100 °C to solve this problem is not possible because of the plasticity and excessive shrinkage of this type of fibre. Disperse dyes on acrylics have good levelling and good fastness properties. They give dyeings of better washing fastness on acrylic fibres than on nylon and there is no gas fume fading problem. Acrylic materials are quite plastic at high dyeing temperatures and rapid cooling of the dyebath may set creases in the fabric. On the other hand, slow cooling may deposit non-absorbed dye particles on the fabric surface and scouring may be needed after dyeing to clean the surface. Unfortunately, the application of disperse dyes on acrylic fibres is limited to rather pale shades.
Segmented polyurethane elastomeric fibres (Lycra) are finding increasing application in a wide variety of products in which they are blended with other fibres. This type of fibre is sensitive to alkaline hydrolysis and severe alkaline scouring must be avoided. Lycra is frequently found in nylon fabrics and both fibres will absorb disperse dyes but not necessarily to the same extent. Like nylon, polyurethanes can also be dyed with acid dyes.

Polypropylene fibres have little substantivity for any of the usual types of dye. These fibres are extremely hydrophobic. They will absorb a limited amount of disperse dyes to give pale dyeings of poor washing fastness. Dye penetration is difficult because the polymer is very crystalline, has a compact structure, and has no polar groups for interaction with dye molecules.

Several chapters in the book 'The Dyeing of Synthetic Polymer Fibres', edited by Nunn [6], provide somewhat dated but still useful information on dyeing synthetic fibres with disperse dyes.

REFERENCES
2. SDC Committee on Disperse Dyes, J.S.D.C., 80 (1964) 237.
3. SDC Committee on Disperse Dyes, J.S.D.C., 89 (1972) 296.
CHAPTER 16

Reactive dyes

16.1 THE DEVELOPMENT OF REACTIVE DYES

Dyeings of cotton with direct dyes (Chapter 14) have rather poor washing fastness because only weak polar and dispersion forces bind the dye molecules to the cellulose polymer chains. Direct dye molecules can therefore easily diffuse out of the cotton during washing. The best fastness to washing requires precipitating an insoluble pigment and mechanically trapping it within the cotton fibres. This type of dyeing process with vat and azoic dyes is, however, much more complicated than direct dyeing (Chapters 17 and 19).

The idea of immobilising a dye molecule by covalent bond formation with reactive groups in a fibre originated in the early 1900s. Various chemicals were found that reacted with the hydroxyl groups of cellulose and eventually converted into coloured cellulose derivatives. The rather forceful reaction conditions for this led to the false conclusion that cellulose was a relatively unreactive polymer. Possibly because of this, a number of dyes now known to be capable of covalent bond formation with groups in wool and cotton were not initially considered as fibre-reactive dyes, despite the good fastness to washing of their dyeings.

In 1955, Rattee and Stephen, working for ICI in England, developed a procedure for dyeing cotton with fibre-reactive dyes containing dichlorotriazine groups. They established that dyeing cotton with these dyes under mild alkaline conditions resulted in a reactive chlorine atom on the triazine ring being substituted by an oxygen atom from a cellulose hydroxyl group (Figure 1.3). This is shown in Scheme 16.1 where Cell–OH is the cellulose with a reactive hydroxyl group and Dye–Cl is the dye with its reactive chlorine atom. Cell–O–Dye is the dye linked to the cellulose by a covalent bond. The role of the alkali is to cause acidic dissociation of some of the hydroxyl groups in the cellulose, and it is the cellulosate ion (Cell–O−) that reacts with the dye.

\[
\begin{align*}
\text{Cell–OH} + \text{HO}^+ & \rightarrow \text{Cell–O}^- + \text{H}_2\text{O} \\
\text{Cell–O}^- + \text{Dye–Cl} & \rightarrow \text{Cell–O–Dye} + \text{Cl}^-
\end{align*}
\]

Scheme 16.1
The dyeings had very good fastness to washing. The only way the fixed dye can bleed from the cotton is after hydrolysis of the covalent bond between the dye and the cellulose. This requires conditions more forceful than those met with in ordinary washing in hot water. Within about five years of this important development, all the major dyestuff manufacturers were marketing reactive dyes for cotton, and also for wool. Reactive dyes, particularly those used for dyeing cotton, have become one of the major classes of dye because of their good washing fastness, their bright shades and their versatile batch and continuous dyeing methods.

16.2 REACTIVE DYES FOR COTTON [1]

16.2.1 Structures of reactive dyes for cotton

The molecular structures of reactive dyes resemble those of acrid and simple direct cotton dyes, but with an added reactive group. Typical structures include the azo (Figure 16.1, (a)), anthraquinone (Figure 16.1, (b)), triphenodioxazine (1, in Figure 16.2) or copper phthalocyanine chromophores (2). The key structural

![Figure 16.1](image-url)

Figure 16.1 Nucleophilic substitution (a) and addition reactions (b) of reactive dyes with cellulose.
features of a reactive dye are the chromophoric system, the sulphonate groups for water solubility, the reactive group, and the bridging group that attaches the reactive group either directly to the chromophore or to some other part of the dye molecule. Each of these structural features can influence the dyeing and fastness properties.

Most commercial ranges of reactive dyes have a complete gamut of colours, many of which are particularly bright. Reactive dyes often have quite simple structures that can be synthesised with a minimum of coloured isomers and biproducts that tend to dull the shade of the more complex polyazo direct dyes. Some colours are difficult to obtain with simple chromophores. Dark blue and navy reactive dyes are often rather dull copper complexes of azo dyes and the production of bright green reactive dyes remains a problem.

A wide range of possible fibre-reactive groups has been examined and evaluated by the dyestuff manufacturers. The final choices for commercial dyes are limited by a number of constraints. The reactive group must exhibit adequate reactivity towards cotton, but be of lower reactivity towards water that can deactivate it by hydrolysis. The hydrolysis of the dye’s reactive group is similar to its reaction with cellulose but involves a hydroxyl ion in water rather than a cellulosate ion in the

Figure 16.2 Triphenodioxazine (1) and copper phthalocyanine reactive dyes (2)
fibre (Scheme 16.2). In addition, the dye–fibre bond, once formed, should have adequate stability to withstand repeated washing. Other factors involved are the ease of manufacture, the dye stability during storage and the cost of the final reactive dye.

Scheme 16.2

Reactive groups are of two main types:

1. Those reacting with cellulose by nucleophilic substitution of a labile chlorine, fluorine, methyl sulphone or nicotinyl leaving group activated by an adjacent nitrogen atom in a heterocyclic ring (Figure 16.1, (a));
2. Those reacting with cellulose by nucleophilic addition to a carbon–carbon double bond, usually activated by an adjacent electron-attracting sulphone group. This type of vinyl sulphone group is usually generated in the dyebath by elimination of sulphate ion from a 2-sulphatoethylsulphone precursor group with alkali (Figure 16.1, (b)).

Although many of the early reactive dyes had only one reactive group in the dyestuff molecule, many of the newer reactive dyes are bifunctional with two or more identical or different reactive groups (Section 16.4). Figure 16.3 shows some typical fibre-reactive groups and the commonly used abbreviations for these groups. Dyes with nicotinyltriazine reactive groups (NT) will react with cotton on heating under neutral conditions.

16.2.2 Basic principle of dyeing cotton with reactive dyes

The relatively simple procedure for batch dyeing of cotton materials with reactive dyes, developed by Rattee and Stephen, is still used for all types of reactive dyes irrespective of their particular reactive group. Dyeing is commenced in neutral solution, often in the presence of salt to promote exhaustion of the dye onto the cotton. During this period, the dye does not react with the fibre and migration from fibre to fibre is possible. Then, an appropriate alkali is added to the dyebath to increase its pH. This initiates the desired dye–fibre reaction. The hydroxyl groups in cellulose are weakly acidic and absorption of hydroxide ions causes some dissociation, forming cellulosate ions. It is these that react with the dye by
nucleophilic addition or substitution (Figure 16.1). In general, the lower the reactivity of the reactive group of the dye towards the alkaline cellulose, the higher the final dyeing temperature and the higher the final pH of the dyebath.

Unfortunately, under the alkaline conditions necessary for the dye–fibre reaction, hydroxide ions also react with the reactive group of the dye in much the same manner as the cellulosate ion. This produces the hydrolysed dye, which is incapable of reaction with the fibre. Hydrolysis of the dye is slower than the reaction with the alkaline cotton but it is significant and reduces the efficiency of the fixation process. After dyeing, any unreacted and hydrolysed dye present in the cotton must be removed by thorough washing. This ensures that no colour will bleed from the cotton on subsequent washing during use. The higher the substantivity of the reactive dye for the cotton, the more difficult it is to wash out unfixed dye from the material. Many of the first reactive dyes had quite simple molecular structures and low substantivity for cotton, so that the removal of hydrolysed dye from the material by washing was relatively easy. This is not necessarily true for reactive dyes of more complicated molecular structure.

Figure 16.3 Typical fibre-reactive groups in commercial reactive dyes
16.2.3 Dye reactivity, application and storage

The reactive groups of the various types of reactive dye have different chemical structures and show a wide range of reactivities. They were originally divided into cold- and hot-dyeing types but many current ranges would be better called warm-dyeing. The most reactive types, such as DCT reactive dyes (Figure 16.3), are applied at lower temperatures (20–40 °C) and only require a weak alkali such as NaHCO₃ or Na₂CO₃ for fixation. The less reactive types, such as MCT dyes, need higher temperatures (80–90 °C) and stronger alkalis such as Na₂CO₃ plus NaOH. Many dyestuff manufacturers now market several ranges of reactive dyes for cotton, each with its own particular recommended dyeing procedure. Table 16.1 gives some typical examples based on the type of reactive grouping.

<table>
<thead>
<tr>
<th>Reactive group</th>
<th>Commercial name</th>
<th>Reactivity</th>
<th>Exhaust dyeing temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCT</td>
<td>Procion MX (BASF)</td>
<td>high</td>
<td>25–40</td>
</tr>
<tr>
<td>MCT</td>
<td>Procion H (BASF)</td>
<td>low</td>
<td>80–85</td>
</tr>
<tr>
<td></td>
<td>Basilen (BASF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cibacron (Ciba)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFT</td>
<td>Cibacron F (Ciba)</td>
<td>moderate</td>
<td>40–60</td>
</tr>
<tr>
<td>DCG</td>
<td>Levalux E (DyStar)</td>
<td>low</td>
<td>50–70</td>
</tr>
<tr>
<td>DFCP</td>
<td>Drimarene K (Clariant)</td>
<td>moderate to high</td>
<td>30–50</td>
</tr>
<tr>
<td></td>
<td>Levalux E-A (DyStar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VS</td>
<td>Remazol (DyStar)</td>
<td>moderate</td>
<td>40–60</td>
</tr>
<tr>
<td>TCP</td>
<td>Drimarene X (Clariant)</td>
<td>low</td>
<td>80–95</td>
</tr>
<tr>
<td>NT</td>
<td>Kayacelon React (Nippon Kayaku)</td>
<td>moderate to high</td>
<td>100–130</td>
</tr>
</tbody>
</table>

* React under neutral conditions

Because most reactive dyes are prone to hydrolysis, their handling and use requires care. Most are readily water-soluble and the dye solution is prepared in the usual way by pasting with water and then adding more water. The temperature of the water used depends upon the ease of solution and the reactivity of the dye. Hot water is not recommended for dissolving dyes of high reactivity, because of the risk of hydrolysis of the reactive group, but is suitable for the less reactive types. Once the dye solution has been prepared, it cannot be stored for later use without some risk of hydrolysis of the reactive group. This decreases its fixation ability and is a particular problem with the most reactive types of dye. Dyes containing a 2-sulphatoethylsulphone group, however, can be dissolved in neutral
water at the boil without risk of hydrolysis. Formation of the reactive vinyl sulphone group (Figure 16.1, (b)) requires the addition of alkali.

Reactive dyes for printing are usually dyes of low reactivity so that the print paste can be stored for some time at room temperature without deterioration from hydrolysis of the reactive group. Reactive dyes of low reactivity and relatively high substantivity are valuable for dyeing using long (high) liquor ratios, using a winch machine. Exhaust dyeing with low reactivity dyes at the higher temperatures required for fixation allows better penetration of the dyes into the cotton fibres. For continuous dyeing with reactive dyes stabilised liquid forms are available. Although these contain special pH buffers and stabilisers to minimise the hydrolysis reaction, they only have a limited shelf life.

Many commercial reactive dyes are dusty powders but all physical forms must be handled with care. These dyes react with the amino groups in proteins in the skin and on mucous surfaces. Inhalation of the dust is dangerous and a dust mask is obligatory during handling. Reactive dye powders and grains are sometimes hygroscopic and drums must be carefully re-sealed. Most reactive dyes have a limited storage period, after which some deterioration can be expected. Standardisation and comparison of reactive dye powders or liquids cannot be done by the usual spectrophotometric procedure involving absorbance measurements of standard solutions (Section 24.2). Both the reactive dye and its hydrolysed form are equally coloured, but only the former is capable of reaction with the cellulose during dyeing. Therefore, dyeings must be prepared and their colours compared with standard dyeings. Chromatographic techniques usually allow separation and quantitative measurement of the relative amounts of a reactive dye and its hydrolysis product in a given dye (Section 24.5).

16.2.4 Fastness properties of reactive dyes on cellulosic fibres
In general, reactive dyes on cellulosic fibres give dyeings with good to very good fastness to washing and other wet processes. Apparent inferior fastness to washing is usually because of incomplete removal of unreacted and hydrolysed dye from the material by washing after dyeing. The presence of unfixed dye can easily be tested for by hot pressing a wet sample of the dyeing sandwiched between two pieces of dry white cotton. Colour transfer to the white material indicates the presence of unfixed dye in the dyeing. It is more likely to be a problem for deep dyeings.

The use of reactive dyes is growing rapidly, faster than for any other dye application class. This is because these dyes also give dyeings of moderate to good
light fastness, allow relatively simple and diverse dyeing methods and are available in a range of bright colours. They have contributed significantly to the decline of direct cotton dyes. Their fastness properties, though generally good, do not match those of pigmented cotton dyed with vat dyes. In particular, the fastness to bleaching by chlorine, and to a lesser extent by peroxides present in modern household detergents, is often only moderate.

16.2.5 Evidence for covalent bond formation with cellulose
The good fastness to washing of dyeings with reactive dyes on cellulosic fibres is a consequence of the stable covalent bond formed between the dye’s reactive group and the cellulose polymer. There is considerable evidence to support the formation of this dye–fibre bond. Dyeings are resistant to colour stripping with hot aqueous pyridine, a solvent that effectively removes direct dyes from cotton. Dyeings of cotton obtained with bifunctional dyes often exhibit reduced swelling and decreased solubility in cuprammonium solution. A dye molecule with two reactive groups crosslinking two different cellulose chains would explain this. If the colour of a dyeing obtained with an azo reactive dye is destroyed by chemical reduction with alkaline sodium hydrosulphite, which cleaves the azo dye into two primary aromatic amines, the amine remaining attached to the cellulose can be diazotised and coupled with an appropriate phenol to reform a coloured fibre. Finally, bacterial degradation of reactive dyed cotton that depolymerises the cellulose, but avoids breaking the dye–fibre bond, gives coloured products containing the original dye still bonded to glucose.

16.3 BATCH DYEING OF COTTON WITH REACTIVE DYES

16.3.1 Preparation for dyeing
Level well-penetrated dyeings require careful preparation of the material. All sizing compounds capable of reacting with the dye, such as starch or polyvinyl alcohol, must be removed from the material and any traces of residual alkali must be uniformly neutralised. Good alkali boiling to remove wax is essential for goods to be dyed with cold-dyeing reactive dyes because penetration of the dyes into the fibres is much more difficult at lower dyeing temperatures. Reactive dyes often give such bright colours that bleaching may not be necessary. Once size has been removed, grey cotton goods can sometimes be simultaneously scoured and dyed using hot-dyeing reactive dyes and an efficient detergent. Because of the
sensitivity to bleaching by chlorine of some reactive dyes, over-chlorinated water must be avoided or treated with a reducing agent such as sodium bisulphite or thiosulphate.

16.3.2 The three-step exhaust dyeing process

A typical exhaust dyeing process for cellulosic materials using reactive dyes has three distinct phases:

(1) the initial exhaustion phase. Dyeing is started in neutral solution so that there is little likelihood of the dye reacting with the cellulose. During this stage of dyeing, some reactive dye will be absorbed by the fibres, the amount depending upon its substantivity. This dye is capable of migration to promote level dyeing. Sodium chloride or sulphate will often be present initially or be added gradually to the dyebath during this phase to promote exhaustion. The temperature of the dyebath may also be gradually increased to aid penetration of dye into the fibres and to assist migration;

(2) the fixation phase. After the initial exhaustion phase, the pH of the dyebath is increased by complete or gradual addition of the appropriate type and amount of alkali. This causes dissociation of some of the hydroxyl groups in the cellulose and the nucleophilic cellulosate ions begin to react with the dye. The fixation process then results in additional dye absorption, to re-establish the dyeing equilibrium. Dye absorption from solution and reaction with the fibre then progress until no further dye is taken up. Figure 16.4 illustrates the variations of the dyebath exhaustion and the extent of fixation during a typical exhaust dyeing;

(3) the post-dyeing washing. The rinsed dyeing contains dye bonded to the cellulose, absorbed but unreacted dye, as well as hydrolysed dye. There will also be residual alkali and salt. The latter are relatively easy to remove by successive rinsing in cold and then warm water. As much unfixed dye as possible must be washed out of the dyeing. If this is not done, desorption of this dye during washing by the consumer can cause staining of other materials in the wash. Some unfixed dye is eliminated during the initial rinsing that removes salt and alkali. Thorough washing of the dyeing using a boiling detergent solution (soaping) eliminates the remainder. The dyeing is then finally rinsed in warm water. Soaping must often be repeated for deep dyeings or the residual unfixed dye must be complexed with a cationic agent (Section 16.3.5).
Reactive dyes are very versatile and allow a variety of different approaches for controlling the rate of dye absorption, and the degree of dye migration and dye fixation. Salt additions, temperature variations and alkali additions are used alone or in combination to control the dyeing process. Reactive dyes have recently been classified as [1]:

(1) alkali-controllable dyes, which have relatively high reactivity and only moderate substantivity. They are applied at relatively low temperatures and level dyeing requires careful control of the addition of alkali to initiate the fixation stage. Examples include DCT, DFCP and VS reactive dyes;

(2) salt-controllable dyes. These are dyes of relatively low reactivity towards cotton under alkaline conditions and therefore the dyeing temperature will be as high as 80 °C. They have appreciable substantivity and level dyeing requires careful addition of salt to promote exhaustion. Examples in this class include TCE, MCT as well as MFT reactive dyes;

(3) temperature-controllable dyes, which undergo fixation at high temperatures even under neutral conditions. The NT dyes are in this class.

The objective of dyeing with reactive dyes is to obtain the maximum degree of reaction between the dye and fibre, with a minimum of dye lost through hydrolysis of the reactive group, and under conditions where the colour of the dyed material is uniform. Dyes with different reactive groups and molecular structures require different amounts of added salt to obtain economical exhaustion. Some reactive dyes, including most of the oldest, have relatively simple molecular structures and quite low substantivity for cellulosic fibres. They need high concentrations of salt, up to 100 g l⁻¹, particularly when dyeing deep shades or using long (high) liquor ratios. At such high salt concentrations, there is always a risk of dye precipitation, particularly when dyeing at low temperatures. Although Glauber’s salt is more expensive than sodium chloride, it is preferred for dyes prone to aggregation at low dyeing temperatures, such as the turquoise copper phthalocyanine reactive dyes. The advantage of dyes with low substantivity is that they diffuse easily in the fibres and are easy to wash out of the material after dyeing. The higher the substantivity of the reactive dye for the cellulose, the higher the bath exhaustion and the greater the chance of reaction with the fibre, but the greater the difficulty of removing unfixed dye during the final washing.

For dyeings with vinyl sulphone dyes, it is advisable to ensure that the residual alkali has been removed or neutralised prior to soaping since hydroxide ion can catalyse hydrolysis of the ether type dye–fibre bond and result in additional colour
bleeding from the goods (Scheme 16.3). Dyeings with vinyl sulphone dyes have
maximum dye–fibre bond stability at around pH 4.5, whereas the corresponding
value for dyes based on halogenated nitrogen heterocycles is 6–7. The latter type
have dye–fibre bonds that are more sensitive to acid-catalysed hydrolysis.

\[
\text{Dye–O–Cell} + H_2O \rightarrow \text{Dye–OH} + \text{Cell–OH}
\]

Scheme 16.3

The dyeing temperature and the nature and concentration of the alkali required
are determined by the reactivity of the dye, its degree of sulphonation and its
substantivity. For tightly twisted yarns and compact woven fabrics, the migration
phase of dyeing with low reactivity dyes can be carried out at higher temperatures
up to 120 °C to promote initial migration and penetration into the textile. This is
well above the later fixation temperature in the presence of alkali (80 °C). Azo
copper complex dyes will not withstand these conditions and tend to loose the
copper ion. For a higher fixation temperature, reaction with the fibre occurs at
lower pH, using a weaker alkali or a lower concentration of the usual alkali. As is
the case for salt addition, a deeper shade, or a higher liquor ratio, will require more
alkali. It is not usual to exceed a dyebath pH of 11, even with the less reactive dyes
since this invariably leads to lower colour yields because of dye hydrolysis.

The effects of increasing the dyeing pH during the fixation phase are complex
but usually involve an increase in the rates of reaction of the dye with the fibre
and with hydroxide ion. For polysulphonated dyes, one effect of dyeing at pH
above 11 is the decrease in substantivity of the dye for the increasingly anionic
dissociated cellulose. The greater negative charge of more cellulose ions repels
the dye anions. In fact, some dyes actually desorb from the fibre into the dyebath
when the alkali is added at the start of the fixation stage giving a sudden decrease
in the degree of exhaustion at that point. In addition, with polysulphonated dyes,
the substantivity decreases as dye fixation proceeds because the cotton contains
more and more bound anionic dye molecules, which also repel the unfixed dye.
These effects can be counteracted by an increased concentration of salt in the
dyebath.

Dye hydrolysis is more pronounced and exhaustion is less at high liquor ratios.
Therefore, in winch dyeing, reactive dyes of higher substantivity are preferred. In
recent years, there has been a considerable shift to dyeing with reactive dyes on
machines with low liquor ratios. This gives more efficient dyeing, and reduces the
consumption of dyes, salt and alkali. Figures 16.4 and 16.5 allow comparison of
typical dyeing procedures in which the alkali for fixation is added to the dyebath in
one portion (Figure 16.4), or gradually using a variable speed metering pump (Figure
16.5). For the latter method, the rates of exhaustion and fixation are relatively
constant.

![Figure 16.4](image1)

**Figure 16.4** Dyebath exhaustion (solid line) and dye fixation (dotted line) as a function of
time during dyeing with low (a) and high substantivity (b) reactive dyes; alkali addition at
30 min.

![Figure 16.5](image2)

**Figure 16.5** (See also Figure 10.3) Dyebath exhaustion (solid line) and dye fixation (dotted
line) as a function of time during dyeing with a reactive dye, with metering of the alkali
solution.
Viscose fibres give higher fixation and exhaustion of reactive dyes than cotton. In fact, for identical conditions, exhaustion and fixation increase in the order: cotton, mercerised cotton, viscose. The washing fastness of reactive dyes on viscose is also somewhat better than on cotton. Because of the ease of swelling of viscose, the dyeing pH and temperature for a given dye may be different than for cotton, particularly if dye penetration may be problematic.

The so-called 'all-in' dyeing method has the advantage that no additions are required during dyeing and is therefore the most rapid dyeing method. The goods are run in the filled machine with all the added salt and alkali and the reactive dye solution then added over 10–15 min. The rate of dye fixation is controlled by gradual heating. The starting temperature and heating gradient must be well controlled for good colour reproducibility. The NT reactive dyes, mixed with disperse dyes, are useful for dyeing cotton/polyester at 130 °C under neutral conditions.

16.3.3 Washing-off of unfixed reactive dyes

Removal of hydrolysed and unreacted dye from the goods is a vital step after dyeing. The amount of unfixed dye remaining in a cotton fabric dyed with reactive dyes may have to be less than 0.002% owf. Although bleeding out of such a small amount during subsequent washing by the consumer will not significantly alter the depth of shade of the material, it can visibly stain adjacent white goods. This is usually unacceptable.

Both batch and continuous washing processes involve three stages. Initially, the goods are rinsed in cold and warm water. This is a dilution stage aimed at removing as much salt and alkali from the goods as possible. This makes the next soaping stage much more efficient since at lower electrolyte concentrations the substantivity of the dye is less, making its desorption easier. The final stage is again a warm rinsing stage to dilute the final dye solution adhering to the fibres to the point that the amount of unfixed dye carried over to the final drying is minimal. This residual quantity of dye will be deposited on the fibre surface on evaporation of the water during drying and will be easily removed by later washing. Obviously, the amount must be as small as possible.

The entire washing operation involves achieving a compromise between the effectiveness of removal of unfixed dye and the cost of the large volumes of water used, including the heating costs. Low liquor ratio washing saves water but gives less dilution of the washing liquors. Some dyeing machines allow overflow rinsing.
but this consumes much more water. For winch and jig dyeing machines operating
at atmospheric pressure, it is not possible to carry out soaping at temperatures
above 90 °C, even when they are closed. For any given dyeing machine, each
rinsing and washing stage should be evaluated and a general satisfactory washing
protocol established. One point requires particular attention. After each stage in
the washing cycle, dye transfers from one bath to the next, in the solution retained
by the fabric. This transfer must be as low as possible. This means that machines
should be completely drained between stages, and wash boxes in continuous
washing must have effective mangles to squeeze out as much solution as possible
from the fabric leaving the box.

16.3.4 Dyeing compatibility of reactive dyes
Ideally, reactive dyes in a mixture should all exhaust and react with the fibre at
about the same rate so that the shade builds up on tone. Dyes from different
ranges, with different reactive groups, can rarely be used together because of their
different dyeing characteristics and reactivities. It is therefore usual to mix dyes
with the same type of reactive group having about the same substantivity. Since
there is often a great deal of uncertainty about the particular type of reactive group
in a given reactive dye, dye selection must often be from one particular
manufacturer’s dye range and based on his recommendations.

Compatible dyeing behaviour is a function of all the process variables and
requires careful control of the dyeing temperature, salt and alkali concentrations,
the dyeing time and the liquor ratio. Once the dye has reacted with the cellulose,
it is completely immobilised and cannot migrate. Control of the process variables
determines whether a given shade will be reproducible from batch to batch. When
dyeing with mixtures of reactive dyes, shading is usually possible by addition of low
substantivity dyes to the alkaline bath. The dyebath may be partially drained and
re-filled with cold water, the solution of shading dyes added and the bath then re-
heated if necessary. Further additions of salt or alkali are often not required.

16.3.5 Problems in dyeing with reactive dyes
One of the major problems in exhaust dyeing with many reactive dyes is the rather
low level of fixation, particularly when dyeing using a high liquor ratio. Often less
than 70% of the original dye reacts with the fibre. This results in appreciable dye
concentrations in the dyehouse effluent. This environmental problem is
compounded if high salt concentrations are also present. Newer ranges of reactive dyes, particularly those with more than one reactive group that give higher fixation, have attempted to address the problem of colour in the effluent with some success. Several dye manufacturers now offer reactive dyes requiring smaller amounts of salt for exhaust dyeing. The use of less salt demands a higher degree of dye substantivity but this impedes efficient washing-off after dyeing. This is counteracted by using dyes that give good fixation.

It is possible to eliminate colour bleeding and staining of adjacent material when an article is first washed during use by aftertreating the dyeing with a cationic fixative. This type of product reacts with any residual unfixed anionic dye, forming an organic salt of greatly increased molecular size and of lower water solubility and diffusion rate. Such cationic fixatives lack permanence on repeated washing but this is not a problem since the unfixed dye will have gradually been removed by that point. They may, however, reduce the light fastness of the dyeing and are therefore more suitable for treatment of deep shades. Such an aftertreatment is not a remedy for inefficient washing-off of unfixed dye. If the amount of unfixed dye remaining in the goods is significant there is a risk of the precipitated dye–auxiliary complex rubbing off, particularly on wet abrasion.

Dyeings with a few red DCT reactive dyes on cotton are prone to increased colour bleeding because of hydrolysis of the dye–fibre bond. Unreacted chlorine atoms in the dye’s reactive group may hydrolyse under warm humid storage conditions, liberating HCl. This catalyses the hydrolysis of the dye–fibre bond. The colour bleeding can be counteracted by adding a polyamine to the final rinse water that reacts with any residual reactive chlorine atoms in the bound dye.

As for direct dyes, some reactive dyes may be reduced by the cellulose when dyeing at high temperatures in presence of alkali. This can lead to a significant decrease in colour strength when dyeing viscose with reactive dyes, for example. Addition of the mild oxidant m-nitrobenzenesulphonate usually prevents this.

There is always a risk of anionic reactive dyes being precipitated by calcium, magnesium or heavy metal ions in the water supply, or of the formation of insoluble hydroxides of these metals under the alkaline dyeing conditions. To avoid these problems, a limited addition of a polyphosphate sequestering agent may be required. EDTA should be avoided with azo copper complex dyes since demetallisation can occur with a dramatic change in hue. The copper in the stable copper phthalocyanine dyes is, however, unaffected by EDTA.

Finally, stripping reactive dyes is by no means easy. Hydrolysis of the dye–fibre bond using hot acetic acid solution, followed by good washing, may give partial
stripping. Complete colour discharge is often possible by treatment with alkaline sodium hydrosulphite solution followed by hypochlorite. Before such treatments, complexed metals should be removed using EDTA.

16.4 BIFUNCTIONAL REACTIVE DYES

Cl Reactive Black 5 (3, in Figure 16.6) has long been known to give a high degree of fixation, because with two potential vinyl sulphone reactive groups there is an increased probability of reaction with the fibre. Many of the new reactive dyes are bifunctional with identical or different reactive groupings in the dye molecule. Adding more reactive groups to a given chromophore increases the molecular weight but decreases the colour per unit weight of dye since the reactive groups

![Chemical Structures](image)

**Figure 16.6** Bifunctional reactive dyes: Cl Reactive Black 5 (3, Remazol Black B, DyStar); Procion H-E dye (4); MCT/VS type (5) used in the Sumifix Supra dyes (Sumilo).
are not part of the chromophoric system. This problem can be partly overcome, for example by linking together two DCT dyes with a suitable diamine to give a dye with two MCT groups, as in the Procion H-E dyes (4). This increase in molecular size usually results in an increase in substantivity that is of value for exhaust dyeing with higher liquor ratios but which can impede washing-off of unfixed dye after dyeing.

Bifunctional dyes with two reactive groups of different reactivity towards the cotton, which have different optimal fixation conditions, give a more uniform degree of fixation over a wider range of dyeing temperature and fixation pH than dyes containing two identical groups. Therefore, process control does not need to be so stringent. These types of reactive dyes give quite high fixation yields and thus less colour in the dyehouse effluent. Other important types of bifunctional reactive dyes include the MFTVS type (Cibacron C, Ciba) and the MCT- VS type (5) used in the Sumifix Supra dyes (Sumito). The Kayacelon React range of dyes (Nippon Kayaku) are also bifunctional reactive dyes, having two NT reactive groups in each dye molecule.

16.5 CONTINUOUS DYEING PROCESSES FOR COTTON

16.5.1 Introduction
The first step in continuous dyeing involves padding dye solution onto full-width woven fabric. This is a very low liquor ratio dyeing method that gives the expected improved exhaustion and fixation, under appropriate conditions. The very rapid fixation (< 60 s) at high temperatures that is possible in fully continuous dyeing gives high productivity for long runs of a given colour. On the other hand, the slow dye fixation achieved during storage of a roll of impregnated fabric at room temperature (4–24 h) results in better dye diffusion and penetration into the fibres (Section 16.5.2).

There are several problems that must be considered in continuous dyeing with reactive dyes:
(1) dyes of low substantivity are desirable to avoid preferential dye absorption during padding and the initial colour tailing that it causes (Section 10.5.2). This is less of a problem with reactive dyes than with direct or sulphur dyes, which have greater molecular size and therefore higher substantivity. Tailing caused by dyes with different substantivities can result in an initial drift of the
hue. These effects can be minimised by adjusting the initial concentration and composition of the feed solution of dyes;

(2) when using pre-prepared alkaline solutions of reactive dyes, reasonable stability of the dye/alkali mixture is essential. Any premature hydrolysis of the dye’s reactive group in the reservoir or pad bath will result in a loss of fixed colour. This can be controlled using a dye solution with the lowest possible pH. When the pre-mixed dye and alkali solution is not sufficiently stable, and it cannot be stored in a reservoir without an unacceptable degree of hydrolysis, metering pumps deliver known flow rates of separate neutral dye and alkali solutions, which are mixed just before entering the pad bath. A constant padding temperature must be maintained for an invariant colour yield. Having two separate padding stages solves the problem of dyes that are very susceptible to hydrolysis. In this case, a neutral solution of the reactive dye is first padded onto the goods and, after drying, the alkali solution is padded on just before the fixation stage. In some cases, a wet-on-wet two-stage padding is possible;

(3) when dyeing very deep shades, concentrated dye solutions are required. Dye solutions containing more than 50 g l–1 of dye may be needed if the solution is to be applied at relatively low wet pick-up to avoid migration problems during drying and excessive drying costs. For example, a 4.2% owf dyeing requires a dye solution of 70 g l–1 at 60% solution pick-up. The desired concentration may exceed the dye solubility, particularly if an appreciable amount of electrolyte is present. Low dye solubility can be improved by addition of relatively large amounts of urea (100 g l–1). Urea helps to break up dye aggregates by hydrogen bonding to the dye molecules. It is sprinkled onto the cooled dye solution before the salt and stirred in to dissolve it;

(4) after padding with a neutral solution of reactive dyes, the fabric will often be dried. This must be done under conditions that minimise migration of unfixed dye to the fibre and yarn surfaces. Heating of the wet material must be as uniform as possible to avoid side-to-centre and back-to-face colour differences due to migration. The padding solution will usually contain salt as an anti-migrant and also a thickening agent such as sodium alginate (1 g l–1);

(5) in fully continuous operations, the final rinsing and soaping of goods dyed with reactive dyes are also carried out continuously. These processes take place at high fabric speeds and the goods are only in contact with the washing solutions for short periods of time. Therefore, washing-off is usually less
effective than washing in a dyeing machine where longer washing times and fresh baths are more easily arranged. The usual eight box washing range allows three dilution rinses, 2–3 soapings and 2–3 final rinses. For initial rinsing, static baths, into which no water flows, are more economical. The concentration of salts accumulating in the static bath must not become so high that soaping efficiency falls because the unfixed dye is too substantive. It is common to have a counter-current flow of water through each short series of boxes before the last bath overflows to the drain. The flow rate of water must provide the required degree of dilution and of unfixed dye removal so that the final fabric has acceptable fastness properties.

16.5.2 Pad–batch dyeing

Pad–batch dyeing involves padding the fabric with a pre-mixed alkaline solution of the reactive dyes and then winding up the impregnated fabric on a suitable roller. Fixation occurs during storage of the batched fabric at ambient temperature. The dye and alkali solutions are usually mixed just before padding using metering pumps to maintain the correct ratio. A 4:1 dye-to-alkali solution volume ratio is very common. During storage, the roller may be continuously rotated at low speed to avoid drainage of the internal liquid within the batch.

Obviously, the dyes must have adequate reactivity under the batching conditions to give good fixation within about 24 h. The more reactive dyes give effective fixation within 2–6 h. To avoid evaporation from the exposed surfaces and edges of the roll, the fabric is stitched to a somewhat wider end-cloth that is padded and finally wrapped around the entire wet roll before it is covered with a plastic film. When padding on solutions with relatively high pH values, which are necessary to promote fixation of less reactive dyes, there is always a risk of carbon dioxide absorption on the selvages of the material even when these have been accurately wound edge-on-edge. This decreases the solution pH since hydroxide ion is converted into carbonate ion. The rate of fixation is then lowered. The effect of this only becomes apparent after the final washing when the selvages appear paler than the rest of the material. In pad–batch dyeing with Remazol dyes (DyStar), the buffering action of sodium metasilicate added to the NaOH solution is claimed to virtually eliminate the problem of paler selvages from carbon dioxide absorption.

After storing, the batch of material must be thoroughly washed to remove unfixed dye and chemicals. If the fabric is wound on a perforated beam, this can
be carried out using a beam dyeing machine. Alternatively, other types of batch dyeing machine or a continuous washing range can be used.

This semi-continuous pad–batch process offers many advantages and is now widely used in place of jig dyeing. Provided that space is available for storage of the fabric batches, the energy requirements for dyeing are minimal and the process is more economic than batch dyeing for lots in the 1000–10,000 m range. The fabric also often has a better handle and surface appearance because it is not continuously circulating around in a winch or jet dyeing machine. The relatively slow fixation process results in good dye penetration into the fibres.

### 16.5.3 Pad–heat dyeing

The pad–dry process is only suitable for reactive dyes with fairly high reactivity. For dyes of lower reactivity, the dried fabric must be baked to promote further fixation. In pad–dry dyeing, the fabric is first padded with a dye solution containing sodium bicarbonate. During drying, bicarbonate is converted into carbonate, which gives a higher pH and more effective fixation (Scheme 16.4). The dye solution also contains a high concentration of urea (100 g l\(^{-1}\)). This helps the cotton fibres retain water during drying, possibly provides a fluid medium for dye diffusion in the fibres at low water contents, and increases dye solubility. Unfortunately, all this urea is removed on washing after fixation and poses a pollution problem. Urea is a source of nitrogen nutrients for algal growth.

\[ 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

**Scheme 16.4**

In the pad–dry process, typically with the reactive DCT dyes, the drying rate is fairly low and the cotton retains at least 18% water. If the fabric is fully dried, the reaction ceases so the drying time must be longer than that for effective reaction with the cotton. Typical conditions are 2–5 min at 105 °C in a hot flue or on heated cylinders at 105 °C. The fabric temperature will not exceed 70 °C. The initial drying cylinders may be much cooler to avoid excessively high initial evaporation rates and migration.

The pad–dry–bake process is suitable for less reactive dyes such as MCT dyes. Today, this type of process is used mainly in combination with the application of
disperse dyes to cotton/polyester materials using the Thermosol process (Section 15.7.6). Baking temperatures of 200–220 °C for 1 min are typical but may be lower (150–170 °C) if only cotton is being dyed. When dyeing deep shades, the degree of fixation is usually lower. The fabric tends to yellow at high baking temperatures and this can influence the hue of pale shades. The most popular variant of this process for dyeing cotton/polyester fabrics is the neutral thermofix method. For this a solution of reactive and disperse dyes containing sodium bicarbonate is padded onto the cotton/polyester using dicyanodiamide, $\text{H}_2\text{N}−\text{C(=NH)}−\text{NH}−\text{CN}$, in place of urea. Both fibres are dyed simultaneously by heating at around 200 °C for 1 min. As in all reactive dyeing processes, the final step is a thorough washing to remove unixed dyes.

16.5.4 Pad–steam dyeing

In this process, the goods are padded with a solution containing the reactive dyes, salt and the appropriate alkali. Again only selected dyes are suitable and the manufacturer’s recommendations should be followed. The hot humid conditions during steaming tend to cause excessive hydrolysis of the reactive group and thus lower the colour yield. In dyeing terry towelling and other pile fabrics, a two-stage wet-on-wet padding version of this process is used to avoid an intermediate drying step. The towelling is first padded with a neutral solution of the reactive dyes, and then with a solution of the alkali prior to steaming. In wet-on-wet padding, the pick-up of the second solution should be sufficiently high to give good fixation, and colour bleeding into the second pad bath must not be excessive.

16.5.5 Pad–dry–pad–steam dyeing

This is the predominant fully continuous reactive dyeing process. The fabric is padded with a neutral solution of the reactive dyes, dried and then padded with the alkali solution containing salt before steaming. The dye solution is quite stable, because there is no alkali present in the dyebath. Some salt or anti-migrant agent helps to minimise migration of the dyes to the yarn surfaces during the initial stages of drying. The intermediate drying ensures a uniform and high pick-up of the alkaline salt solution and minimises bleeding of dye into the chemical pad. After drying, the fabric must be cooled on cold cylinders to avoid heating the chemical pad solution. Since sodium carbonate is difficult to dissolve in salt solution, sodium hydroxide is the preferred alkali. There are a number of
variations of this type of process and it is also incorporated into the continuous dyeing of cotton/polyester materials using disperse and reactive dyes (Sections 10.5.3 and 23.7.3).

16.5.6 Application of reactive dyes and finishing chemicals

Reactive dyes may be applied to undyed cellulosic materials at the same time as the usual crease-resist and durable press resin finishes, thus combining dyeing and finishing into one step. During curing, when the methylolamino groups (–NHCH₂OH) of the polyfunctional finishing chemicals react with hydroxyl groups in the cellulose (Section 25.3.1), the dye reacts with free amino groups in these agents rather than with the fibre. Since the dye is fixed to the finishing agent, the fastness properties of the final dyeing depend on the permanence of the finish.

16.6 REACTIVE DYES FOR WOOL [2]

16.6.1 Introduction

The somewhat late development of fibre-reactive dyes was partly caused by a lack of appreciation of the considerable reactivity of fibres made of cellulose or proteins. A number of dyes developed for wool with 2-sulphatoethylsulphone or chloroacetylamino groups were not immediately recognised as reactive dyes. In fact, the development of reactive dyes really started with the introduction of the Procion dyes for cotton by ICI in 1955.

Despite the many possible reactive groups in dyes capable of covalent bond formation with nucleophilic groups in wool, only a limited number of types of reactive dye have been commercially successful. Figure 16.7 shows the major types of reactive groups. The dye chromophores are essentially those used for cotton reactive dyes.

The most important reactive groups in wool are all nucleophilic and are found mainly in the side-chains of amino acid residues. They are, in order of decreasing reactivity, thiol (the –SH of cysteine), amino (–NH– and –NH₂ of say histidine and lysine) and hydroxyl groups (–OH of serine or tyrosine). Difluoro-chloropyrimidines undergo aromatic nucleophilic substitution of one or both fluorine atoms, the fluorine between the two nitrogen atoms being the most reactive. Bromoacrylamido groups are stable in boiling water at pH 7 and react by
Figure 16.7 Types of reactive dyes for wool

Dye—NH—CO—C=CH₂

Bromoacrylamido

Dye—SO₂CH₂CH₂OSO₃Na

Sulphatoethyl sulphone*

Dye—SO₂CH₂CH₂SO₂Na

N-Methyltaurine ethyl sulphone*

(*give vinyl sulphone)

Figure 16.8 Reactions of bromoacrylamido reactive dyes with wool

Dye—NHCOCH₂Cl + Wool—SH → Wool—S—CH₂CONH—Dye + HCl

Scheme 16.5
both nucleophilic addition to the double bond and nucleophilic substitution of the bromine atom (Figure 16.8). They can form a three-membered aziridine ring that can react further with the protein resulting in a new crosslink. The actual dyes are probably dibromopropionamides, which eliminate HBr on dissolving in hot water. Methyltaurine-ethylsulphones and 2-sulphatoethylsulphones form the vinyl sulphone reactive group relatively slowly at pH 5–6 (1 h at the boil). This allows some levelling during dyeing before the vinyl sulphone dye reacts with the wool and becomes immobilised. This is useful in hank and winch dyeing where the liquor/goods interchange is less favourable. In fact, all commercial reactive dyes for wool have absorption rates that are greater than the rate of reaction with the fibre to allow some migration. Chloroacetylamino groups (–NHCOCH₂Cl) react by an S₂N₂ mechanism (Scheme 16.5).

Wool reactive dyes are applied like acid dyes in weakly acidic solution. The degree of exhaustion and fixation are usually very high and clearing of unfixed dye from the goods may only be needed for deep shades. Reactive dyes for wool tend to be unlevel dyeing and are prone to give skittery dyeings. They are used more on loose fibre and slubbing than on piece goods, where they accentuate fibre non-uniformity and poor, uneven fabric preparation. A number of amphoteric or weakly cationic auxiliary products are available to assist level dyeing. Despite their good light fastness and very good washing fastness, they are still not widely used, partly because of their high cost. Red to maroon shades are very popular but there are no black reactive dyes available that can match the chrome blacks on wool.

16.6.2 Batch dyeing of wool with reactive dyes

Reactive dyes are usually applied to wool at pH 5–6 using ammonium salts, and acetic acid as required. At higher pH values, exhaustion is too low, and at lower values rapid dye uptake gives unlevel dyeings. Slightly higher pH values are used for dyeing paler shades (pH 5.5-6.0) and lower values (pH 5.0-5.5) for deep shades. Reactive dyes often give quite good exhaustion at temperatures below the boil but the dyeing temperature will eventually be raised to 100 °C to ensure that reaction with the wool is as complete as possible. Some procedures recommend a holding stage at an intermediate temperature of 65–70 °C for 15–20 min to allow the dye to migrate before it reacts with the wool.

Because of their tendency to give unlevel, skittery dyeings, reactive dyes are usually applied to wool in the presence of proprietary levelling agents. These are often amphoteric, having both cationic and anionic groups in the molecule. In contrast to most levelling agents, which decrease the dyeing rate, the auxiliary
products for dyeing wool with reactive dyes accelerate dyeing. The anionic dye complexes with the cationic site in the auxiliary product but the remaining anionic site provides substantivity for the wool surface. The bulky dye–auxiliary complex exhausts well onto the fibre surface at relatively low temperature, better than the dye alone, but cannot penetrate into the fibres. The complex breaks down as the dyeing temperature increases so that the smaller liberated dye molecules can then absorb into the wool. The use of such products avoids unlevel, skittery dyeings and provides better compatibility of dye mixtures.

Deeply dyed goods must be aftertreated to remove unfixed dye so as to give the best wet fastness. This is particularly important to ensure that there is no staining of adjacent undyed material during washing. After dyeing, the material can be washed at 80 °C for about 15 min using a dilute ammonia solution at pH 8.0–8.5, and then rinsed in water with a little acetic acid. To avoid any alkali damage to the wool, washing can be done with hexamine (hexamethylenetetramine from formaldehyde and ammonia) at pH 6.5, or with sodium bicarbonate. Certain proprietary chemicals can be added to the dyebath on completion of dyeing and their hydrolysis increases the bath pH to around 7. For example, hydrolysis of sodium trichloroacetate gives chloroform, carbon dioxide, both of which are volatile, and sodium hydroxide (Scheme 16.6). The actual colour removed may consist of unreacted dye, hydrolysed dye and products of the reaction of the dye with soluble wool hydrolysis products such as ammonia and hydrogen sulphide or amino acids.

\[
\text{CCL}_3\cdot\text{CO}_2\text{Na} + \text{H}_2\text{O} \rightarrow \text{HCCl}_3 + \text{CO}_2 + \text{NaOH}
\]

Shrink-proof wool, which has been treated with resins in the Hercosett process, remains cationic on the surface and gives rapid uptake of reactive dyes. The usual auxiliary levelling agents may be less effective in this case. The deposited resin protects the wool from damage and the best fastness results for deep shades are obtained by dyeing at 110 °C for 30 min.

Wool dyed in deep shades with reactive dyes is better protected from damage during dyeing. A number of explanations for this have been proposed. These involve protein chain crosslinking, reaction with thiol groups that interferes with
the reformation of disulphide links, and reaction with non-keratinous proteins in the cell membrane complex and endocuticle.

### 16.6.3 Semi-continuous methods for reactive dyes on wool

Reactive dyes can be applied to both wool cloth and tops by padding followed by batching for 24–72 h. A thickener is added to the pad liquor to give a high solution pick-up. High concentrations of urea are used and the solution also contains sodium metabisulphite. Urea breaks up dye aggregates and sodium metabisulphite reduces cystine crosslinks in the wool, generating more reactive thiol groups. This promotes higher and more uniform fixation. The combination of urea and metabisulphite (Na2S2O5, gives NaHSO3 on hydrolysis) in the padding solution results in greater fibre swelling and better dye penetration. Dyes with activated double bonds react with bisulphite by nucleophilic addition and are converted into non-reactive forms so the pad solutions are not particularly stable. The pad–batch method can be used with reactive dyes normally applied to cotton, such as Procion MX and Drimarene K dyes. The dyed goods are then treated with dilute ammonia, rinsed and neutralised with acetic acid to remove unfixed dye. This type of process is very economical and reduces fibre damage.

### REFERENCES

CHAPTER 17

Vat dyes

17.1 INTRODUCTION

This chapter discusses vat, indigo and sulphur dyes together because their use in dyeing involves the same principles. Vat dyes are one of the oldest types of dye. Vat dyes in particular give dyeings on cellulosic fibres with the best overall fastness properties. Because of the popularity of blue jeans, Indigo is still one of the most important of all dyes in present use. Natural Indigo was obtained by extraction from leaves, by fermentation in wooden vats, the origin of the term 'vatting'. Today, Indigo is synthesised from manufactured intermediates. Its application involves reduction to the water-soluble leuco compound, dyeing the cotton and re-oxidation of the leuco dye in the fibres to the insoluble pigment, the three basics steps involved in vat dyeing (Figure 1.4).

Vat dyes are water-insoluble pigments. They are called dyes because chemical reduction in alkaline solution converts the pigment into a water-soluble leuco form with substantivity for cotton. The vat pigment and the leuco compound often have quite different colours – blue and pale yellow in the case of Indigo – so the progress of the reduction is often easy to observe. After dyeing with the leuco compound, the pigment is regenerated in the dyed cotton by oxidation. The overall process therefore involves three key steps:
(1) reduction of the pigment to the soluble leuco compound, a process called vatting;
(2) absorption of the leuco compound by the cotton during dyeing;
(3) oxidation of the absorbed leuco compound in the cotton, reforming the insoluble pigment inside the fibres.

The use of strongly alkaline solutions (pH 12–14) for vatting and dyeing limits the use of most vat dyes to cellulosic fibres.

17.2 CHEMICAL CONSTITUTION OF QUINONE VAT DYES

In the case of Indigo, vatting involves reduction of a pair of conjugated carbonyl groups (Figure 1.4). For most vat dyes, these carbonyl groups are present in an
anthraquinone or polycyclic quinone. The parent quinone is an insoluble pigment (1, in Figure 17.1). The leuco compound is the sodium salt of the diphenol or hydroquinone formed by reduction in NaOH solution (2). It is reasonably soluble in water, substantive to cotton and easy to oxidise back to the red pigment. Reduction is carried out in strongly alkaline solution to avoid formation of the vat acid (3). This is the free diphenol formed by protonation of the anionic leuco derivative. The vat acid is insoluble in water; has no substantivity for cotton and is more difficult to oxidise.

Quinone vat dyes are usually either anthraquinone derivatives (1) or polycyclic quinones. Indanthrone (4), the first quinone vat dye, was discovered by accident during attempts to make an Indigo-type derivative from 2-aminoanthraquinone. The structures of most vat dyes are often quite complex and have no ionic groups. Many of the polycyclic derivatives have no attached substituents, but a few have halogen, hydroxyl, methoxyl or amide groups. The more complex dyes may have several reducible quinone groups (Figure 17.2).

The molecular structure of a vat dye influences the water solubility, substantivity and rate of diffusion into the cotton of the leuco compound used in dyeing. A classification of quinone vat dyes according to dyeing characteristics is more useful for our purpose and will be given later in this chapter.

Figure 17.1 CI Vat Red 42 (1); leuco compound formed by reduction (2); vat acid formed by protonation of the anionic leuco derivative (3); CI Vat Blue 4 (4)
17.3 THE REDUCTION OF QUINONE VAT DYES

17.3.1 Vat dye dispersions

Quinone vat dyes are available as fine powders or grains, and as liquid dispersions or pastes. The insoluble pigment is extensively milled with dispersants such as sodium lignosulphonates to produce very small particles (Section 15.3). Typically, at least 50% of the particles will have diameters less than 1 μm. All forms must disperse readily in water and any aggregates of particles must easily break up to give a fine, stable dispersion. The rate of reduction to the leuco form is usually faster, the finer the pigment dispersion.

Solid forms contain much dispersing agent and more may be added to the dyebath to keep any unreduced dye in suspension. Addition of sodium hydrosulphite (dithionite) (Na₂S₂O₄) to the alkaline aqueous dispersion of the vat dye brings about rapid reduction. In pigmentation dyeing methods, the fine pigment particles are uniformly deposited in the goods by padding or liquor circulation before reduction occurs. Very fine dispersions are needed for these processes.
pigmentation processes and the proportion of fine particles is higher than for vat pigments in the traditional vatting process. Dye powders for pigmentation dyeing have higher dispersant content. Pastes and liquid forms are useful for printing and continuous dyeing. They will usually have less dispersant but contain appreciable amounts of water. Some ranges of dyes are deliberate mixtures of vat and disperse dyes for dyeing cotton/polyester blends.

17.3.2 Reducing vat dyes with hydros
Reduction of quinones is not easy and vatting requires a strong reducing agent. The dihydrate of sodium dithionite, or hydrosulphite, Na₂S₂O₄·2H₂O, is used almost exclusively and goes by the common name of ‘hydros’. Vatting is carried out under strongly alkaline conditions for a number of reasons:

(1) the reduction of the quinone (QO₂⁻) with hydros to give the leuco dye (QO₂⁻), and the oxidation of the hydros by oxygen, consume alkali (Scheme 17.1);
(2) it is important that the insoluble vat acid does not precipitate;
(3) hydros is unstable in solution, particularly under acidic or neutral conditions and at higher temperatures. Its decomposition forms thiosulphate and bisulphate. This decomposition reaction consumes hydroxide ion and it is faster as the solution becomes more acidic (Scheme 17.2).

\[
\begin{align*}
\text{QO}_2^- + \text{Na}_2\text{S}_2\text{O}_4 + 4\text{NaOH} & \rightarrow \text{QO}_2^{2-} + 2\text{Na}^+ + 2\text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O} \\
\text{Na}_2\text{S}_2\text{O}_4 + 2\text{NaOH} + \text{O}_2 & \rightarrow \text{Na}_2\text{SO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}
\end{align*}
\]

Scheme 17.1

\[
\begin{align*}
2\text{Na}_2\text{S}_2\text{O}_4 + 2\text{NaOH} & \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
\end{align*}
\]

Scheme 17.2

The decomposition of hydros is exothermic. Decomposition of solid Na₂S₂O₄·2H₂O can lead to spontaneous ignition. Cool, dry conditions are therefore necessary for storage. Decomposition of hydros occurs rapidly in acidic solution. Alkaline hydros solutions are more stable provided oxygen is absent.
Because hydros reacts readily with oxygen (Scheme 17.1), the material being dyed with the leuco dye should not be over-exposed to air. Oxidation of the excess hydros can lead to subsequent oxidation of the leuco dye and precipitation of the quinone, giving uneven surface deposits of pigment on the goods. A large excess of hydros in the bath is usual. The amount used depends on the dyes and the type of machine. The suppliers give suitable recommendations for their dyes. Other more stable reducing agents, such as sodium sulphoxylate-formaldehyde (HOCCH₂SO₂Na), are used in printing with vat dyes to ensure stability of the pastes. Steaming of the printed material activates this reducing agent and the vat dye in the print paste is reduced (Scheme 23.3). Sodium sulphoxylate-formaldehyde is a poor reducing agent at 25°C and is more stable than hydros. Other reducing agents such as thiourea dioxide (Scheme 23.3) and glucose are now being suggested as more environmentally friendly alternatives to hydros.

17.3.3 Vatting

Traditional vatting involves adding hydros to a fine, relatively concentrated aqueous dispersion of the vat dye pigment containing NaOH. The vatting temperature is often higher than the subsequent dyeing temperature. This gives rapid reduction. The concentrated solution of the leuco form is then diluted by adding it to water in the dyebath. The bath water also contains NaOH and some hydros to avoid any oxidation from dissolved atmospheric oxygen. Vatting may also be carried out directly in the dyebath if the dye is readily reduced.

Dyeing takes place at temperatures lower than the vatting temperature to avoid decomposition of the hydros. This also decreases the risk of over-reduction of polyquinone dyes such as Indanthrone. Over-reduction is the reduction of more than one pair of conjugated carbonyl groups in a polyquinone and often results in poor colour yields and off-shade dyeings. Reduction inhibitors, such as sodium nitrite or glucose, prevent over-reduction during vatting. Anthraquinone and polycyclic vat dyes give leuco solutions with intense colours, often very different from those of the original pigment dispersion. The vat dye flavanthrone is a yellow pigment that produces a deep blue vat. It is often used in paper strips for the detection of excess hydros.

Vatting conditions for quinone vat dyes vary widely. Three main types of vatting process are used depending upon the dyes being used. These involve:

1. a concentrated NaOH solution and a high vatting temperature (60°C);
(2) a moderate concentration of NaOH and a lower vatting temperature (50 °C);
(3) a low concentration of NaOH and a low vatting temperature (30–40 °C).

17.3.4 Redox potentials and rate of vatting
Dyes that are easy to reduce are more difficult to oxidise, and vice versa. The standard redox potential ($E^\circ$) gives a measure of the ease of reduction at a given pH. In strongly alkaline solution, the redox potential $E$ is given by

$$E = E^\circ + \frac{RT}{2F} \ln \left( \frac{a_{\text{ox}}}{a_{\text{red}}} \right)$$

where $R$ is the gas constant, $T$ the absolute temperature, $F$ the Faraday constant, and $a_{\text{ox}}$ and $a_{\text{red}}$ are the activities of the oxidised and reduced forms of the vat dye.

The value of $E^\circ$ is related to the standard free energy change for the reduction process.

$$\Delta G^\circ = \Delta E^\circ F = RT \ln(K)$$

![Figure 17.3](image-url) Potentiometric titration curve for oxidation of a leuco vat dye showing hydros, ferricyanide and dye potentials and total dye content.
Anthraquinone vat dyes have large negative standard redox potentials, giving unfavourable positive values of $\Delta G^\circ$, and therefore their reduction requires strong reducing agents. Conversely, the leuco compound in alkaline solution is readily oxidised. The potentiometric titration of the leuco compound in solution with an oxidising agent is complicated by the precipitation of the insoluble quinone pigment, even in the first stages of the titration. This usually results in unstable potentials and the usual form of the titration curve is not followed. Complete oxidation of the leuco form can, however, usually be detected and the titration is useful for analysis of the actual dye content of vat dye samples (Figure 17.3). The titration is usually performed using potassium ferricyanide solution as oxidising agent. The reaction involved is:

$$\text{QO}_2^{2-} + 2\text{Fe(CN)}_6^{3-} \rightarrow \text{QO}_2 + 2\text{Fe(CN)}_6^{4-}$$  \hspace{1cm} (3)

The number of moles of leuco dye oxidised is given by:

$$\text{mmol dye} = 0.5 \times V (\text{ml}) \times M (\text{mmol ml}^{-1})$$  \hspace{1cm} (4)

where $V$ is the volume of ferricyanide solution for quantitative oxidation and $M$ its molarity.

A typical vat dye has a redox potential around $-0.80$ V with respect to a standard hydrogen electrode. Alkaline hydros solution has a potential of about $-1.10$ V. The standard potential for the reduction reaction is calculated as follows:

$$\text{QO}_2^{\text{(ox)}} + 2e^- \rightarrow \text{QO}_2^{2-} \text{(red)} \hspace{1cm} E^\circ = -0.80 \text{ V}$$

$$2\text{SO}_3^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{S}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} \hspace{1cm} E^\circ = -1.10 \text{ V}$$  \hspace{1cm} (5)

Combination of the first with the reverse of the second equation gives:

$$\text{QO}_2 + \text{S}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{QO}_2^{2-} + 2\text{SO}_3^{2-} + 4\text{H}^+$$

which is essentially the same as the first equation in Scheme 17.1.

$$E^\circ = -0.80 - (-1.10) = +0.30 \text{ V}$$  \hspace{1cm} (6)

$$\log(K) = \frac{2E^\circ}{2.303RT} = \frac{2 \times 0.30 \times 96485}{2.303 \times 8.314 \times 298} \approx 10^{10}$$
Obviously, such a large equilibrium constant for the reduction means that hydros solution is a sufficiently powerful reducing agent to completely reduce the vat dye pigment to the leuco form. Similar considerations apply to the oxidation of the leuco derivative. Any oxidising agent with a redox potential below about –0.60 V will give quantitative oxidation back to the quinone form of the dye.

\[
\begin{align*}
\text{QO}_2^{(ox)} + 2e^- & \rightleftharpoons \text{QO}_2^{2-} \quad E^\circ = -0.80 \, \text{V} \\
\text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightleftharpoons \text{HO}_2^- + \text{HO}^- \quad E^\circ = -0.10 \, \text{V}
\end{align*}
\]

Thus, combination of the second with the reverse of the first equation gives

\[
\begin{align*}
\text{QO}_2^{2-} + \text{O}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{QO}_2 + \text{HO}_2^- + \text{HO}^- \\
E^\circ = -0.10 - (-0.80) & = +0.70 \, \text{V}
\end{align*}
\]

For oxidation of the leuco derivative with oxygen, \(E^\circ = +0.70 \, \text{V}\) and the equilibrium constant is enormous.

Standard redox potentials are thermodynamic values related to the position of equilibrium and give no information about reaction rates. Hydros is a very strong reducing agent, more effective at high pH and at higher concentration. Its potential is unstable but negative enough that it will reduce almost all vat dyes, but not necessarily rapidly. Indigo dyes, for example, have less negative standard potentials than anthraquinone vat dyes but reduce more slowly. Attempts to control the amount of hydros needed in vatting and during dyeing, based on redox potential measurements of the dyebath solution, have not been particularly successful. It is difficult to interpret the recorded potentials in a way that allows calculation of the amount of excess hydros and to keep the required platinum electrodes in good condition.

The reducing action of hydros is complex. The dithionite ion is a good reducing agent but much of its reducing power depends upon formation of the dithionite radical formed by breaking the weak bond between the two sulphur atoms in dithionite (Scheme 17.3). The kinetics of the reduction process depend on the temperature and concentrations of chemicals in solution, the rate increasing with increase in the temperature and the concentration of hydros. The rate of reduction of a vat pigment is, however, complicated by the heterogeneous nature of the system and depends upon the size distribution and habit of the crystals in dispersion. The crystalline form affects the rate of vatting more than the particle.
size but, in general, the rate of reduction is higher for finer particles. The effects of these physical parameters are far less significant than the differences between dyes of different structures. Vatting rates are fairly easy to measure since the solution of the leuco compound usually has a colour quite different from the quinone pigment. Times of half reduction (the time required to achieve 50% reduction of the pigment dispersion under given conditions) vary by a factor of over 600.

\[ \text{SO}_2\text{O}_2\text{S} \rightarrow \text{SO}_2^+ + 2\text{SO}_4^- \]

Scheme 17.3

Rates of vat dye reduction show no correlation with their redox potentials. Redox potential values allow calculation of the extent of reduction at equilibrium with a given reducing agent of known concentration and potential; they do not give the rate at which equilibrium is reached. A rapid rate of reduction of the vat pigment is much more important in continuous dyeing and printing where reduction and adsorption are concurrent. In printing, the rate of reduction must be higher than the rate of decomposition of the reducing agent under the given steaming conditions. Whenever possible, dyes that reduce slowly are vatted at higher temperature unless decomposition is a problem.

17.4 THE SUBSTANTIvITY AND DYEING CHARACTERISTICS OF VAT DYES FOR CELLULOSIC FIBRES

17.4.1 Basic steps in the dyeing process
The dyeing of cellulosic materials with quinone vat dyes follows a four-step sequence:
(1) preparation of the vat containing the leuco forms of the dyes;
(2) dyeing of the material, in which the fibres absorb the water-soluble leuco compound;
(3) oxidation of the absorbed leuco compound back to the parent pigment inside the fibres;
(4) soaping of the dyed material to remove pigment loosely adhering to the fibre surfaces and to develop the true shade and fastness properties.
17.4.2 Classification of vat dyes

For quinone vat dyes, there is no single classification according to dyeing properties as is the case for the direct dyes. The German Interessen Gemeinschaft für Farbenindustrie (IG) developed one popular classification for their Indanthrene range of vat dyes based on leuco compound substantivity and the required dyeing conditions. There were three main types:

1. the IN (indanthrene normal) group of dyes require the use of concentrated NaOH and high vatting (60 °C) and dyeing temperatures (60 °C). No salt is added to the dyebath because of the high substantivity of the leuco dyes for cotton;
2. the IW (indanthrene warm) group of dyes require only moderate amounts of NaOH and lower vatting (50 °C) and dyeing temperatures (50 °C). The leuco forms of these dyes have moderate substantivity for cotton and some addition of salt is needed during dyeing to aid exhaustion;
3. the IK group of dyes only need a low concentration of NaOH with low vatting (40 °C) and dyeing temperatures (20 °C). These dyes have low substantivity for cotton and need considerable salt for good dyebath exhaustion. Some have amide groups that would be hydrolysed under the vatting and dyeing conditions used for IN and IW dyes.

There are special processes for some black vat dyes that require an oxidative aftertreatment to develop the full black colour. Table 17.1 compares the characteristics of these three types of vat dye. The required concentrations of hydros, caustic soda and salt increase with increasing amounts of dye in the bath and with increasing liquor ratio.

<table>
<thead>
<tr>
<th>Table 17.1 Characteristics of the three main types of vat dye</th>
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<tbody>
<tr>
<td><strong>Val dye type</strong></td>
</tr>
<tr>
<td>NaOH concentration (g l⁻¹)</td>
</tr>
<tr>
<td>NaCl concentration (g l⁻¹)</td>
</tr>
<tr>
<td>Dyeing temperature (°C)</td>
</tr>
<tr>
<td>VATTING temperature (°C)</td>
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</tbody>
</table>
There are various other classifications of vat dyeing methods. The SDC recommend tests to determine the best dyeing method [1]. In this, the colour strengths of dyeings produced under different dyeing conditions are compared with those of standard dyeings using a grey scale. This test applies only to anthraquinone dyes. There are also SDC tests for determining the strike, migration and levelling characteristics of vat dyes. Different companies have different classification systems for their vat dyes. Because vatting and dyeing conditions vary from one dye to another, the suppliers’ recommendations should be consulted.

17.4.3 The high substantivity of leuco vat dyes

The origin of the substantivity of leuco vat dyes for cotton is far from clear. Hydrogen bonds between cellulose hydroxyl groups and phenolate ion groups, or amino or amide substituents, in the leuco dye may be involved in dye-fibre binding. The substantivity of the leuco dye is very dependent on the position of the phenolate ion groups and on the actual molecular structure. Substantivity tends to be greater the larger the surface area of the leuco dye molecule and van der Waals interactions between the dye and fibre are important. Molecules of leuco vat dyes tend to be large and, although coplanarity of the structure is essential, the structures are often not long and linear as for direct dyes. Although the planar molecular structures of leuco vat dyes should promote aggregation, there is not much evidence of this in dyeing solutions.

In the dyeing process, the influence of salt addition and increasing dyeing temperature are similar to the effects found in dyeing cotton with direct dyes. Unlike direct dyes, however, dyeing with many leuco vat dyes is very rapid at relatively low temperatures and usually gives high exhaustion at equilibrium. The ability to control the dyebath exhaustion by salt addition is very limited since the bath initially contains a high concentration of sodium ions from the added hydros and caustic soda. Because of this, many dyes have a rapid strike. The dyebath may be 80–90% exhausted within 10 minutes. Because there is little diffusion into the fibres within such a short period, there is a strong tendency for cotton yarns and fibres to be ring dyed in the early stages of dyeing. Diffusion only becomes important well after the time of half dyeing. The high strike must be controlled to avoid unlevel dyeing since the low dyeing temperatures do not favour migration. The behaviour of the leuco dyes is assessed by the usual migration and strike tests in comparison with the behaviour of standard dyes [1]. The dyeing methods
The initial strike can be retarded using polyethylene oxide complexing agents. The initially formed dye–auxiliary complex presumably slowly breaks down to gradually liberate free leuco dye, thus controlling the initial rate of adsorption. Both non-ionic and cationic retardants are used but these decrease the exhaustion. They can also be used for levelling of uneven dyeings. Such dyeing auxiliaries should be added to the dyebath after vatting. The dye manufacturer’s recommendations should be consulted since these agents are often dye-specific. Similar chemicals can be used for stripping faulty dyeings. This is not easy because of the high substantivity of the leuco vat dyes and the stripping auxiliaries used form much more stable complexes with the leuco dyes than those obtained from levelling agents.

17.5 DYEING COTTON WITH LEUCO VAT DYES

17.5.1 Preparation
As always, good preparation of the goods is essential to avoid a non-uniform distribution of residual impurities that might hinder level dyeing or that might interact with the dyes. Water quality is important since the calcium and magnesium salts of some leuco dyes may precipitate if hard water is used. The use of sequestrants or protective colloids is often recommended.

17.5.2 Dyeing conditions
Quinone vat dyes are used on all forms of cellulosic materials. The vat is usually pre-prepared and added to the dyebath containing the goods, possibly in successive portions. Vat dyes of high substantivity are often used for dyeing deeper shades where the effect of poor levelling is less visible. They usually follow a Freundlich adsorption isotherm (Section 11.1.1) so that using more dye gives
deeper shades, but with diminishing returns. The dyeing temperature may be increased to promote migration, if the dye is stable. This gives better penetration into tightly constructed materials. Subsequently cooling the dye bath promotes better exhaustion. Any required salt may be added in portions towards the end of the process for dyes of lower substantivity.

The liquor ratio is usually in the range from 10:1 to 20:1. The actual amounts of caustic soda and hydros required for vatting, and for addition to the dye bath, depend on many factors, such as the dyeing temperature and time, and particularly on the degree of exposure to air during dyeing. The latter is mainly a characteristic of the particular dyeing machine used. As in dyeing cellulosic fibres with some direct dyes, the rate of dyeing with leuco vat dyes is higher at higher temperature, lower liquor ratio and lower dye concentration. It is not much affected by the relatively high NaOH and hydros concentrations. Many leuco compounds have high substantivity and level dyeing requires careful control of the dyeing temperature, the total salt concentration and gradual addition of the concentrated leuco dye vat to the dye bath. Figure 17.4 shows a typical procedure for dyeing cotton with a quinone vat dye.

![Figure 17.4](image)

**Figure 17.4** A typical procedure for dyeing cotton with a quinone vat dye

### 17.5.3 Problems with anthraquinone dyes

A number of chemical problems arise with some quinone vat dyes. These include:

1. multiple reduction steps for polyquinones such as indanthrone;
(2) isomerism of leuco compounds to oxanthrones;
(3) hydrolysis of amide groups;
(4) over-oxidation after dyeing;
(5) dehalogenation of some dyes.

To minimise these types of problems, the supplier’s recommendations for vatting and dyeing must be followed.

Indanthrone (CI Vat Blue 4) and some of its derivatives show a number of these problems. Indanthrone has two anthraquinone residues in its molecule. The normal blue leuco compound used in dyeing is that corresponding to the reduction of one of the anthraquinone groups (5, in Figure 17.5). If both anthraquinone groups are reduced, the final product (6) gives a brownish yellow solution, has poor substantivity for cotton and is more difficult to oxidise. Such over-reduction produces duller blue dyeings of lower colour yield. Indanthrone is also one of the quinone vat dyes whose leuco compound will tautomerise via the vat acid to an oxanthrone (7) if the concentration of NaOH in the solution is not sufficiently high. Oxanthrones are not easily oxidised to the parent quinone and their formation results in dyeings of poor colour yield. Mild oxidation of leuco vat dyes of the indanthrone type with hypochlorite produces a much greener azine derivative (8).

Figure 17.5
This is responsible for the rather poor chlorine fastness of indanthrone. The reaction is reversible and treatment of an over-oxidised dyeing with dilute alkaline hydros solution followed by air oxidation regenerates blue Indanthrone.

Partial formation of the green azine derivative can occur during air oxidation if the fabric still contains a relatively high concentration of NaOH solution. Rinsing out the excess alkali from the dyeing is therefore necessary before significant oxidation by oxygen has occurred. Some of the chlorinated indanthrone vat dyes are prone to elimination or substitution of a chlorine atom unless vatting is carried out with care. Although the indanthrone type dyes represent a rather special case, it is obvious that vatting of the insoluble pigment to produce a solution of the leuco derivative for dyeing is not always a simple operation. It is important to follow the supplier’s recommendations for all stages of the dyeing process.

17.5.4 Aftertreatment of the dyeing

Once the actual dyeing process is complete, the goods go through a series of operations:

1. Rinsing to remove adhering exhausted dye liquor and chemicals. A reductive rinse with dilute alkaline hydros solution may be needed for heavy shades;
2. Oxi-inising the leuco dye to the pigment form using hydrogen peroxide and acetic acid;
3. Soaping at or near the boil. For soaping in a package machine, the first step may be dispersion at 60 °C to remove loose surface colour, followed by soaping at or near the boil. This is important to avoid filtration of eliminated dye particles by the package;
4. Neutralising the dyeing with acetic acid solution and final rinsing.

These processes are an essential part of the overall procedure and must be correctly carried out if the dyeing is to have the optimum fastness properties. The oxidation and soaping stages are discussed in the following section.

17.6 OXIDATION AND SOAPING AFTER DYEING

17.6.1 Oxidation

An oxidising agent has a much more positive redox potential than the compound that it can oxidise or, considered from the opposite perspective, the compound being oxidised has a more negative redox potential than the oxidising agent that it
Quinone vat dyes are generally difficult to reduce and easy to oxidise. For sulphur dyes (Section 17.11) the reverse is true. A typical vat dye has a redox potential around $-0.80 \text{ V}$ and oxidising agents with redox potentials more positive than about $-0.50 \text{ V}$ will in principle give complete oxidation of the leuco dye to the quinone. The rate of oxidation must also be acceptable. Oxidation of a leuco vat dye can be achieved by exposing the goods to air, after an initial rinse to remove adhering liquor, and therefore appears quite simple. Air oxidation, however, is of little use for compact goods such as yarn packages, and is quite slow, often requiring 30–40 min for complete oxidation. It may also result in side reactions and off-shade dyeings. Chemical oxidants are therefore generally preferred because they give more rapid and uniform oxidation throughout the material. Sodium dichromate, hydrogen peroxide, or sodium perborate or percarbonate are used at up to $40 \degree \text{C}$. It is important that the initial oxidation is carried out under alkaline conditions to avoid forming the vat acid, which is much less soluble and hard to oxidise. Over-oxidation of some dyes, such as Indanthrone, leads to changes in hue of the dyeing (Section 17.5.3).

17.6.2 Soaping

Soaping removes pigment deposited on the fibre surface that would wash or rub off in use. The deposit is formed by oxidation of the leuco dye in the solution adhering to the fibres after dyeing. Thorough rinsing after dyeing, using a weak solution of alkaline hydros, helps to minimise this problem. Soaping involves thoroughly washing the goods in a detergent solution at or near the boiling point. It improves the light, washing and rubbing fastness of the dyeing. Some vat dyes give a slight shade change on soaping so a standardised procedure is necessary for exact colour reproducibility.

The soaping process probably involves re-crystallisation of the dispersed vat dye particles obtained from the initial oxidation of the leuco dye. This is not a spontaneous process and requires heat and water. The growth of the pigment crystals inside the cotton fibre is limited by the pore size. It is this crystallisation process that is responsible for the slight change in hue and the improvements in the fastness properties.

17.7 PRE-PIGMENTATION DYEING METHODS

In many cases, leuco vat dyes have too high a substantivity for continuous dyeing and preferential absorption by the cotton fibres would result in exaggerated tailing.
The pigment form, however, has no substantivity for cotton at all. The pre-pigmentation dyeing methods are simple processes in which a fine dispersion of the vat pigment is uniformly circulated through the goods that are then treated with alkaline hydros solution to cause reduction. Dyeing takes place around each original pigment particle with almost no migration. The dyeing is subsequently oxidised and soaped as before. Either of the two operations, the initial pigmentation or the reduction, may be batch or continuous processes. This leads to a variety of possible dyeing methods, some of which are described below.

17.7.1 Pre- and semi-pigmentation batch dyeing methods

In the pre-pigmentation method, a fine dispersion of the vat dye pigment is first circulated through the goods. In the second step, reduction to the leuco dye is carried out using NaOH and hydros. The latter may be added all at once or gradually. This method is useful for light and medium shades where levelling and penetration may be a problem in dyeing with a fully reduced vat dye. It is, however, less suitable for compact forms of material. In package dyeing, the pigment dispersion must not be filtered out in the packages but rather gradually deposited into the package by salt addition that causes the particles to slowly flocculate.

In the semi-pigmentation process, all the chemicals are circulated through the goods at room temperature before gradual heating to start reduction. The rate of vatting is very slow at the low starting temperature. As in the pre-pigmentation method, a fine dispersion is required.

The vat acid process is another alternative for package dyeing. After reduction of the vat pigment, in alkaline solution, the leuco vat acid is precipitated in the presence of a dispersing agent by acidification. This is then circulated in the goods and dyeing takes place by gradual addition of caustic soda to reform the soluble and substantive leuco form.

17.7.2 Semi-continuous processes

In semi-continuous vat dyeing processes, the fabric is pigmented by padding with the insoluble vat dye dispersion. Subsequent reduction to the leuco form is a batch operation using a jig or beam dyeing machine. Some dye comes off the fabric during development with the alkaline hydros solution and some vatted dye liquor may be added to the bath in the machine beforehand. This prevents ending in jig
dyeing. In some cases, an intermediate drying of the padded fabric may be included to minimise colour bleeding into the development bath.

17.7.3 The fully continuous pad–steam process

The pad–steam process for dyeing cellulosic materials with vat dyes is a particularly important process. It involves five stages:

1. Padding the fabric with the fine vat pigment dispersion containing a wetting and an anti-migration agent;
2. Drying of the padded fabric and cooling;
3. Padding of the dried, pigmented fabric with hydros and caustic soda solution;
4. Steaming in air-free steam at about 102–105 °C;
5. Rinsing, oxidation and soaping using a series of wash boxes.

Liquid forms of vat dyes are preferred for continuous dyeing as they give less migration on drying and are more convenient for preparing the large volumes of dye liquor required. The drying of the fabric after padding ensures a high pick-up of alkaline hydros solution from the chemical pad. Some dye invariably bleeds from the fabric into the alkaline hydros solution. This is less when padding a dried fabric, and an initial addition of some dye to the chemical pad solution minimises colour tailing. Drying of the initially padded fabric is usually carried out in two steps involving a gentle pre-drying stage before the complete drying process. Pre-drying is to control migration of the pigment particles to the yarn surfaces where water is evaporating. The heating should be as uniform as possible. It is also common practice to use an anti-migrant such as sodium alginate in the first padding solution. The anti-migrant causes flocculation and aggregation of pigment particles during drying thus limiting their movement within the fabric. Some anti-migrant agents may also increase the solution viscosity. The ease of migration depends on the fibres and fabric, the solution pick-up and the pigment particle size (Section 10.5.3).

After the chemical pad, the fabric is steamed for 30–60 s in saturated, slightly superheated, air-free steam (Section 12.6.3). It is essential to avoid condensation falling onto the fabric in the steamer as this causes a spotty colour (Section 12.6.3). The steamer has a water seal at its exit with water flowing through the trough to maintain a temperature of not more than 40 °C. After steaming the fabric is rinsed by spraying to remove alkali and hydros. This is followed by rinsing, oxidation, soaping, rinsing and neutralising in a series of wash boxes.
17.7.4 Wet-on-wet processing

The usual pad-dyeing process cannot be used for corduroy or terry cloth because of flattening of the pile and excessive migration during drying. A wet-on-wet dyeing process is used. In this, the cloth is padded with the pigment dispersion and then, while still wet, it is padded again with the alkaline hydros solution. The solution pick-up at the chemical pad may go from values of around 70 up to 150–200%. The goods then go through the steamer and the usual aftertreatments.

17.8 FASTNESS PROPERTIES OF VAT DYES

Many quinone vat dyes provide outstanding colour fastness. The colour gamut is somewhat restricted as there are no bright colours, particularly in the red and turquoise areas. Only azoic and sulphur dyes have smaller colour gamuts. The colour gamut is the size of the ‘colour space’ for the colours obtainable with a particular type of dye either alone or in combinations (Section 21.8.2).

Vat dyes are very expensive, like reactive dyes. A high degree of overall colour fastness is characteristic of vat dyes. They usually have excellent fastness to washing, chlorine bleaching, alkali boiling and light. Vat dyes also have the advantage of being the only dyes for cellulosic materials that do not give shade changes on application of topical reactive finishes for cotton, such as flame resist finishes (Section 25.3.1). One minor problem is that of photochemical catalytic fading or cotton tendering by a small group of vat dyes. These are mainly yellow and orange vat dyes that photosensitise the tendering of cotton, as in drapery fabrics. The dye functions as a catalyst for the photo-oxidation of the cellulose. Others photosensitise fading of other vat dyes.

17.9 DYEING WITH INDIGO AND INDIGOID VAT DYES

Natural Indigo was rapidly displaced from the market once the synthetic product became available. The quality of natural Indigo was quite variable because of the presence of other coloured impurities. The fastness properties of Indigo dyeings are not up to the standards expected from the vat dye class as a whole. It is, however, the appearance of faded Indigo in denim that is so fashionable today. After dyeing, various wet processes, such as stone washing, deliberately enhance this faded effect. Indigo builds up primarily on the cotton fibre surface. This is one reason for the somewhat inferior fastness properties of Indigo compared to quinone vat dyes.
17.9.1 Application of Indigo to cotton

Dyeing cotton yarn for blue jeans is an important use of Indigo. In a typical batch operation, concentrated reduced Indigo is added to a dyebath from which oxygen has been removed with a little alkaline hydros. The goods are entered and fully immersed to avoid oxidation. After about 15 min at 20–25 °C, the goods are removed and well squeezed before air oxidation. Indigo does not exhaust well because of its limited substantivity for cotton, not surprising considering its small molecular size (Figure 1.4). Deep shades must be built up by repeated dipping in the dyebath after each oxidation. The use of too concentrated a dyebath is not effective for deep shades as it results in poor rubbing fastness. Some salt may be added to aid exhaustion. After dyeing, the goods are well soaped. The final dyed material may be aftertreated to produce a faded, worn look.

Continuous methods are used for dyeing ball warps, warp beams and piece goods with Indigo. This is usually carried out in a series of 4–6 wash boxes with upper and lower rollers and nips at the exits. The goods are threaded through each box and may be skyed at the mid-point. The first box is used to wet out the material. In subsequent boxes, the goods are immersed in the leuco Indigo solution for 10–30 s at a linear speed of about 25 m min\(^{-1}\), squeezed and skyed for 2 min to oxidise the leuco dye to Indigo. The boxes are fed with a stock vat of leuco Indigo and the liquor in the boxes is circulated to maintain constant dyeing conditions. This process of several dips and oxidations is then repeated in a second series of boxes, and so on. Several rinsing and washing boxes complete the process.

17.9.2 Indigoid vat dyes

Besides Indigo itself, there are a number of other important indigo and thioindigo derivatives used for dyeing cellulosic fibres. These include chlorinated and brominated indigo and thioindigo dyes in which the nitrogen atoms of Indigo are partially or totally replaced by sulphur atoms (9, in Figure 17.6). Compared to the

![Figure 17.6 Structure of thioindigo](image)
VAT DYES

anthraquinone type vat dyes, Indigoid vat dyes give much paler yellow to brown leuco compound solutions. The vatting process is also slower and requires less alkali.

17.10 SOLUBILISED VAT DYES

The solubilised vat dyes provided a means of avoiding the difficult vatting process required for quinone and indigoid vat dyes. The preparation of a solution of a leuco vat dye requires care and time, and protection of the solution from excessive exposure to air. The solubilised vat dyes avoid these problems. These dyes are pre-prepared sulphate esters of the leuco vat acid. The first product of this type was that derived from Indigo (10, in Figure 17.7). Later solubilised leuco dyes derived from quinone vat dyes were marketed.

![Image of 10](10)

Figure 17.7

Cotton absorbs these dyes directly from a neutral or slightly alkaline solution but they are not very substantive even in the presence of added salt. Although a leuco sulphate ester has the same negative charge as the normal leuco dye, its charge is localised in the sulphate groups whereas that of the phenolate ion is delocalised. Cotton therefore repels a leuco sulphate ester molecule more strongly than the normal leuco compound. Because of their limited substantivity, solubilised vat dyes are generally only suitable for pale shades. After dyeing, the goods are rinsed or hydroextracted to remove superficial dye solution, and the vat dye pigment is developed in the fibre by oxidation with sodium per sulphate or acidified sodium nitrite solution. After neutralising with dilute soda ash solution, the goods are soaped as in the case of normal vat dyeing. The dyeing has the same fastness properties as one prepared from the original vatted pigment.

The low substantivity of the leuco sulphate esters avoids the problems of the high strike of leuco vat dyes. Since they can be used in solutions close to neutrality, they can also be used for wool dyeing. Unfortunately, the dyeing and
oxidation conditions for each dye vary so it is important to follow the supplier’s instructions. The use of these dyes was never widespread and has declined in recent times. They are not particularly competitive because of their high cost.

17.11 SULPHUR DYES

17.11.1 Chemical nature of sulphur dyes

Sulphur dyes are a type of vat dye used for dyeing cellulosic fibres. The insoluble pigment is converted into the substantive leuco compound by reduction with sodium sulphide and the leuco form is subsequently oxidised inside the fibre. Sulphur dyes are manufactured by heating organic materials with sodium polysulphide in aqueous or alcoholic solution, or by baking with sodium sulphide and sulphur. A variety of organic compounds are used including amines, nitro compounds, and phenols and their derivatives. These dyes almost always contain loosely bound sulphur and liberate hydrogen sulphide when treated with acidic solutions of reducing agents such as stannous chloride.

The chemistry of sulphur dyes is very complex and little is known of the molecular structures of the dyestuffs produced. The Colour Index only gives the structures of the starting materials that are used to produce these dyes and even then the information can be quite misleading. Two products manufactured from the same starting materials are unlikely to have similar properties even though they may have the same CI number. The actual dyestuffs produced from the same materials by different processes may have quite different dye contents, dyeing characteristics and environmental impacts. Because of the large amounts of sodium sulphide used in the manufacture and application of these dyes, much of which will eventually be found in the effluent, they pose a significant environmental problem. In this respect, sulphur dyestuffs produced in the developed Western nations are much more environmentally friendly.

A variety of structural units have been proposed for various sulphur dyes. It is generally accepted that these dyes are polymeric having sulphur containing aromatic heterocyclic units such as thiazines and thiazoles linked by dis- or polysulphide bonds (Figure 17.8). On treatment of an aqueous dispersion of the insoluble pigment with sodium sulphide, the sulphide links are reduced forming individual heteroaromatic units with thiol groups (Scheme 17.4). These are soluble in the alkaline solution in the form of thiolate ions that have low to medium substantivity for cellulose. Over-reduction is possible if other groups are
affected and the more powerful hydros is rarely used as the reducing agent. After
dyeing of the cellulosic material, the thiolate ions in the fibres can be re-oxidised
back to the polymeric pigment with di-sulphide bonds linking the aromatic units.
Sulphur dyes often have dull yellow vats and sulphide and polysulphide
solutions are usually pale yellow. For these reasons, the colour content of a given
product cannot be assessed by the usual spectrophotometric method (Section
24.1) and it is necessary to prepare dyeings and compare their colours.

17.11.2 Dyeing with sulphur dyes of various types

There are a number of different types of sulphur dye. The Colour Index lists
sulphur, leuco sulphur, solubilised sulphur and condensed sulphur dyes, although
the latter are no longer manufactured. The sulphurised vat dyes, which are
intermediate between sulphur and quinone vat dyes, will also be mentioned in this
section. Of these types, only the sulphur, leuco sulphur and the sulphurised vat
dyes are of real importance in dyeing. Sulphur dyes are available as powders,
pastes, and as pre-reduced liquids. The latter type is possible because a solution of
a leuco sulphur dye containing sodium sulphide is much less sensitive to oxidation
than a leuco solution prepared from an anthraquinone vat dye with hydros.
Leuco sulphur dyes are either solutions of the leuco dye or granular mixtures of
leuco compound and reducing agent, usually sodium sulphide. They can be diluted
with or dissolved in hot water and the solution used directly for dyeing, or after
addition of more sodium sulphide. These dyes eliminate the difficulties of vatting,
because reduction of sulphur dyes is not rapid.

Solubilised sulphur dyes are thiosulphate derivatives of the leuco compounds
and are available in powder or liquid form. They are prepared by reacting
disulphides with sodium sulphite to give the thiosulphate ester of the thiol. These
are called Bunte salts (Scheme 17.5). These dyes are applied in the presence of
alkali and reducing agent (Na₂S) to generate the sulphur dye that then undergoes
further reduction to the leuco dye. Like the sulphate esters of leuco vat dyes, the
thiosulphate esters have little substantivity for cotton. They are also used in paper
dyeing where they are precipitated by the fillers added to the pulp.

\[
\text{Dye} - \text{S} \rightarrow \text{Dye} + \text{Na₂SO₃} \rightarrow \text{Dye} - \text{S} \rightarrow \text{Dye} \cdot \text{Na} \\
2\text{Dye} - \text{S} \rightarrow \text{SO₃Na} + \text{Na₂S} \rightarrow \text{Dye} - \text{S} \rightarrow \text{Dye} + 2\text{Na₂SO₃} \\
\text{Dye} - \text{S} \rightarrow \text{S} \rightarrow \text{Dye} + \text{Na₂SO₃} \rightarrow \text{Dye} - \text{S} \rightarrow \text{Dye} + \text{Na₂S₂O₃}
\]

Scheme 17.5

The sulphurised vat dyes, such as CI Vat Blue 43 and Sulphur Red 10, bridge
the vat and sulphur dye classes. They are manufactured by the same kinds of
procedures as for sulphur dyes but are applied like vat dyes using hydros for
vatting.

17.11.3 Characteristics of sulphur and leuco sulphur dyes on cotton

Sulphur dyes have the dullest range of colours of all dye classes but are relatively
inexpensive. They are used to dye medium to deep, dull shades on cellulosic
materials. There are several excellent blacks giving dyeings with good wet fastness
properties. In fact, when black, and deep brown, blue and dull olive green shades
are needed, with good washing and satisfactory light fastness at reasonable cost,
sulphur dyes are irreplaceable. There are few green sulphur dyes and no true reds.
There are, however, an abundance of blacks, blues, yellows and browns. On a
world basis, sulphur dyes constitute one of the major dye classes.

Sulphur dyes are used in cotton dyeing for woven goods using jigg dyeing machines
and also in continuous dyeing. They are commonly used for the continuous dyeing
of corduroy. They are now being used more widely in jet machines. Sulphur dyes are also used for dyeing denim olive, brown and maroon, rather than the traditional Indigo blue, as well as to 'bottom' or 'top' Indigo dyed cotton warps. To 'bottom' or 'top' means that a sulphur dye is applied either before or after the Indigo. The fastness to wet processes and to crocking can be varied almost as required to satisfy the demand for the faded look so popular for denim. This is achieved by allowing premature oxidation of the leuco dye during dyeing, by using short dyeing times so that there is inadequate time for dye penetration into the fibres, and by poor rinsing and soaping after dyeing. The dyeings can then be subsequently treated to produce the faded worn look by removing the surface colour.

Although cellulosic goods dyed with sulphur dyes usually have good washing fastness, it can be further improved by resin finishing. The light fastness varies from moderate to good in heavy shades. A major characteristic of sulphur dyes is the poor fastness to chlorine, which distinguishes them from most quinone vat dyes. Dyeings with sulphur dyes cannot be bleached with hypochlorite. In fact, these dyes are readily distinguished from other cotton dyes by their dark, dull colours and the bleaching that occurs when a dyeing is spotted with hypochlorite and allowed to dry.

Cotton dyed with some sulphur blacks becomes tendered on storing under warm humid conditions. This is a consequence of the formation of sulphuric acid from oxidation of the sulphur dye in the fibres. It can be minimised by thorough washing after dyeing before the oxidation of the leuco dye, by a final alkaline rinsing with soda ash solution, and by resin finishing. Such tendering is avoided by dichromate oxidation of the leuco dye.

17.12 BATCH DYEING PROCEDURES WITH SULPHUR DYES

17.12.1 Vatting sulphur dyes

The major reducing agent for sulphur dyes is sodium sulphide, possibly containing some polysulphides. Sulphide ion is strongly hydrolysed in solution and gives a pH almost as high as the same concentration of NaOH (Scheme 17.6). Since hydrogen sulphide is a diprotic acid, the species present in an alkaline solution depends upon the pH and may be sulphide or hydrosulphide. Polysulphide ions are all in equilibrium with themselves and sulphide and hydrosulphide ions. Formation of polysulphide ions decreases the pH of solutions of sulphide ion (Scheme 17.6). These polymeric ions are not very sensitive to air. They therefore inhibit oxidation of sulphide and hydrosulphide and help to prevent 'bronzy' dyeings with a metallic
lustre and low wet rubbing fastness resulting from deposits of pigment on the fibre surfaces.

Vattin involves pasting the sulphur dye with water and sodium carbonate, diluting and adding sodium sulphide. The mixture is then boiled. Reduction is often slow. The leuco dye solution is added to the dyebath containing a small amount of hydros and caustic soda, which serve to remove any dissolved oxygen. The vatted dye is usually strained into the dyebath since sulphur dyes tend to have more insoluble impurities than other types of dye. Because of limited solubility of the leuco compounds, some dyes may have to be vatted in the bath if large quantities must be dissolved for heavy shades.

Hydros is usually unsuitable for vattin in most cases. Its use increases the risk of over-reduction, which decreases the colour yield since the over-reduced dye cannot be readily re-oxidised. Compared to vat dyes, leuco sulphur dyes are more difficult to oxidise. Alkaline solutions of glucose reduce some sulphur dyes at 90–95 °C. Reduction is achieved by the aldehyde group of the glucose. This type of reduction is much more environmentally friendly since there will be less sulphide in the dyehouse effluent. It should be used whenever possible.

17.12.2 Dyeing method
Initially the goods are wet out in the bath. Since the dyeing liquor contains appreciable amounts of sulphide, copper fittings must be avoided. If wetting or penetrating agents are used these should be of the anionic type since non-ionic surfactants form stable, non-substantive complexes with the leuco thiol. An anionic product such as phosphated 2-ethylhexanol is suitable. The bath may then be set at 40 °C with some sodium polysulphide and some EDTA. Polysulphides in the leuco dyebath prevent premature oxidation of the dye and reduce the tendency to bronzing of deep dyeings of blues, navies and blacks. An addition of a sequestrant such as EDTA avoids precipitation of the leuco thiocarbonate by calcium and magnesium ions. The leuco dye is then added slowly and, since the leuco dyes only have low to moderate substantivity for cellulose, some salt may be added.
initially, or in portions during dyeing, to promote exhaustion. After dyeing the goods are rinsed, the leuco dye oxidised and the dyeing is soaped as for a conventional vat dye.

Sulphur dyes usually have acceptable substantivity, particularly in the presence of salts, so that stripping in a fresh reducing bath is not easy. Dyeing is often conducted at the boil but this decreases the degree of exhaustion. Sulphur dyes require less salt than reactive dyes and usually have reasonable exhaustion. Low sulphide leuco dyes require more salt and no polysulphide. They do not give good exhaustion in heavy shades and the use of a low liquor ratio is recommended. For popular shades such as black, it has long been common practice to use a standing bath. This is a dye bath that is re-used for subsequent dyeings after addition of more reduced dye. Any free sulphur that tends to accumulate is dissolved by addition of sodium sulphite to give thiosulphate. This prevents it sticking to the goods. The actual dyeing temperature can vary. At higher temperatures around the boil, the bath exhaustion is less but penetration of the leuco dye into the fibres is better than at lower temperatures.

17.12.3 Post-dyeing treatments

After dyeing, good rinsing before oxidation helps reduce bronzeness and poor rubbing fastness by removing loosely adhering surface leuco dye solution before oxidation precipitates the insoluble pigment. Once the rinsing is completed, the leuco dye in the fibres is oxidised to the insoluble pigment.

Some leuco dyes can be oxidised in air, others need chemical oxidation. Sodium dichromate, hydrogen peroxide, or sodium percarbonate or perborate are used in warm, weakly alkaline solution. The peroxy compounds used for vat dyes can be used for sulphur dyes, but some leuco dyes (red-browns) are not oxidised by these agents. Some blues are over-oxidised, probably by oxidation of the disulphide links between the heteroaromatic units to form ionic sulphinate and sulphonate groups. This increases the water solubility, decreases the wet fastness and results in staining of other goods during washing. Even sulphur blacks oxidised with peroxides tend to be bluer, lighter and somewhat less fast to washing. The best washing fastness is obtained by oxidation of the leuco dye with sodium dichromate and acetic acid. Sodium bromate (NaBrO₃) is now more widely used as an oxidant, particularly in North America. It requires a small amount of metavanadate ion (VO₂⁻) as catalyst for the oxidation of the more resistant red-brown dyes. This catalyst can be prepared in situ during sodium bromate manufacture. Commercial products usually contain
this and some sodium nitrite to minimise stainless corrosion. Sodium bromate oxidation is carried out in dilute acetic acid solution at about pH 4.

Colour bronzing and crocking problems arise once a critical depth of shade has been exceeded. Deep shades must therefore be well soaped to remove residual surface colour. This improves shade stability, decreases bronzing and improves the colour brightness and washing fastness. Soaping is less critical in pale and medium depths. Unlike the quinone vat dyes, however, crystallisation of sulphur dye particles does not occur in this process. Excessively bronzy black dyeings can be treated with alkaline sodium sulphide solution to remove the surface pigment responsible for the bronzey appearance. Bronzing can be minimised by ensuring that the dye in the dyebath is always fully reduced, that the fabric is not over-exposed to air during dyeing, and that it is well rinsed immediately after dyeing. Blacks may be soaped with olive oil and soap.

Some dyeings are treated with copper sulphate, or with this and sodium dichromate, to improve the light fastness, and in some cases the wet fastness. Fabrics for use inside rubber articles should not be copper treated. Some yellow-brown dyes are treated with copper sulphate to improve light fastness but the effect is lost on washing. The use of chromium salts is now declining because of their adverse environmental impact.

Because of their dull colours, dyeings with sulphur dyes are often topped with the much brighter basic dyes. The sulphur dye pigment acts as a mordant for the cationic dyes. Dyeings with sulphur dyes may also be shaded with some sulphide stable direct dyes, but this tends to lower the washing fastness.

Alkylation of the leuco thiols under alkaline conditions with epichlorohydrin derivatives (3-chloropropene oxide) before oxidation renders them insoluble. Oxidation is then no longer required. Some dyes, however, may benefit from an oxidative treatment so as to develop the full colour. The alkylating agents may have high molecular weight or be polyfunctional so that the alkylated product has very good washing fastness in the presence of the peroxide compounds in domestic detergents.

17.12.4 Dyeing with soluble sulphur dyes

Large amounts of such dyes are sold in liquid form. They are of two types – water-soluble reduced leuco dyes, and solubilised sulphur dyes – the former being far more important. The water soluble leuco dyes are completely in solution and contain far less insoluble matter than a sulphur dye powder. This is beneficial in
package dyeing. They often still require a small addition of sodium sulphide or another reducing agent. These liquids contain the stabilised leuco dye, sodium sulphoxinate-formaldehyde or sulphide and sodium carbonate. The solubilised sulphur dyes are thiourea esters prepared from the leuco thiols with sodium sulphite (Scheme 17.5). They usually have low substantivity for cellulosic and are useful for package, padding and pad–jig applications. Reduction is necessary before or during dyeing and the usual aftertreatments are needed.

17.13 CONTINUOUS DYEING WITH SULPHUR DYES
Sulphur dyes are used for continuous dyeing of cotton goods using a pad–steam–wash process, with three groups of wash boxes for rinsing, oxidising and soaping. Padding may take place at up to 80 °C to reduce the substantivity of the leuco dye for the cotton fibres. This reduces the problems of selective absorption and the resulting initial colour tailing that it causes. As for other vat dyes, steaming is carried out in air-free saturated steam. Then the dyeing is rinsed at 40–60 °C and oxidised with sodium bromate plus metavanadate catalyst at pH 4 in the presence of acetic acid. In the remaining wash boxes, the best possible soaping and rinsing is done. For black dyes tending to produce sulphuric acid by oxidation on storage, a final soda ash rinse may be added. In some instances a better appearance results using a two-pad method. This involves padding with the sulphur dye suspension or solution, followed by intermediate drying, padding with sodium sulphide solution, steaming, and the usual aftertreatment sequence.

17.14 ENVIRONMENTAL CONCERNS
Waste sulphur dye baths, and the sulphide ion they contain, liberate hydrogen sulphide on acidification. These solutions cannot be directly released into water streams without treatment. Residual pad bath liquor from continuous dyeing is usually mixed with the residual oxidising bath liquor to oxidise the excess sulphide. Exhausted dyebaths can be oxidised with hydrogen peroxide. Oxidation of sulphide ions generates the less noxious thiosulphate and sulphate ions. This particular effluent problem can be partially solved by using glucose and caustic soda as the reducing agent but the vatting temperature must be 90–95 °C. This particular reducing system can be used with solubilised sulphur dyes, with leuco sulphur dyes as the additional reductant, and even with sulphur dyes, replacing part of the sodium sulphide.
One manufacturer has introduced new brands of low-sulphide dyes. Vatting is carried out with a new proprietary reducing agent. This acts by gradually reducing the sulphur dye as the dyeing temperature is increased so that the exhaustion is also controlled.

In addition to the present development of low-sulphide dyeing techniques using sulphur dyes, the use of chromium salts for oxidation and aftertreatment is gradually declining.

Sulphur based reducing agents such as sodium hydrosulphite and sodium sulphide are used in considerable excess to provide adequate control over the vatting and vat dyeing processes. The residues of these reducing agents and their oxidation products in the dyehouse effluent pose a serious environmental threat.

Many of the difficulties associated with vat and sulphur dye reduction can be overcome by using electrolytic reduction. Since vat dyes are not soluble in water, a reduction mediator is needed. This is for example a soluble iron(II)-amine complex that is stable in alkaline solution. It is reduced at the working cathode to the Fe(II) form, whose redox potential is sufficiently negative to permit complete reduction of the vat dye pigment to its soluble leuco derivative. The reformed Fe(III) complex is then reduced back to Fe(II) at the cathode (Scheme 17.7).

At the end of the dyeing process, the leuco compound can be re-oxidised and the insoluble vat pigment removed by filtration so that the remaining solution containing the mediator can be re-used. For sulphur dyes direct cathodic reduction is possible since a small amount of soluble leuco dye acts as the reduction mediator [2–4].

REFERENCES

CHAPTER 18

Cationic dyes

18.1 INTRODUCTION

Many of the initial synthetic dyes, such as Mauveine, had free basic amino groups capable of reacting with acids (Scheme 18.1). They were therefore originally named basic dyes. Molecules of these dyes are invariably organic cations and they are preferably called cationic dyes. They usually have brilliant colours and high tinctorial strength; some are even fluorescent. Many basic dyes are now obsolete because of their very poor light fastness on natural fibres but a few are still used for dyeing paper and leather and for making inks.

Cationic dyes will dye fibres with anionic sites by a process of ion exchange (Scheme 1.2). This is usually a simple direct dyeing process. Anionic auxiliary products must be avoided as they may precipitate cationic dyes in the form of an organic salt (Scheme 18.2). In dyeing protein fibres with cationic dyes, acids retard dye absorption by suppressing the dissociation of the anionic carboxylate groups in the fibres (Scheme 7.1), thus making the fibre more cationic and inhibiting adsorption of dye cations. Cationic dyes have very low substantivity for cotton unless excessive oxidation has generated anionic carboxylate groups. For dyeing cotton with cationic dyes, the cotton was usually mordanted with tannic acid fixed with tartar emetic. The insoluble, anionic tannin attracts coloured dye cations (Section 1.1.2), just as it repels dye anions when on a nylon surface after back-tanning (Section 13.9.7).

\[
\text{Dye}^{-\text{NH}_2} + \text{H}^+ \rightarrow \text{Dye}^{-\text{NH}_3^+}
\]

Scheme 18.1

\[
\text{Dye}^{(\text{aq})} + \text{Aux}^{(\text{aq})} \rightarrow \text{Dye}^{(\text{s})} - \text{Aux}^{(\text{s})}
\]

Scheme 18.2
Today, the major use of cationic dyes is in dyeing anionic acrylic and modacrylic fibres and, to a much lesser extent, modified nylons and polyesters. Dye adsorption by acrylic fibres involves interaction between anionic sulphonate and sulphate polymer end groups and the cationic dye molecules (Scheme 4.5). In some acrylic fibres, anionic carboxylate groups are also involved (Section 18.4.1). Disperse dyes do not build up well on acrylic fibres and are only useful for pale shades. Dyeings of natural fibres with cationic dyes invariably have poor fastness to light. In direct contrast to this, acrylic fibres dyed with cationic dyes exhibit fairly good light fastness, and good fastness to washing. The improved resistance to fading is because of the limited access of water and oxygen into the more hydrophobic acrylic fibres. Access of both water and oxygen enhance the rate of colour fading on exposure to light (Section 24.3.4). Good washing fastness of acrylic materials dyed with cationic dyes is usual since most washing procedures are at temperatures well below the glass transition temperature of the fibrous polymer and the dye is therefore less likely to diffuse out of the fibre.

18.2 CHEMICAL STRUCTURES OF CATIONIC DYES
Cationic dyes belong to a variety of different chemical classes. Many of the older basic dyes were di- and triphenylmethane, heterocyclic azine, oxazine or polymethine, or aminoazo compounds (Figure 18.1). In many cases, the cationic charge is extensively delocalised over the entire dye molecule. Typical anionic counter ions include chloride, oxalate (C\(_\text{2O}_4\)\(^{2–}\)) and tetrachlorozincate (ZnCl\(_4\)\(^{2–}\)) ions. Since the introduction of acrylic fibres in the 1940s, new cationic dyes have been developed specifically for dyeing these fibres. Many of these have quaternary ammonium groups with a localised cationic charge that is not part of the chromophore (Figure 18.1).

18.3 PREPARATION FOR DYEING ACRYLIC FIBRES
18.3.1 Preparing the material
Poor preparation of the goods is usually the major cause of poor quality dyeings and preparation should be of the highest quality consistent with the final price of the material. The preparation of acrylic fibre materials may involve desizing of woven materials, scouring and bleaching. Combined desizing and scouring are often possible since relatively soluble sizing materials such as modified starch or...
CATIONIC DYES

Polyvinyl alcohol are normally used. Scouring with weakly alkaline solutions of ammonia or trisodium pyrophosphate ($\text{Na}_3\text{HP}_2\text{O}_7$) is common. A non-ionic detergent is essential. Cationic auxiliary products may have substantivity for the anionic groups in the fibres and block dyeing sites whereas residues of anionic products will interact with and even precipitate the cationic dyes in the bath.

Acrylic materials sometimes have a slight yellow cast, usually a sign that drying was too severe. Bleaching is possible with sodium chlorite ($\text{NaClO}_2$) and formic acid or brightening with a fluorescent whitening agent. Some fluorescent whitening agents can be used in the presence of sodium chlorite, allowing combination of the two methods. Stabilisers that control chlorine dioxide emission (Scheme 18.3), such as borax or polyphosphates, should be used. A corrosion inhibitor such as sodium nitrate is essential when using steel equipment. Some cationic dyes are very sensitive to traces of chlorine and will rapidly fade giving poor colour yields, particularly when dyeing pale shades. An anti-chlor treatment

![Chemical structures of some typical cationic dyes](image)

Figure 18.1 Chemical structures of some typical cationic dyes
of fabric bleached with sodium chlorite may be necessary and small additions of sodium bisulphite or thiosulphate to the dyebath will avoid problems with cationic dyes sensitive to traces of chlorine in municipal water.

\[
\text{Scheme 18.3}
\]

18.3.2 Dyebath preparation

The dye powder is usually pasted with acetic acid and then mixed with boiling water. Cationic dyes with delocalised cationic charges are intensely coloured and it is essential to avoid dust escaping from the powders. Concentrated liquid dyes avoid this problem. Solid forms of these dyes are often not easy to dissolve because of their tendency to form gummy material. Preparation of a paste with methanol and addition of warm or hot water is sometimes a useful alternative. Some cationic dyes are not stable in boiling water. Many react with alkali to give colourless products such as the free amine from neutralisation of an ammonium ion group (reverse of Scheme 18.1), or a carbinol by reaction of the cationic group with hydroxide ion (Scheme 18.4). Dyeing with cationic dyes therefore invariably takes place in weakly acidic solution to avoid these problems.

\[
\text{Scheme 18.4}
\]

18.4 DYEING ACRYLIC FIBRES WITH CATIONIC DYES

18.4.1 Dyeing procedure

Acrylic fibres may contain a variety of different anionic groups. These include a limited number of terminal sulphate and sulphonate groups arising from the persulphate polymerisation initiator (Figure 3.2). In other types, there may be appreciable numbers of carboxylate groups from acrylic acid or similar comonomers added to the acrylonitrile before polymerisation (Section 4.4.1). These anionic groups are responsible for the substantivity of cationic dyes for such fibres. Figure 18.2 compares equilibrium dye adsorption as a function of pH for two types of acrylic fibres (A and B). Dyeing acrylic fibres with cationic dyes is carried
Figure 18.2 Equilibrium dye adsorption by acrylic fibres with only sulphate and sulphonate end-groups (a) and with carboxylate groups (b) out in weakly acidic solution containing acetic acid and sodium acetate and a non-ionic wetting agent and dispersant. A small amount of sequestrant ensures that heavy metals do not interfere with chemicals in the solution. The dye solution is often prepared by pasting with acetic acid, and a stable pH of 4.5 to 5.5 can be obtained by addition of sodium acetate to buffer the solution. Dyeing at around pH 5 suppresses the dissociation of any carboxylic acid groups in the fibre and thus controls the dyeing rate. Note the increased dye uptake of the acrylic fibre with carboxylic acid groups (b) in Figure 18.2 as the acid groups dissociate and become anionic above pH 6. The number of carboxylate groups in an acrylic fibre varies from one type to the next. Level dyeing requires strict control of the pH and dyeing temperature, as well as the use of cationic retarding agents. The latter initially block the anionic sites in the fibre and are gradually replaced by the more substantive dye cations. An addition of up to 2.5 g l\(^{-1}\) of anhydrous sodium sulphate helps to offset the negative surface charge and sodium ions weakly block anionic sites in the fibre. Both effects decrease the initial rate of dye absorption. Sodium sulphate is not as effective as cationic retarding agents that have some substantivity for the fibre.

Figure 18.3 shows a typical dyeing procedure. If dye additions are needed to give the correct shade, the bath temperature is first slowly reduced to below 80 °C. Acrylic materials are quite thermoplastic. They easily form crack marks and creases and texturised acrylic filaments also readily lose their characteristic...
bulk. After dyeing is complete, the bath is slowly cooled to 50–60 °C to avoid these problems. Rapid cooling by addition of cold water to the dyebath can be disastrous as it causes immediate setting of creases in the goods. The material is finally rinsed, and possibly given a mild scour with a non-ionic detergent and a little acetic acid plus a softening agent.

18.4.2 Problems in dyeing acrylic fibres with cationic dyes

Cationic dyes rapidly adsorb on all available surfaces of the acrylic fibres because of the polymer’s negative surface potential in water. Once the fibre surfaces are saturated, the rate of isothermal dyeing is independent of the bath concentration and of the liquor ratio since the rate of diffusion of dye into the fibre is slow. Addition of sodium sulphate to the dyebath suppresses the rapid strike as sodium ions counteract the negative charge on the fibre surface.

Above the dyeing transition temperature ($T_D$) under the actual dyeing conditions, cationic dyes tend to exhaust very rapidly over a small range in temperature. Great care is needed at temperatures just above $T_D$ to avoid unlevel dyeing. The rate of diffusion of the cationic dyes into the acrylic fibre is very slow below $T_D$ because of the absence of the required polymer chain mobility. The rate of dyeing increases rapidly above $T_D$, and can double for every 2.5–3.0 °C increase in temperature. The corresponding increases in temperature needed to
double the dyeing rates of nylon and polyester are typically 10 and 5 °C, respectively, but at higher temperatures for polyester. Once the acrylic fibre becomes accessible, very careful temperature control is required. For this reason, once the bath temperature reaches 70-75 °C, the rate of heating is usually significantly decreased (Figure 18.3).

The careful temperature control required when dyeing acrylic fibres with cationic dyes is necessary to avoid unlevel dyeings. These dyes on acrylic materials have at best poor migration ability. Some newer types of more hydrophilic cationic dyes have low molecular weights and lower substantivity. They migrate more readily but attempted levelling by extended heating, or heating to a higher dyeing temperature, is dangerous because of the thermoplasticity of the fibre.

If the acrylic fibre has a significant number of carboxylate groups present, the dyeing pH will greatly influence the dyeing rate. The rate of exhaustion will increase with increase in the pH as more carboxylic acid groups dissociate. Thus, it is important to know the characteristics of the particular acrylic polymer in advance.

### 18.4.3 Dyeing mechanism

Although a simple ion exchange mechanism explains many effects in the dyeing of acrylic fibres, the process is probably more complex than this. Over-dyeing is not usually a problem as the fibres rarely accept more dye than corresponds to the number of anionic sites. The sulphonate and sulphate groups do not change with variation of the dyebath pH but this is not true for carboxylate groups. In acidic solution, carboxylate groups are protonated and their negative charge neutralised. For dyeings carried out at constant pH, the Langmuir isotherm provides a good description of the dyeing equilibrium (Section 11.1.1). The number of anionic sites in an acrylic fibre \( C_{\text{max}} \) can be determined from the intercept of the graph of \( 1/C_f \) versus \( 1/C_s \) for a series of dyeings at equilibrium:

\[
\frac{1}{C_f} = \frac{1}{C_{\text{max}}} + \left( \frac{1}{K C_{\text{max}}} \right) \frac{1}{C_s}
\]

### 18.4.4 Dyeing retarders

The presence of either cationic or anionic auxiliary products in the dyebath controls the rapid strike and high rate of dying of cationic dyes on acrylic fibres. Cationic
retarders are organic ammonium salts with hydrophobic chains. Their adsorption on the fibre surface reduces the negative surface potential. They also compete with the cationic dye for anionic sites in the fibre, thus slowing the rate of adsorption. They have moderate substantivity for acrylic fibres and may even be adsorbed before the dye is added to the bath to decrease the strike. During dyeing, the cationic auxiliary in the fibre is gradually displaced by the cationic dye. Boiling in the presence of some cationic retarder may give some degree of levelling although this invariably increases the risk of damaging the thermoplastic material. Other types of retarder are cationic polymers that adsorb on the surface of the fibres, decrease the negative surface potential and prevent easy passage of the dye into the fibre.

Anionic retarders complex with the cationic dye in the bath (Scheme 18.2) and decrease the number of free dye molecules in solution. Such anion–cation complexes easily precipitate and an anionic agent may have a non-ionic component to keep the complex in dispersion. They are less widely used than cationic retarders. Boiling a dyeing in a blank bath containing an anionic retarder will remove some dye. For complete stripping, bleaching with hypo chloride in the presence of acetic acid at around pH 6 is possible.

18.4.5 Compatibility of cationic dyes

Dyeing on shade with mixtures of dyes is most successful when the dyes used are compatible with one another. Ideally, the colour of the dyeing builds up gradually as the dyes are adsorbed, but always with the same hue. The complex behaviour of cationic dyes in mixtures complicates the determination of their dyeing compatibility. The rate of dyeing of any given dye, under given conditions, often changes significantly when other dyes are present. The rate is also dependent on the type and amount of retarding agent present in the dyebath. The dyer must rely on the dye supplier for information on the behaviour of the dyes and must often conduct his own dyeing trials. Because many variables influence the determination of cationic dye compatibilities, different dye suppliers use different methods of evaluation.

The key parameters determining the compatibility of dyes are the fibre saturation value and the combination constant or compatibility value. Knowledge of these parameters facilitates the selection of compatible dyes. The fibre saturation value determines the amounts of cationic dye or cationic retarder that will saturate all the fibre's anionic sites. The combination constant or compatibility value is based on the rate of dyeing.
One standard test (AATCC Test Method 141 [1]) evaluates a dye’s combination constant or compatibility value \( k \), a number from 1 (rapid dyeing) to 5 (slow dyeing). Dyeings of a given cationic dye are carried out in mixtures with each dye of a standard series of five blue or five yellow dyes. The series selected will have a yellow or blue hue markedly contrasting with the test dye. Thus, a violet cationic dye would be tested in mixtures with the series of yellow dyes rather than the blue series. The five dyes in each standard series have compatibility ratings from 1 to 5. At pre-selected times during the dyeing trials with mixtures of the test and standard dyes, a piece of the dyed material is replaced by undyed material and dyeing continued. For each mixture of test dye and standard dye, the colours of the successively dyed samples are examined. The combination constant \( k = 1 \) to 5) for the test dye is that of the standard dye for which the series of dyeings are on shade. Compatible dyes should therefore have about the same \( k \) values. This type of information is available from the dye manufacturers.

Fibre saturation values give the number of anionic sites in the fibre (mmol kg\(^{-1}\)). This value ranges from about 25 up to 115 mmol kg\(^{-1}\). The fibre saturation value determines the % owf of cationic dye or retarder that will saturate all the anionic sites. These amounts can be calculated if the molecular weight, total cationic charge and purity of the dye or retarder are known. Consider a cationic dye powder containing 50% pure dye with a single positive charge and a molecular weight of 400 g mol\(^{-1}\). For an acrylic fibre with 25 mmol kg\(^{-1}\) of singly charged anionic sites, 2.0% owf of dye in the dyebath will saturate all the anionic sites if the dyebath exhaustion is 100%:

\[
\text{Mass of dye} = 25 \frac{\text{mmol}}{\text{kg}} \times 400 \frac{\text{mg}}{\text{mmol}} \times \frac{100}{30} = 20000 \frac{\text{mg}}{\text{kg}} = 2.0\%\ \text{owf}
\]  

Knowing how much dye will saturate the available sites in the fibre avoids excess dye adsorbed on the fibre surface, which leads to poor washing and rubbing fastness. When the total amount of dye is close to that required for fibre saturation, rapidly adsorbed dyes with low \( k \) values can block out slow dyeing dyes with high \( k \) values. For dyeing deep shades, the amount of cationic retarding agent is usually calculated so that its total charge plus that of the dye is that required to balance the charge of the fibre’s anionic sites. Use of more than this quantity of retarder is wasteful and may reduce the exhaustion. The effect of cationic retarders is greater for dyes of higher \( k \) value. One of the difficulties in assessing cationic
dye compatibility values is that the values are different in the presence of cationic and anionic retarders.

18.5 DYEING MODIFIED POLYESTERS AND NYLONS

Polyester modified to have anionic sites by incorporation of 5-sulphophthalic acid (Figure 4.3) has a more open polymer structure and dyes more readily with disperse dyes. Because of the anionic groups, it can also be dyed with cationic dyes. This modified polymer is also more easily hydrolysed and more sensitive to heat setting before dyeing. Heat setting is carried out at a maximum temperature of 180 °C. Dyeing is usually under pressure in weakly acidic solution at temperatures not exceeding 120 °C.

Cationic dyes diffuse quite slowly into modified polyester fibres, even with added carrier. As in dyeing with disperse dyes, the carrier serves to open up the internal molecular structure of the polymer to allow more rapid dye diffusion into the fibres. Any carrier residue must be completely removed after dyeing to avoid reduced light fastness. When dyeing two-colour effects on blends of cationic-dyeable and regular polyester, with a mixture of cationic and disperse dyes, sufficient non-ionic emulsifier must be present to prevent precipitation of the cationic dye by anionic dye dispersing and carrier emulsifying agents.

Cationic-dyeable nylon fibres are also produced by incorporation of 5-sulphophthalic acid during polymerisation. They are used mainly for tone-in-tone and multi-colour effects in batch dyeing carpets from blends of regular and modified nyons. Dyeing is carried out at the boil in weakly acidic solution. A non-ionic emulsifying agent prevents the cationic dyes from precipitating in the presence of the anionic acid dyes used for the regular nylon.

REFERENCES
19.1 INTRODUCTION

An ingrain dye is an insoluble pigment formed in situ by means of a chemical reaction between colourless, soluble precursors already inside the particular fibre. There are a number of different types of ingrain dye. The Colour Index includes ingrain or developed dyes under different headings:

1. azoic dyes prepared by impregnating the material with an alkaline solution of an azo coupling component and subsequently reacting this with an appropriate diazonium ion to produce an azo pigment within the fibres. The Colour Index lists Azoic Coupling Components and Azoic Diazo Components. The latter are given as the primary aromatic amines from which the diazonium ions are prepared;

2. condensed sulphur dyes (Colour Index Condensed Sulphur Dyes). These are polythiols that behave like the leuco compounds of sulphur dyes. On oxidation inside the fibre, they form an insoluble polymeric dye (reverse of Scheme 17.4);

3. black pigments based on the oxidation of aniline or other primary aromatic amines (Colour Index Oxidation Bases);

4. copper phthalocyanine pigments synthesised in the fibre by reaction of copper salts and appropriate isoindole derivatives under reducing conditions, or alternatively by precipitation of water-soluble copper phthalocyanine precursors (Colour Index Ingrain Dyes).

The developed azoic dyes used in cotton dyeing are the most important ingrain dyes but have gradually lost their market share. Reactive dyes have superseded them, apart from a few deep red and bordeaux combinations that give shades unobtainable with any other class of dye. The oxidation bases and ingrain dyes are used mainly for printing but are not particularly significant.
19.2 AZOIC DYES

19.2.1 Introduction
These usually are water-insoluble mono- or bisazo compounds precipitated in the fibre by reaction of a diazonium ion with a suitable coupling component. The name 'azoic dye' is somewhat confusing, since many soluble dyes are also azo dyes. The name 'azoic combination' is preferable.

The production of dyeings with Para Red, one of the first azoic combinations (1880), illustrates the basic principle of dyeing with this type of dye. Cotton fabric was first impregnated with an alkaline solution of 2-naphthol (1, in Figure 19.1). It was dried and then padded with an acidic solution of diazotised p-nitroaniline (2). A deep red pigment formed in the cotton fibres (3). A final soaping at the boil removed pigment particles adhering to the fibre surfaces. This gave the optimum fastness to washing, light and rubbing, although these were not outstanding. Intermediate drying was necessary because 2-naphthol has poor substantivity for cotton and tended to bleed out of the wet fabric into the diazonium ion bath causing pigment formation, particularly on the fibre surfaces. The introduction of coupling components with much higher substantivity for cotton overcame this problem, and also decreased the migration of the coupling component to the yarn surfaces during the intermediate drying.

![Figure 19.1](image)

Azoic combinations are still the only class of dye that can produce very deep orange, red, scarlet and bordeaux shades of excellent light and washing fastness. The pigments produced have bright colours, and include navies and blacks, but
there are no greens or bright blues. The actual hue depends on the choice of the
diazonium and coupling components. Their use on cotton today is more and more
limited, largely because of the success of fibre-reactive dyes for cotton. Black
shades on polyamide, polyester and acetate fibres are also often azoic combinations
(Section 15.5). For azoic dying of these artificially-made fibres, a dispersion of the
primary amine and coupling component is used. The fibres absorb these like
disperse dyes. The amine is then diazotised in the fibre and reacts with the
coupling component to give the azo pigment.

19.2.2 Coupling components

Azoic coupling components are often called Naphtols (note the difference in
spelling from naphthol), after Naphtol AS, the original commercial name of the
anilide of 2-hydroxy-3-naphthoic acid (beta-oxyo-naphthoic acid or BON acid).
Naphtol AS (CI Azoic Coupling Component 2) was introduced in 1912. Many
other Naphtols are also anilides of BON acid (Figure 19.2). The Naphtols are
phenols, soluble in alkaline solution and substantive to cotton, particularly in the
presence of salt. A cotton fabric impregnated with the Naphtol solution does not
usually require intermediate drying before development with the diazonium ion
solution. Their dyeings have better fastness properties than those of Para Red.
Deep red and bordeaux are the predominant shades obtained with azoic
combinations. The Naphtols used for yellow and orange azoic combinations are
usually arylamides of acetoacetic acid (Figure 19.2), which dissolve in dilute
alkaline solution as the enolate ions.

The anilides of BON acid are soluble in dilute NaOH solution and form the
corresponding naphtholate ion. These relatively small molecules are of only low to
moderate substantivity for cotton, but they diffuse rapidly into the fibres. In
general, the higher the substantivity the better the rubbing fastness as less azo
pigment forms on the fibre surfaces. The naphtholate ions are always coplanar and
preferably have elongated molecular structures. They behave essentially as
colourless, low molecular weight direct dyes. The substantivity increases with
increase in the molecular size of the naphtholate ion, but the diffusion rate in the
fibres and solubility in dilute aqueous alkali decrease. Addition of salt promotes
better exhaustion of the bath, more being needed for Naphtols of lower
substantivity. Low substantivity is preferred in continuous dying so that the bath
composition does not vary because of preferential absorption (Section 10.5.2). For
batch dyeing, the higher substantivity Naphtols give better bath exhaustion and the dyeings have better rubbing fastness.

Preparation of the naphtholate ion solution is a key step. Dissolving solid Naphtols requires care and the supplier’s recommendations for the amount of alkali, temperature and time should be adhered to. Aqueous alkaline solutions of Naphtols often contain a colloidal dispersion of the sodium naphtholate. The addition of protective colloids, or surfactants such as sulphated castor oil, minimises the risk of precipitation. The dissolution of the less soluble Naphtols is assisted by initially dissolving the solid in hot methanol, or by pasting it with a
solution of a dispersing agent, before addition to the aqueous alkali solution. Soft water is essential to avoid precipitation of the insoluble calcium and magnesium naphtholates. Many Naphths are available as liquids that only require dilution and additional alkali. Although the liquid forms are more expensive, their use does avoid many of the problems associated with bath preparation.

Sometimes, the addition of formaldehyde to a concentrated Naphtol solution at room temperature is recommended. This forms the 1-hydroxymethyl derivative that prevents hydrolysis of naphtholate ion to the insoluble free phenol. The 1-hydroxymethyl-2-naphthol is much more acidic than the original Naphtol because of the intramolecular hydrogen bond (4, in Figure 19.3). The hydroxymethyl group is cleaved during coupling with the diazonium ion.

Figure 19.3

Azoic dyeing usually involves a single coupling component and a single diazonium ion. To obtain a specific shade, a mixture of two Naphths of similar substantivity may sometimes be necessary, but usually with only a small amount of the second component. Mixtures of diazonium components are not used. The production of green dyeings with azoic dyes has always been a problem. No suitable combination of a single diazonium ion and single coupling component will generate a pigment of this colour. Combinations of components producing a mixture of blue and yellow azoic pigments are also not particularly satisfactory.

19.2.3 Diazo components

A solution of a diazonium ion requires diazotisation of a primary aromatic amine. These are available as the free amine base or as amine salts such as the hydrochloride. Commercial names can be confusing, and only give a guide to the colour obtained by coupling with typical Naphths. Fast Red GG, for example, is a name for p-nitroaniline (CI Azoic Diazo Component 37), whose diazonium ion gives a red pigment on coupling with simple anilides of BON acid. Many of the
amines used are simple substituted aniline derivatives with no ionic substituents. More complex amines give violet and blue shades.

The so-called Fast Colour Bases require diazotisation. This usually involves reaction of the primary aromatic amine in acidic solution or dispersion with sodium nitrite, at or below room temperature. Successful diazotisation requires careful weighing of all the chemicals and regard for the supplier’s recommendations. Diazotisation of a primary aromatic amine is often difficult and solutions of diazonium ions are inherently unstable. They undergo decomposition even at low temperature and particularly on exposure to light. Storing prepared diazonium ion solutions is not usually possible.

Because of the many difficulties that arise in the diazotisation reaction, dye manufacturers market a variety of stabilised diazonium components. These diazonium salts are soluble in water and are then immediately ready for the coupling reaction. Some of these products are stable diazonium ion salts such as borofluorides (R–N$_2$BF$_4$), naphthalene sulphonates (5, in Figure 19.4) or tetrachlorozincates (6). Diazonium ions can also be stabilised by conversion into a diazoamino compound with an amino acid (7) or into trans-diazotate ions (8).

Both 7 and 8 are stabilised forms of the phenyldiazonium ion (diazoised aniline). The formation of both diazoamino and diazotate derivatives (Scheme 19.1) is reversible and acidification of their solutions regenerates the diazonium ion. One

\[
\begin{align*}
&\text{(a) Borofluoride (5)} \\
&\text{(b) Naphthalene sulphonate (6)} \\
&\text{(c) Trans-diazotate (8)} \\
&\text{(d) Phenyldiazonium (7)}
\end{align*}
\]

![Figure 19.4](image) CI Azoic Diazo Component 17 (5); CI Azoic Diazot Component 18 (6); stabilised forms of the phenyldiazonium ion (7 and 8).
advantage of diazoamino or diazotate derivatives is that frequently both the stabilised diazonium component and the coupling component can be padded or printed onto the cotton together using a weakly alkaline solution. Subsequent treatment with an acidic solution liberates the free diazonium ion that then reacts with the coupling component to give the azoic pigment.

\[
\begin{align*}
D
\text{NN}^+ & + \text{H}_2\text{NRCO}_2\text{H} \rightarrow D
\text{NN}^+\text{HNRCO}_2\text{H} + \text{H}^+
n\text{DN}^+ & + \text{NaOH} \rightarrow \text{D} + \text{Na}^+ + \text{H}_2\text{O}
\end{align*}
\]

Scheme 19.1

19.3 APPLICATION OF AZOIC DYES

19.3.1 Batch dyeing methods

The production of dyed cotton using an azoic combination involves four steps:

1. absorption of the naphtholate ion by the cotton;
2. removal of the excess naphthol solution from the fibre surfaces;
3. treatment with the diazonium ion solution to bring about coupling;
4. soaping the fabric at the boil to remove superficial pigment, followed by rinsing and drying.

The process can be carried out in almost any type of dyeing machine determined by the form of the goods.

The depth of shade of an azoic dyeing is not always easy to predict. The amount of azoic pigment produced cannot be specified as a % owf as for other dyes. The depth of shade produced depends on the amount of coupling component in the cotton and hence on the substantivity of the naphtholate ion. This is usually low and dependent upon the liquor ratio and the quantity of salt added to the bath. To improve the substantivity, it is usual to limit the liquor ratio to relatively low values and to apply the coupling component from a bath at room temperature with additions of salt. The suppliers provide tables or graphs showing the relationship of the concentrations of coupling component in the solution and in the fibre. The procedure usually specifies all quantities and conditions. Rinsing the naphtholated
Fabric with alkaline brine removes excess coupling solution adhering to the fibres. If this is not done, azoic pigment forms in excessive amounts on the fibre surfaces giving a product with reduced fastness to rubbing and washing. The cotton material containing the naptholate ion must be kept cool and not allowed to dry out.

Coupling is carried out at room temperature using an excess of the diazonium ion component. It is common to add some salt to the development bath to prevent bleeding of the coupling component into the solution and formation of suspended azoic pigment. Addition of a non-ionic surfactant assists penetration of the diazonium ion into the cotton and helps to disperse any pigment that forms in the solution so that it does not deposit on the fibre surfaces. The rate of coupling varies widely depending on the electrophilic nature of the particular diazonium ion and depends on the pH value of the bath. This must be close to the optimum value. If the solution is too acidic, coupling may be very slow. If it is too alkaline, the diazonium ion may react with water or decompose. The addition of buffering salts, such as sodium acetate, bicarbonate or phosphate, helps to neutralise the strong acid in the diazonium ion bath. The more electrophilic high-energy diazonium ions have electron-attracting substituents and can couple at pH values as low as 4–5. Under these conditions, the concentration of free naptholate ion is very small. As the electrophilic nature of the diazonium ion decreases, the pH of the coupling bath must increase to allow a higher concentration of free naptholate ion. Low energy diazonium ions only couple in weakly alkaline solution around pH 8 or higher.

After coupling, the goods are rinsed with a weakly acidic solution and then with water. Soaping under alkaline conditions with good mechanical action is essential to remove azoic pigment that has formed or deposited on the cotton fibre surfaces. This ensures the optimum fastness to washing and rubbing. It also helps to develop the true shade of the dyeing. During soaping there is often a noticeable change in shade of the dyeing associated with changes in the physical form of the pigment particles within the fibres. This may involve both crystallisation and aggregation of the particles. Soaping helps to achieve the maximum light and chlorine fastness.

Correction of faulty dyeings by stripping is not easy. Treatment with an alkaline solution of hydros in the presence of a cationic surfactant destroys the colour of the azoic pigment by reduction of the azo group. It is essential to remove the primary amines produced to avoid coloration from their oxidation by air. Boiling alkaline solutions will remove most Naphtols.
19.3.2 Continuous dyeing methods

A variety of procedures are used for the continuous dyeing of cotton fabrics with azoic combinations. Some involve continuous padding of the fabric with a solution of the coupling component followed by batch development and soaping in a dyeing machine.

A pad–dry–pad process is fairly common. For padding with an alkaline solution of the coupling component, good fabric absorbency and effective size removal from the warp are essential. The water used should also be soft since calcium and magnesium ions readily precipitate insoluble salts of the naphtholate ion. Even though the naphtholate ions are usually of only low to medium substantivity, a small pad trough is used and padding with a solution as hot as 80 °C is common. This decreases the substantivity even further, minimises bath concentration changes and tailing and ensures complete solubility of the naphtholate and its good penetration into the cotton. Intermediate drying of fabric padded with a solution of a low substantivity Naphtol minimises bleeding and azo pigment formation in the development bath. Addition of salt to the Naphtol solution helps to suppress migration of the coupling component during drying. The impregnated fabric should not be over-dried, to ensure rapid re-wetting in the development pad bath. This second pad bath, with the diazonium ion solution, may contain a non-ionic surfactant to ensure rapid fabric re-wetting and dispersion of any azo pigment formed in the bath. Coupling takes place in a bath at a pH usually between 4.0 and 6.0 at 20 °C, depending on the electrophilic nature of the diazonium ion. After padding with the diazonium component, the fabric will be skyed for a minute or so to allow time for the coupling reaction. The aftertreatment involves the usual combination of rinsing and good soaping.

The application of azoic combinations to cotton fabrics such as terry cloth by a wet-on-wet pad method is also popular. The fabric is padded with a solution of the coupling component at 80 °C and skyed for up to a minute. This allows the coupling component to penetrate into the fibres, and cooling of the fabric to the point that there will be no thermal decomposition of the diazonium ion solution in the next stage. Padding with a solution of the diazonium ion immediately follows before skying again to complete development. The use of the more substantive Naphtols prevents bleeding into the second, diazonium ion bath. Soaping with a solution of a non-ionic surfactant and sodium carbonate is carried out in either a rope or open-width machine.
In azoic dyeing, the dyer must choose appropriate components to produce the required shade. He must select the method for application of the coupling component and calculate the initial concentration required in the bath. This usually involves considering which Naphtols have the appropriate substantivity for the application method selected and which will give a shade close to the desired colour with appropriate diazonium ion developers. A method of preparing the diazonium ion solution must be selected and its concentration calculated. Finally, the amounts of alkali for the coupling component solution and the amounts of acid and buffers for the development bath must be calculated. Without prior experience, this is a formidable task given today's greater emphasis on being able to dye on shade at the first attempt. Fortunately, the chemical suppliers provide much practical information to make these steps as easy as possible. Even so, the dyer must optimise the diazotisation and coupling steps and pay attention to the conditions of soaping to obtain a dyeing with the correct shade and optimum fastness.

19.4 FASTNESS PROPERTIES OF AZOIC DYEINGS ON COTTON

Correctly prepared dyeings with azoic combinations on cotton have fastness properties often comparable, or only slightly inferior, to those produced using quinone vat dyes. They complement the vat dyes because of the wide range of orange, red and bordeaux shades that they provide.

The fastness to washing of azoic combination dyeings on cotton is usually very good to excellent but only after careful elimination of particles of azo pigment loosely adhering to exposed fibre surfaces. Intermediate drying or rinsing of fabric containing the Naphtol, and the soaping of the final dyeing, are key processes ensuring optimum fastness. The same argument applies to rubbing fastness. Deep dyeings that have not been well soaped easily transfer colour onto adjacent white fabric, even under conditions of gentle rubbing.

There are two other problems associated with the fastness properties of azoic combinations on cotton. In pale shades, the dyeings often have much reduced light fastness, particularly under humid conditions. Some sensitive azoic combinations also give dyeings of only fair resistance to chlorine and peroxide bleaching. Table 19.1 shows the typical variations in fastness grades for azoic dyeings.
Table 19.1 Typical fastness properties of azoic dyeings

<table>
<thead>
<tr>
<th>CI Diazo component</th>
<th>CI Coupling component</th>
<th>Hue</th>
<th>Soda boiling</th>
<th>Light</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>2</td>
<td>Yellowish red</td>
<td>1.2</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>37</td>
<td>7</td>
<td>Red</td>
<td>3.4</td>
<td>5.6</td>
<td>4.5</td>
</tr>
<tr>
<td>37</td>
<td>23</td>
<td>Black</td>
<td>2 - 3</td>
<td>7</td>
<td>3.4</td>
</tr>
<tr>
<td>42</td>
<td>13</td>
<td>Bordeaux</td>
<td>4 - 5</td>
<td>6.7</td>
<td>4</td>
</tr>
</tbody>
</table>

19.5 OTHER TYPES OF INGRAIN DYE

19.5.1 Oxidation bases

Oxidation bases represent a type of ingrain dye that finds limited application, mainly in cotton printing. They give intense blacks of excellent fastness to washing and light; comparable shades with black vat dyes require uneconomical quantities of dye. The major oxidation dye is known as Aniline Black. The cotton fabric is impregnated with a solution of aniline hydrochloride, appropriate oxidising agents and an additional acid. 'Ageing' of the goods occurs on heating in air at around 95 °C. During this process, vaporisation of the free amine and the acid poses an environmental problem. After ageing, a chroming treatment using a solution of potassium dichromate develops the characteristic full black. This completes the oxidation reaction and avoids 'greening' of the black shade on exposure. The dyeing is finally well soaped. The oxidation of aniline generates a high molecular weight, insoluble pigment of complex chemical constitution. Other typical oxidising mixtures include potassium ferrocyanide and sodium chlorate, as well as vanadium salts. The major difficulties are avoiding tendering of the cotton under the hot acidic conditions and ensuring that the pigment forms predominantly inside the fibres and not on their surface, the latter leading to poor rubbing fastness.

In addition to aniline salts, derivatives of 4-aminodiphenylamine are also used. This has the advantage of not requiring the chroming treatment. Oxidation bases find their major textile application in printing and in the dyeing of hair and fur.
19.5.2 Other ingrain dyes

Condensation dyes are usually organic thiosulphate derivatives, absorbed by cotton fibres and subsequently insolubilised by treatment with an alkaline solution of sodium sulphide. The reactions involved are illustrated in Scheme 19.2.

\[
\begin{align*}
2\text{Dye} + S_{2}\text{O}_3^{2-} & \rightarrow \text{Dye-S-S-Dye} + 2\text{SO}_3^{2-} \\
\text{Dye-S-S-Dye} + S_{2}\text{O}_3^{2-} & \rightarrow \text{Dye-S-S-Dye} + S_2\text{O}_5^{2-} \\
\text{Dye-S-S-Dye} + S_{2}\text{O}_3^{2-} & \rightarrow \text{Dye-S-Dye} + S_2\text{O}_5^{2-} \\
2\text{Dye-S} + O_2 + 2H^+ & \rightarrow \text{Dye-S-S-Dye} + H_2O_2
\end{align*}
\]

Scheme 19.2

The former Alcian dyes (ICI) were water-soluble isothiourea derivatives of copper phthalocyanine bearing chloromethyl substituents. They dyed cotton directly and aftertreatment with an alkaline solution precipitated the final insoluble pigment (Scheme 19.3).

\[
\begin{align*}
\text{CP-CH}_2\text{-Cl} + S_{2}\text{O}_3^{2-} & \rightarrow \text{CP-CH}_2\text{-S-S-C} + \text{Cl}^- \\
\text{CP-CH}_2\text{-S-S-C} + H^+ & \rightarrow \text{CP-CH}_2\text{-OH} + S_{2}\text{O}_5^{2-}
\end{align*}
\]

Scheme 19.3

The phthalogen dyes are precursors of copper phthalocyanine, which is generated in the fibre by a complex chemical reaction (Figure 19.5). For example, impregnation of cotton with di-imino-isouindoline in the presence of a special
reducing solvent and a copper salt or copper complex, followed by heating, generates copper phthalocyanine pigment. The final dye or print has excellent fastness properties.

**Figure 19.5** Formation of copper phthalocyanine from appropriate precursors

**REFERENCE**

CHAPTER 20

Union dyeing

20.1 FIBRE BLENDS

For the seven major types of textile fibre (wool, cotton, viscose, acetate, nylon, polyester and acrylic – given in bold face in Table 1.1, Section 1.2.1), there are 21 possible blends, or combinations, of two different components. This number excludes any blends of fibres of the same generic type such as two differentnylons. For each binary mixture, there is obviously a vast choice of the proportions of the two component fibres. For combinations of three fibres, the number of possibilities is very much larger. The major commercial blend by far is cotton/polyester, estimated to consume about 15% of world fibre production. Other important combinations include cotton/nylon and wool/polyester. In addition, the dyeing of blends of nylon or polyester variants is becoming more popular, especially in the USA.

At one time, wool/cotton fabrics were called unions and the dyeing of fibre blends became known as union dyeing. This chapter only covers dyeing of the most important blends. The dyeing of cotton/polyester blends, and of one or two other types, will serve to illustrate the principles of union dyeing. In general, the methods used for union dyeing are similar to those used for dyeing the individual component fibres with the particular types of dyes selected. This is so because many binary blends are mixtures of a synthetic and a natural fibre. In such cases, the type of dye selected to dye one fibre in the blend often does not significantly colour the other component. In other words, there is minimal cross-staining.

The actual distribution of the different fibres is an important characteristic of a fibre blend. For example, a woven cotton/polyester fabric may consist of a polyester filament warp and a spun cotton filling, or of yarns spun from intimate blends of staple polyester and cotton fibres. Many speciality yarns of complex construction, such as core spun yarns, are also blends of fibres. Different fibres are combined and assembled into a fabric for both aesthetic and functional effects. The blending of expensive fibres with cheaper ones often has economic advantages. Many blends provide fabrics with superior performance. This is particularly true for materials containing a mixture of natural and synthetic fibres where the desirable properties of both types of fibre contribute to the quality. For example, the polyester in a
cotton/polyester fabric improves the tensile strength, abrasion resistance and dimensional stability, while the cotton provides reduced pilling, good moisture absorbency and wearer comfort. The polyester also minimises the loss of tear strength and abrasion resistance that occurs on treating cotton with crosslinking agents in the presence of acid catalysts.

The four main classes of dyes are:
(1) anionic acid dyes;
(2) cationic dyes;
(3) the various kinds of anionic dyes for cellulosic fibres;
(3) disperse dyes.

This leads to six major binary combinations of these dye types. Table 20.1 lists the fibre blends that can be dyed with these combinations plus those dyed with acid dyes alone. Because of the significance of union dyeing, dye manufacturers go to considerable lengths to develop and recommend suitable combinations of dyes, in some cases even marketing ready-made mixtures.

Table 20.1 Important fibre blends that can be dyed with the major dye combinations

<table>
<thead>
<tr>
<th>Dye type combinations</th>
<th>Fibre blends that can be dyed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid dyes</td>
<td>Nylon/wool, nylon/cationic nylon, nylon/urethane</td>
</tr>
<tr>
<td>Acid dye/basic dye</td>
<td>Nylon/anionic nylon, nylon/acrylic</td>
</tr>
<tr>
<td>Acid dye/cotton dye</td>
<td>Nylon/cellulose, wool/cellulose</td>
</tr>
<tr>
<td>Acid dye/disperse dye</td>
<td>Nylon/polyester, wool/polyester</td>
</tr>
<tr>
<td>Basic dye/cotton dye</td>
<td>Acrylic/cellulose</td>
</tr>
<tr>
<td>Basic dye/disperse dye</td>
<td>Acrylic/polyester, anionic polyester/polyester</td>
</tr>
<tr>
<td>Cotton dye/disperse dye</td>
<td>Cellulose/polyester, cellulose/acetate</td>
</tr>
</tbody>
</table>

20.2 UNION DYEING

In union dyeing, there are several possibilities for colouring the different fibres:
(1) solid shade dyeing – all the fibres are identically coloured;
(2) reserve dyeing – at least one fibre is undyed and remains white;
(3) cross-dyeing – the different fibres are dyed different hues;
(4) tone-in-tone dyeing – the different fibres have the same hue but with different depths.
Union dyeing often involves colouring each fibre component separately using appropriate dyes in two different dyebaths. This will be the longest type of union dyeing process. Ideally, the dyeing of each type of fibre is so selective that the dyes for colouring one fibre completely reserve the other. This is rarely the case. Some of the dyes selected for colouring one component of the blend often stain the other type of fibre. Such cross-staining must be distinguished from cross-dyeing. Staining of a fibre implies that the dye is not well fixed and the colour will have poor fastness properties. In most union dyeing, therefore, minimising the degree of cross-staining is essential.

It is obviously desirable that union dyeing takes less time than that required for dyeing each fibre in separate steps. Direct dyeing processes, in which both fibres are dyed simultaneously with a mixture of different or similar types of dyes in a single bath, are more economical. A number of factors, however, must be considered. These include:

1. the colour effects and fastness properties required;
2. the compatibility of different dyes in the dyebath;
3. the degree of anticipated cross-staining of each fibre;
4. the influence of the dyeing conditions on the different fibres present;
5. the stability of the dyeings to finishing processes;
6. the type and availability of dyeing equipment;
7. the process costs.

One-bath union dyeing to give a solid shade is difficult to achieve and there are few union dyeing processes of this type. For example, there are several important limitations in the dyeing of unions containing wool or cotton because of their different sensitivity to alkalis and acids. Thus, the cotton in cotton/wool blends cannot be dyed with vat dyes because the high alkalinity required for the leuco dye solution causes extensive wool degradation. Large amounts of cotton/polyester blends are still dyed in two separate processes, one for application of disperse dyes to the polyester, followed by a second dyeing of the cotton with reactive or direct dyes.

20.3 DYEING COTTON/POLYESTER BLENDS

20.3.1 Introduction

There is a major market for 65/35 and 50/50 polyester/cotton fabrics for a variety
of end-uses, in weights ranging from light shirting to heavy industrial fabric. A variety of different batch and continuous dyeing processes are used for these. The dyeing of blends of polyester with other cellulosic fibres such as viscose and linen follows much the same principles outlined here, although there are some slight differences in the actual details.

The dyeing properties of polyester and cotton fibres are quite different and most of the dyeing methods for their unions involve separate steps for the colouring of the two fibres. The polyester component is invariably dyed first with a mixture of disperse dyes. For the cotton, there is a choice of dyes, the actual selection depending on the desired colour, the type of finishing required, the demanded fastness properties, the costs and the type of machinery available. The cotton is usually dyed with reactive, direct, sulphur, vat, or azoic dyes. The use of the latter three types is decreasing because of increased costs and environmental problems. The reactive/disperse dye combination for dyeing cotton/polyester clothing fabrics is very popular. If the cotton is dyed first, subsequent pressure dyeing of the polyester at 120–130 °C can change the shade of the dyed cotton because the cotton dyes are less stable at high temperatures. Dyeing the polyester before the cotton allows an intermediate reduction clearing of any disperse dye on the polyester surface or remaining in the cotton (Section 15.7.4). An alkaline solution of hydros destroys several types of cotton dyes so that reduction clearing is precluded after dyeing the cotton. In addition, once the polyester is dyed any detrimental effects of required cotton dyeing assistants such as alkali and salt on the disperse dyes are avoided.

Cross-staining of the cotton by disperse dyes can be a problem. The stained cotton has poor light and washing fastness and the weakly held disperse dyes will transfer colour to other synthetic fibres such as nylon during washing. For deep shades, alkaline scouring, or preferably reduction clearing with alkaline hydros and a non-ionic detergent, removes the disperse dyes staining the cotton. Because cotton crosslinking agents used in the finishing of cotton/polyester fabrics require the use of relatively high curing temperatures, the disperse dyes used for the polyester must be of the types that have higher sublimation fastness. Therefore, high-energy disperse dyes are preferred (Section 15.7.6). For fabrics with more than 60% polyester, the cotton component may not even be dyed if the required shade is only pale and the two fibres are well blended in the yarn.

As always, careful fabric preparation is essential for production of high quality dyeings. The aim is to produce a fabric that is easily wetted and absorbs dyes as uniformly as possible. It is imperative that singeing does not produce small masses
of melted polyester on the fibre ends since these tend to dye more deeply than the fibres resulting in a fabric with a spotty appearance. Heat setting the polyester before dyeing, to stabilise the fabric dimensions, must be uniform since it influences both the rate and extent of dyeing with disperse dyes. Heat setting after dyeing helps to remove creases in the fabric and to set its final dimensions. It can, however, cause thermal migration of the disperse dyes in the polyester fibres. In the case of poorly penetrated fibres, disperse dyes may migrate further into the polyester fibre interior, thus deepening the shade. Alternatively, if any hydrophobic chemical such as non-ionic surfactant or fabric softener remains on the polyester fibre surfaces, disperse dyes may migrate into this layer, in which they are very soluble. This results in greater ease of colour removal by washing or rubbing during use, and is undesirable.

In many cases of union dyeing, the dyes and dyeing conditions for colouring one of the fibres influence the other fibre and its dyes. The major areas of concern are:

1. the degree of cross-staining. Although disperse dyes will stain cotton, the anionic cotton dyes usually completely reserve the polyester. The disperse dyes selected should be those that give minimal cotton staining;
2. interactions between dyes and auxiliaries when present in the same bath. For example, many disperse dyes are not stable under the alkaline reducing conditions used in leuco vat dyeing. The salt and alkali required for dyeing cotton with reactive dyes often have a deleterious effect on the dispersing agent for disperse dyes and cause particle aggregation;
3. the conditions for fixation or aftertreatment of one type of dye on the other types often limits the processing methods that are possible. Thus, if direct dyes are used for continuous dyeing in combination with disperse dyes they must be stable to the high temperatures used in the Thermosol process. This factor influences when reduction clearing can be used. It is not possible to clear disperse dyes staining the cotton with an alkaline hydrosol solution if the cotton is already dyed. All the types of dyes used to colour cotton will be reduced under these conditions and the colour destroyed.

Even when staple polyester is the predominant fibre in intimate blends with cotton, the cotton fibres have a tendency to migrate to the yarn surfaces and have higher visibility. The colour and the fastness properties of the dyed cotton are therefore important, even though it is the minor component.

One of the major problems in dyeing cotton/polyester fabrics is that of colour control. This is true for cross-dyeings and for solid shades. To examine the colours
of the individual fibres after dyeing, they must be separated. This is not easy. For simple evaluation of dyeing, small swatches of 100% polyester and 100% cotton fabrics, with characteristics close to those of the fibres in the blend, can be sewn onto the cotton/polyester material and their colours examined after dyeing. This avoids having to separate the two kinds of fibres. Alternatively, a widely used technique is to evaluate the colour of the dyed blend and then to dissolve out the cotton with 70% aqueous sulphuric acid. The polyester is unaffected by this and a polyester ‘skeleton’ remains, the colour of which can be examined. The colour of the cotton is assessed from the difference between the colours of the original fabric and the residual polyester skeleton.

Because a mixture of dyes is needed for dyeing this type of fibre blend, and because there are a number of potential problems, consultation with a dye manufacturer is recommended in selecting dyes and processes. Suppliers are able to recommend disperse dyes that minimise staining of the cotton, suitable dyes for the cotton, and point out inappropriate dye combinations.

### 20.3.2 Batch dyeing of cotton/polyester

Since the dyeing of polyester is invariably carried out at 120–130 °C under pressure, enclosed beam and jet dyeing machines are widely used for dyeing cotton/polyester blend fabrics. For lightweight materials in beam dyeing machines, the multiple layers of the fabric on the beam must be permeable to the circulating dye liquor. Knit goods do not have adequate dimensional stability for continuous dyeing and are often dyed in jet machines. Good desizing, scouring and bleaching are essential for bright or pale shades, and are usually carried out in the dyeing machine before the actual dyeing. Heat setting at 180–200 °C for 30–40 s reduces pilling and increases dimensional stability and crease recovery.

A dyeing carrier is not essential but will assist levelling of disperse dyes on the polyester. To minimise staining of the cotton by the disperse dyes, it is common practice to drain the dyeing machine while the liquor is still at high temperature. Under these conditions, most of the unexhausted disperse dyes are still in solution. Cooling the bath before draining tends to cause precipitation of dyes on the fabric. Unfortunately, some disperse dyes do exhibit substantivity for cotton, but this is low if the dye bath is above 100 °C. In the case of jet dyeing machines, blowing out the exhausted dye liquor at high temperature may not be possible because of the risk of setting creases into the fabric. In this case, the bath is cooled slowly and then drained at the highest possible temperature that avoids creasing.
To minimise staining of the cotton and the need for clearing, dye selection is important. The use of jet dyeing machines allows low liquor ratios, reduced chemical and energy requirements and good colour reproducibility. A liquor-to-goods ratio of say 10:1 for a 65/35 polyester/cotton fabric represents a liquor ratio of 1000/35 or 28:1 with respect to the cotton. This high ratio for the cotton clearly has an influence on the exhaustion of the cotton dyes, particularly reactive dyes that may have low substantivity for cotton.

### 20.3.3 Disperse/reactive dye combinations

For bright shades of superior washing fastness, reactive dyes are the best choice for colouring the cotton in a blend with polyester, despite their greater cost for deep dyeings.

There are four major types of process used for the batch dyeing of cotton/polyester materials using a combination of reactive and disperse dyes. There are also a number of variants designed to take advantage of specific dye products. Most procedures are quite lengthy, the major problem being the long times needed for complete removal of the hydrolysed reactive dyes from the cotton.

The most conservative method uses four separate steps:

1. dye the polyester with the disperse dyes at 130 °C;
2. reduction clear to remove any disperse dyes staining the cotton;
3. apply the reactive dyes to the cotton;
4. rinse and scour to remove hydrolysed reactive dyes from the cotton.

The overall process can take as long as 10–12 h. The required time is less if the reactive dyes are added to the cooled exhausted disperse dye bath without draining, re-filling and reduction clearing. Some clearing of loosely held disperse dye particles from the fabric occurs during scouring to remove unfixed reactive dyes from the cotton.

In the reversed form of this two-bath process, the reactive dyes are applied first, the fabric rinsed with warm water to remove salt and alkali from the cotton, and then the polyester is dyed with the disperse dyes under pressure. The high temperature dyeing of the polyester helps to eliminate much of the residual hydrolysed reactive dye from the cotton. Pressure dyeing the polyester may require a bath pH of 6.5 to minimise reactive dye–fibre bond hydrolysis during dyeing at 130 °C. It is essential that the disperse dyes do not significantly cross-stain the cotton since the usual hydros reduction clearing is not possible without some
attack on the reactive dyes already present on the cotton. Some types of disperse dyes can be cleared by alkaline scouring (Section 15.7.4) so that the reactive dyes are not affected. This process only takes 7–8 h.

One rapid single-bath dyeing method adds both types of dyes to the initial dyebath set at pH 6.5. The solution is heated to 80 °C and Glauber's salt added to aid exhaustion of the reactive dyes onto the cotton. Dyeing is then completed at 130 °C for the polyester component. The bath is then cooled and alkali added to fix the reactive dye to the cotton. A final scouring is required. The dispersion of disperse dyes must be stable to salt and the reactive dye must have good stability in the neutral bath at high temperature or be capable of fixation under neutral conditions (NT reactive dyes). Cross-staining of the cotton must be minimal because reduction clearing is impossible. Obviously, careful dye selection is essential. This process takes up to about 5 h. Figure 20.1 compares the two- and one-bath dyeing methods.

Selected reactive and disperse dyes will dye cotton/polyester fabrics using a single dyebath initially buffered at pH 9.0–9.5 and then heated to 125 °C. The dyeing pH is lower than is usual for fixation of the reactive dyes but the method uses a high dyeing temperature to compensate for this. Not many disperse dyes are

Figure 20.1 Rapid stepwise and all-in-one dyeing processes for cotton/polyester (time of rinsing and scouring not included)
stable at 125 °C in a dispersion with a pH above 9. The overall dyeing time is just over 5 h.

By using single-bath dyeing processes with combinations of reactive and disperse dyes, it is possible to reduce dyeing times. The major limitation in this respect is the long time required for removal of hydrolysed reactive dyes from the cotton. The reactive dyes must also be stable to high temperature dyeing if they are applied together with the disperse dyes. In addition, colour reproducibility of the cotton fibres is more difficult when using reactive rather than simpler dyes such as direct dyes.

20.3.4 Disperse/direct dye combinations

This combination allows relatively simple dyeing methods and the use of the less expensive direct dyes. Because of the lower fastness to washing of direct dyes on cotton, complete clearing of the disperse dyes staining this fibre is less essential.

There are two major methods for dyeing cotton/polyester with a combination of direct and disperse dyes. In the two-bath method, the polyester and cotton are dyed separately using the appropriate dyes. Disperse dyes are used for the polyester, dyeing at 130 °C under pressure. For medium and heavy shades, an alkaline reduction clear with hydros solution reduces and removes azo and anthraquinone disperse dyes staining the cotton fibres. After rinsing and neutralising the fabric, the direct dyes are applied to the cotton at 90 °C, with addition of salt if required. This two-bath dyeing cycle takes about 6 h.

In the rapid one-bath dyeing method, dyeing takes place with a mixture of disperse and direct dyes at 130 °C. This results in lower initial exhaustion of the direct dye onto the cotton but good levelling. The bath is then cooled to 80–90 °C and the direct dye further exhausted by addition of Glauber’s salt. The bath is drained at 60–70 °C, and the fabric given two cool rinses. The total time required is about 4 h. The direct dyes used must be stable at 130 °C and the disperse dye should give minimal cross-staining of the cotton. Reduction clearing of any disperse dye staining the cotton destroys the direct dyes. This process is therefore less suitable for deep shades.

A major problem with using direct dyes on cotton is the poor washing fastness of deep dyeings, which normally only satisfies the lowest requirements. The washing fastness improves after the usual aftertreatments (Section 14.5), or after resin finishing. The latter provides shrinkage control and dimensional stability for knit goods and crease resistance for woven fabrics. The polyester avoids the usual
losses of tear strength and abrasion resistance of the cotton with these resin finishes. Cationic fixatives (to improve the washing fastness of the direct dyes on the cotton) and softeners, can alter the shade of the dyeing and decrease the light fastness. The possibility of thermal migration of the disperse dyes from the polyester fibres into any hydrophobic softener on the fibre surface during final drying and curing must also be considered. Any disperse dye transferred into the surface layer of softener is easily removed during use.

So, when considering a combination of disperse and direct dyes for dyeing a cotton/polyester blend, the fastness properties of the final dyeing are often decisive. Direct dyes are more likely to be used in combination with disperse dyes for colouring polyester/viscose fabrics since the washing fastness of direct dyes on viscose is somewhat better than on cotton. Dyeing in a jet machine preserves the characteristic soft handle of this type of fabric.

20.3.5 Disperse/vat dye combinations
Cotton/polyester can be dyed with a mixture of vat and disperse dyes using a single-bath dyeing process. Both types of dyes are added at the beginning of the dyeing cycle and, after the initial temperature increase, dyeing of the polyester is completed at 130 °C. Some dye producers sell ready-mixed vat and disperse dyes that reduce the number of required weighings. Shade control may be more difficult with these. Additional dispersant maintains the dispersion of both types of insoluble dye. Some vat dyes, of lower molecular weight, significantly stain the polyester component, and should be avoided.

After dyeing at 125–130 °C, the cotton is already pre-pigmented with the vat dye. The bath is then cooled and reduction of the vat dye carried out at around 60–70 °C by addition of caustic soda and hydros. The chemicals for vatting do not affect disperse dyes since ionic species do not penetrate into the hydrophobic polyester fibres. Reduction of the vat dye to the substantive leuco compound for dyeing of the cotton and reductive clearing of superficial vat and disperse dyes from the fibre surfaces occur simultaneously. The dyeing is then rinsed and the leuco vat dye oxidised. The usual soaping follows. It is best to use closed, fully flooded dyeing machines to minimise oxidation of the leuco vat dye. The process requires about 5 h. Some vat dyes give better results when added after the pressure dyeing of the polyester, but this takes longer because pre-pigmentation of the cotton fibres takes more time. This latter process is useful if staining of the
cotton by the disperse dyes is heavy because a reduction clearing can be carried out before the vat dyes are added to the bath.

20.3.6 Disperse/sulphur dye combinations
Because of the low price of sulphur dyes, this combination is useful for dyeing deep shades where the fastness requirements are less demanding. A two-bath dyeing procedure is common, initially dyeing the polyester with disperse dyes under pressure. The cotton is dyed in the second bath with the leuco sulphur dye maintained in solution with some sodium hydrosulphide rather than sodium sulphide, which can attack the polyester fibre. The reducing conditions help in clearing disperse dye from the cotton. Finally, the dyeing is rinsed, the leuco dye oxidised and the fabric well soaped. The process takes a long time but is useful for relatively inexpensive dull, deep shades. The reversed procedure, in which the cotton is first dyed with the sulphur dye, is not recommended because the alkaline solution must be completely neutralised before application of the disperse dye.

20.3.7 Semi-continuous dyeing methods
This type of process offers high productivity for batches of material that are larger than is usual for exhaust dyeing but too small to justify fully continuous operation. There are a number of possible variants. In the case where the polyester is dyed by padding and thermofixation, the dyeing of the cotton may be carried out in a batch process. This process may involve:
(1) cold pad–batch application of reactive dyes;
(2) batch treatment of the fabric in any suitable dyeing machine with a solution of salt and alkali if the reactive dyes were padded simultaneously with the disperse dyes;
(3) a separate dyeing process for the cotton in a jet or beam dyeing machine.

Alternatively, the polyester may be pressure dyed and the cotton dyed with reactive dyes by the cold pad–batch process. The reverse of this, cold pad–batch dyeing of the cotton followed by batch dyeing of the polyester, is particularly economic because the padded cotton can be batched directly onto the perforated beams for a beam dyeing machine and no intermediate drying is required. It is less successful in deep shades because reduction clearing of disperse dye from the
cotton is not possible. In addition, a number of methods depend upon padding the cotton/polyester fabric with a solution containing all the dyes for both fibres. The colour develops on treatment with a solution of the appropriate chemicals in a suitable dyeing machine. This might involve treatment with a carrier for dyeing the polyester with the disperse dyes, followed by treatment with a solution of the assistants for dyeing the cotton with the selected cotton dyes. The residual pad liquor is usually added to the treatment bath. This procedure only requires one set of weighings.

Cold pad–batch dyeing of cotton and cotton in cotton/polyester fabric has been a big success and is widely practised. This process involves much less investment in equipment than a continuous dyeing range and minimum energy requirements.

20.3.8 Continuous dyeing of cotton/polyester

The Thermosol process for dyeing polyester was discussed in Section 15.7.6. It is used for dyeing woven cotton/polyester fabric. Vat, sulphur and reactive dyes for the cotton component give good results in the pad–thermosol–pad–steam process. This type of dyeing range (Figure 10.7) is so long that economic operation requires large batches of woven fabric. Direct and azoic dyes may also be used for the cotton component.

The dye pad contains a mixture of the dyes for the cotton and the polyester along with an anti-migration agent. The dyes selected must therefore be compatible at this stage and the dyes for the cotton must be stable to the conditions of the subsequent Thermosol process.

The fabric is then carefully dried to avoid excessive dye migration, and 'Thermosolled'. During this process, the disperse dyes, which are located mainly in the more absorbent cotton fibres, vaporise and transfer to the polyester. After cooling, the fabric passes into the chemical pad containing the appropriate solution of cotton dying assistants that will allow dyeing of the cotton fibres during subsequent steaming. The hydros for reduction of the vat dyes will clear any disperse dye from the polyester surface. This cannot occur when using direct or reactive dyes, so that effective sublimation of disperse dye from the cotton is essential. The operation of a pad–thermosol–pad–steam dyeing range involves a high degree of control to produce thousands of metres of uniformly dyed fabric of high colour consistency. The method is useful for the dyeing of large lots of material, usually well in excess of 10 000 m. Cotton/polyester fabrics can also be dyed on a Thermosol range using solubilised vat dyes. These dyes colour both fibres and in pale shades the colour difference between the two is often acceptable.
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20.4 DYEING WOOL/POLYESTER BLENDS

Fabrics containing a blend of polyester and wool have superior abrasion and crease resistance to those made from wool alone, yet they retain the valued warmth and handle of wool fabrics. In many cases, where the highest quality and good fastness properties are essential, the two fibres may be dyed separately before blending and fabric construction.

The dyeing of wool/polyester mixtures, using acid dyes for the wool and disperse dyes for the polyester, allows the production of solid shades and all types of cross-dyeing. In the two-bath dyeing process, the polyester is first dyed with the disperse dyes under pressure at up to 130 °C using a weakly acid dyebath at around pH 5. Dyeing times should be short since the wool is more prone to damage at temperatures above 105 °C. In dyeing wool/polyester unions, the disperse dyes may stain the wool fibres in the blend and the long time required for their migration to the polyester can cause a loss of wool quality. Any residual disperse dyes in the wool must be removed under the mildest conditions possible by soaping with a non-ionic detergent solution at 70 °C. Alternatively, reduction clearing with a weakly alkaline ammonia solution of hydros or formaldehyde-sulphoxide avoids damaging the wool. Acid dyes then dye the wool under weakly acidic conditions in a second bath.

In the one-bath process, fast acid and disperse dyes are applied simultaneously from a weakly acidic dyebath, followed by soaping. In deep shades, staining of the wool by disperse dyes is heavy and unless the soaping treatment is effective, the washing fastness of the dyeings may be inferior. The one-bath dyeing method is useful mainly for pale to medium depths of moderate fastness. Both the acid and disperse dyes are applied simultaneously using a polyester dyeing carrier at the boil at pH 4–5. The use of a carrier avoids the lengthy times for the transfer of disperse dye held by the wool to the polyester. The wool must be cleared of disperse dye by scouring with non-ionic detergent. Reduction clearing is not possible in this case, since the wool is already dyed with dyes sensitive to reducing agents. Alternatively, a one-bath process at 120 °C uses a wool protection agent and there is little cross-staining of the wool by the disperse dye.

20.5 DYEING COTTON/ NYLON BLENDS

In dyeing polyamide/cellulosic blends, there is a diversity of blends types and dyeing methods. The polyamides include wool, silk, nylon and the polyurethanes, although the latter are not strictly polyamides. Dyeing at pH values above 10 may
damage polyamides because of hydrolysis. The risk of this is also higher for extended dyeing times and at higher temperatures. Nylon fibres can be dyed with acid, reactive or disperse dyes. The cellulosic component is usually cotton or viscose, dyed with direct, vat, sulphur, reactive or azoic dyes. The high alkalinity in dyeing cotton with vat, sulphur and azoic dyes excludes their use in the presence of animal fibres. These dyes are, however, useful for dyeing the cotton in nylon/cotton blends since the nylon is more resistant to alkaline solutions, provided the dyeing temperature is limited. In the presence of wool, even reactive dyes for the cellulose must be capable of fixation at lower temperature and pH values than are normally used in cotton dyeing with these dyes.

Cotton/nylon fabrics can be dyed using disperse or acid dyes for the nylon, and direct dyes for the cotton. Some direct dyes will give a solid shade dyeing both cotton and nylon directly at pH 4–5. Alternatively, some direct dyes do not stain nylon in the presence of a syntan, or do not stain the nylon at 80–90 °C in a weakly alkaline bath. These can be used to correct the shade of the cotton. Better washing fastness is obtained with a combination of fast acid dyes for the nylon, and reactive dyes for the cotton.

If the percentage of cotton or nylon is below 20%, the production of a uniform solid shade is not too difficult. For intimately blended fibres, it is even possible to dye only the major component and leave the other fibre undyed. It is even easier if one of the fibres predominates at the fabric surface as in a fabric with a cotton pile on a nylon backing. Solid shades are more difficult to dye with 50/50 cotton/nylon blends as both fibres will be visible.

Military cotton/nylon fabrics have a limited range of shades and orders of large batches are common. For batch dyeing such fabrics, direct dyes of reasonable wet fastness are used for the cotton in conjunction with a syntan to avoid their staining of the nylon and, in a second bath, milling or metal-complex dyes are applied to the nylon. The milling and metal-complex dyes do not cross-stain the cotton and have good light and wet fastness.

Some interesting continuous dyeing methods are known using vat dyes for the cotton component of cotton/nylon blends. This is possible because nylon is much more resistant than wool to alkalis and reducing agents. For example, the cotton/nylon fabric is padded with a mixture of vat and acid dyes, steamed to fix the acid dye on the nylon, then padded wet-on-wet with hydros and caustic soda solution, and steamed to reduce and fix the vat dye on the cotton. Rinsing, oxidising the leuco vat dye, and scouring to remove superficial colour, complete the process. This requires two steamers in the dyeing range. Since some acid dyes will
penetrate adequately into the nylon at relatively low temperatures around 120–125 °C, under conditions that avoid total drying, a conventional Thermosol unit can be used in place of a steamer. Some leuco vat and sulphur dyes have sufficient substantivity for nylon that a solid shade is obtained with a combination of vat or sulphur dyes alone. The dyes may not give exactly the same colour on the cotton and the nylon fibres but they may be close enough to be acceptable.

20.6 DYEING NYLON AND POLYESTER VARIANTS

20.6.1 Dyeing mixtures of polyamide variants
Nylons are available with a range of amino group contents varying from ultra deep to ultra light dyeing with acid dyes. Disperse dyes cover all these types of nylon to about the same extent but the amount of acid dye absorbed is usually dependent on the number of available amino groups in the nylon. The sole object of dyeing blends of the different types of nylon with acid dyes is to achieve contrasting tone-in-tone colour effects. The objective is purely aesthetic. Generally, the colour contrast between two nylon variants is greater the higher the dyeing pH, the greater the number of sulphonate groups per dye molecule and the lower the amount of anionic levelling agent added to the dyebath. In some cases, the reproducibility of the colour contrast effect is poor, since it is very sensitive to the dyeing conditions. In addition, the pale dyeing nylon may give a dyeing of lower light fastness and the deep dyeing nylon lower washing fastness.

20.6.2 Dyeing nylon/urethane mixtures
Polyurethane elastomeric fibres (spandex) are not major fibres in terms of consumption but their use in clothing is growing. They may often consist of a polyurethane filament core wrapped with other fibres. Their dyeability with acid and disperse dyes is similar to that of nylon. Disperse dyes cover polyurethane more evenly than nylon but again the wet fastness of the dyeings is only poor to moderate. Dark shades cannot be recommended. With acid dyes, polyurethanes dye more rapidly than nylon at lower temperatures even though the nylon will contain more acid dye if dyed to equilibrium. In dyeing nylon/urethane blends, cationic and amphoteric levelling agents are useful for dyes that do not level well, such as disulphonated acid dyes. More cationic auxiliary is need for higher dye concentrations. Anionic retarders are useful for dyeing with monosulphonated and
pre-metallised acid dyes. Less retarder is required at higher dye concentration to avoid over-saturating the fibre.

20.6.3 Dyeing blends of polyester variants

The typical blend of polyester variants contains regular polyester and polyester with anionic groups. It is possible to dye this blend in a single bath with a combination of disperse dyes and cationic dyes to achieve very attractive tone-in-tone dyeings. The dyeing behaviour of basic-dyeable polyester is similar to that of acrylic fibres. It can be dyed with disperse dyes towards which it is more accessible than regular polyester. The shade of the regular polyester should therefore be relatively pale because both types of polyester will absorb the disperse dyes. The colour of the anionic polyester variant will then depend on the colour of the absorbed disperse dyes topped with the basic dyes. When using only basic dyes, a complete reserve of the regular polyester is possible since they only lightly stain the polyester surface. The fabric is dyed with basic dyes at the boil with carrier, or at 120 °C. The surface stain on the regular polyester surface is stripped with hydros, ammonia, non-ionic detergent and Glauber’s salt. Basic-dyeable polyester is less resistant to both acid and alkali catalysed hydrolysis than regular polyester. Such hydrolysis is minimised using about 5 g l⁻¹ of Glauber’s salt in the dyebath, dyeing at a pH value of 5–6 and at temperatures not exceeding 120 °C for the shortest possible time.

In dyeing of basic-dyeable polyester, the strike is much less rapid than with acrylics and levelling agents are not needed. Cationic dyes on anionic polyester have somewhat lower light fastness than on acrylics. The major problem is the lack of compatibility of the cationic dyes with the anionic dispersing agents in the disperse dyes. This is overcome by use of suitable emulsifying agents called compatibilisers that prevent precipitation of any anion–cation complex.

REFERENCE

CHAPTER 21

Colour measurement

Colour measurement has become an essential tool in textile dyeing for matching coloured samples, determining colour differences and for formulating dyebaths. Numerical colour information is rapidly becoming an indispensable, integrated part of the entire textile production sequence. Understanding the fundamentals of colour measurement, or colorimetry, is essential for the optimum use of this technology.

The primary objective of colorimetry is the numerical description of colours by means of physical measurements. Any two samples with the same numerical colour specification, for a given set of viewing conditions, will always have identical perceived colours under those conditions. The difference in the numerical descriptions of two colours should also correlate with the actual degree of colour difference seen by an observer. Such a system of colour specification is extremely valuable. It allows rapid and objective communication of colour information, the specification of acceptable colour differences and the resolution of colour matching disagreements between observers. Many industries producing coloured materials now use colorimetry. It is a key technique in textile dyeing.

21.1 FACTORS INFLUENCING COLOUR PERCEPTION

What is colour and how do we see it? Despite our familiarity with colours, this is not an easy question to answer. Colour vision begins when the sensitive cells in the retina lining the back of the eyeball absorb light, and culminates when the visual cortex of the brain interprets the transmitted nerve impulses as a colour. Only a little is understood of these complex processes.

In the illuminant mode of observation, light enters the eye directly from the light source. In the object viewing mode, the colorants present in a material selectively absorb part of the light illuminating it and transmit or reflect the remainder into the eye of the observer. It is this light that stimulates the sensation of what we call the 'colour' of the material. This 'colour' is not an intrinsic property of the object and its perception may vary depending on three important factors:
(1) the wavelength distribution, or colour, of the light source illuminating the object;
(2) the degree of reflection or transmission of each wavelength of the incident light by the object;
(3) the visual response of the observer’s eye to the wavelengths of light entering from the object.

The numerical specification of a colour requires numerical descriptions of each of these factors.

21.2 LIGHT SOURCES AND ILLUMINANTS

In daylight, an orange and a lime have quite characteristic colours. When seen under a red light, however, the orange is much duller and redder while the ‘green’ lime now appears dark grey. Red light has a low colour rendering ability. This is the ability of the light to reveal what we consider to be the true colour of an object. White lights such as daylight consist of all wavelengths of visible light in about equal proportions. They have the best colour rendering properties.

Visible light sources include those with:
(1) discontinuous line spectra from a source only emitting certain discrete wavelengths of light, such as a low pressure mercury lamp. These are often coloured lights of low colour rendering ability;
(2) continuous emission spectra from sources emitting at all wavelengths, such as an incandescent tungsten lamp or the sun. These are usually white lights;
(3) both line and continuous emissions, as in the light from a fluorescent tube. These often give good quality white light.

The spectral power distribution (SPD) of a light source provides the required numerical description of it. The SPD gives the emitted power (watts per square metre of emitter surface per unit wavelength interval, W m⁻² nm⁻¹) as a function of the wavelength. For colour measurement, a relative rather than an absolute spectral power distribution is adequate. Daylight, which has an irregular, continuous SPD similar to that labelled D₆₅ in Figure 21.1, is a white light composed of all the wavelengths in the visible region in about equal proportions. It has a high colour rendering ability. The light from an incandescent source (tungsten bulb, A in Figure 21.1) is yellower than daylight. It has a smooth SPD, the emitted power gradually increasing from 400 to 700 nm. Fluorescent tubes
generate light with an irregular SPD showing the strong line emission characteristic of mercury at wavelengths of 405, 436, 546 and 578 nm, plus the continuous background emission from the fluorescence of the phosphors lining the inside of the tube (F7 in Figure 21.1). This fluorescence arises from the phosphors absorbing the mercury emissions in the ultraviolet region of the spectrum (257 and 366 nm) and then re-emitting this energy as visible light (Scheme 21.1).

Luminous sources are often characterised by their colour temperature given on the absolute temperature scale (absolute temperature in Kelvin, $K = °C + 273.15$). The colour temperature of a light source corresponds to the operating
temperature of a black body emitter generating light with a colour that is identical or as close as possible to that of the source. A black body is an ideal thermal radiator. Its heated hollow cavity emits light through a small hole in the wall. The inner surface of the cavity re-emits all the incident radiation it absorbs. The SPD of the emitted light from a black body is continuous and ideally depends only on the temperature of the surface and not on its nature. The higher the temperature of the emitting surface, the greater the total power of the emitted radiation, and the lower the wavelength of maximum emission. As the temperature of the black body increases, the colour of the emitted light changes from dull red to orange, to yellow. Eventually, at a temperature around 6000 K, the emitted light is white. The sun’s surface temperature is around this value and it emits white light with an SPD similar to that from a black body at 6000 K.

The SPD of a real light source such as the sun, with a particular colour temperature, is not necessarily similar to that of a black body operating at that temperature, but the colours of the two lights will be identical or almost so. It is important to recognise that a source of illumination with a given SPD always generates the same colour sensation, but other lights with quite different SPDs can also stimulate the identical colour sensation.

The Commission Internationale de l’Éclairage (CIE) has proposed SPDs for lights for colorimetric purposes. These are called CIE standard illuminants. The distinction between real sources and defined illuminants is important. The SPDs of some illuminants correspond to those from real sources. For example, an incandescent lamp with a tungsten filament, operating at a colour temperature of 2856 K, will give the SPD of Illuminant A (A in Figure 21.1). For other illuminants, such as Illuminant D65 (Figure 21.1), there may be no corresponding real light source. The SPD of daylight is extremely variable. It may have colour temperatures ranging from 4000 up to over 30000 K. The CIE has specified the SPD for a number of illuminants corresponding to typical phases of daylight, with different colour temperatures, for example CIE Illuminant D65. For these illuminants, the label D represents daylight, and the number gives the colour temperature in hundreds (65 = 6500 K). The CIE has also defined the SPD of a number of F illuminants (F7 in Figure 21.1). These correspond to different types of fluorescent light. There are also many real sources whose SPDs are not part of the CIE recommendations. These include CWF (cold white fluorescent), TL-84 and Ultralume 30 lamps used for interior lighting.

Daylight simulators often consist of tungsten bulbs behind blue filters, or fluorescent tubes. They are important for the inspection and comparison of
coloured samples under controlled conditions in a viewing booth. Their labels, however, may be misleading and unrelated to the CIE recommendations for colorimetry. A daylight simulator labelled D_65, even though it provides 'daylight' illumination, will not have the same SPD as that of CIE Illuminant D_65.

21.3 REFLECTION OR TRANSMISSION OF LIGHT BY AN OBJECT

21.3.1 Reflection spectrophotometry

Spectrophotometric measurements provide the numerical description of the reflection or transmission of light by an object. The reflection or transmission spectrum gives the fraction of the incident light that an object reflects or transmits as a function of wavelength.

In most reflection spectrophotometers, the reflection of light by the sample is measured at each wavelength relative to that of a white standard such as a plate coated with MgO or BaSO₄. These standards give almost 100% diffuse reflection (light rays reflected in all directions) between 380 and 750 nm. They are, however, rather fragile and often a working standard such as a ceramic tile of known reflectance is used. Calibration of the instrument with a white standard tile allows calculation of the reflectance of the sample relative to that of a perfect diffuse reflector having 100% reflection of the incident light at all wavelengths.

There are many different types of spectrophotometer. They may have continuous or pulsed light sources, different angles for the beams of incident and detected reflected light, double or single beam optics, different systems for dispersion of the light into its component wavelengths and different wavelength ranges and measurement intervals. In some cases, white light illuminates the sample (all wavelengths, polychromatic illumination) followed by dispersion of the reflected light into its component wavelengths and measurement of the intensity of each wavelength. In others, there is initial dispersion of the light and sequential illumination of the sample with each discrete wavelength (monochromatic illumination), followed by measurement of the reflected intensity.

There are three common instrument geometries (Figure 21.2):

1. Illumination of the sample at an angle of 45° to its surface and detection of the reflected light at close to right angles (45/0 geometry);
2. the reverse of this (0/45 geometry);
3. diffuse illumination of the sample from all directions, using an integrating sphere, and detection of reflected light at close to perpendicular to the sample (d/0, or more often d/8 geometry).
Some spectrophotometers are capable of continuously scanning through the entire visible spectrum, while others, called abridged instruments, only measure at selected wavelengths. Because of the large number of instrument variations, two different instruments often do not give exactly the same data for identical samples, even when optimally calibrated and operated. This section presents a brief account of a spectrophotometer with an integrating sphere that illustrates several important points.

In double beam instruments with an integrating sphere (Figure 21.3), the sample and working standard are placed against small openings in the surface of the sphere. A highly reflecting white paint coats the interior wall of the sphere.
The total area of the sphere's reflecting surface is large compared to that of the sample ports and the light entry and exit ports. White light from the source reflects off the walls and then off the sample or white standard. Light reflected from the sample or white standard at an angle of 8° from the perpendicular leaves the sphere and a diffraction grating disperses it into its component wavelengths. The intensity of each wavelength is then measured. The detector may be a photomultiplier tube measuring in turn the intensities of the beams reflected from the white calibration plate and the sample at each wavelength selected by the dispersion unit. The ratio of these intensities gives the percentage reflectance. In some abridged instruments, sixteen appropriately spaced light-sensitive diodes simultaneously measure the beam intensities for the sixteen selected wavelengths (400 to 700 nm at 20 nm intervals), thus avoiding any motion of optical components and giving excellent long term reproducibility.

The light source illuminating the integration sphere must have good stability and emit adequate energy at each wavelength. A small baffle projecting from the sphere wall prevents direct illumination of the sample and standard. Since the reflectance factor is the ratio of the reflected intensities from the sample and the white standard, it does not depend upon the SPD of the light source illuminating the sphere walls, provided the sample is non-fluorescent.

Specular reflection involves true mirror reflection where each light ray reflects from the surface at an angle identical to its angle of incidence, with no penetration into the surface and no absorption. For diffuse reflection, each point on the surface appears to reflect light equally in all directions. Textile materials reflect the incident light diffusely. Specular reflection by textiles is usually minor except for certain smooth fabrics and those made with lustrous synthetic fibres. For lustrous surfaces at certain viewing angles, the true colour of the surface, seen by the diffusely reflected light, is diluted with the white light from specular reflection. The colour is thus desaturated by the specular component. When using the d/8 geometry described above (Figure 21.3), some of the light passing to the detector can come from specular reflection from the sample. The reflection spectrum thus includes the specular component. This is not possible with the 45/0 geometry. To record a reflection spectrum not including any specular component, an absorbing surface or a light trap is placed at the appropriate point on the sphere surface. This prevents direct reflection from there with the correct angle of incidence for specular reflection. In textile work, the specular reflection is normally included because a non-uniform fabric surface specularly reflects light rays whose envelope of angles of incidence and reflection is quite wide. Complete exclusion of the
specular component is thus difficult. A colour measurement report should indicate whether the specular component was included or excluded (often referred to as ‘sin’ or ‘sex’).

Transparent materials or solution cells can be placed in the light beam where it leaves the integrating sphere after reflection from a white standard in the sample port. The spectrophotometer is calibrated to read 100% reflectance with a solution cell containing only a colourless solvent in the reflected light beam. When a coloured solution replaces the solvent, absorption of the light at some wavelengths reduces the apparent reflectance readings and the instrument gives the percentage transmission of the solution directly.

Reflection or transmission measurements represent the characteristics of the object and provide the numerical description of the object’s colour used in calculating colour coordinates. The precision and accuracy of the numerical specification of a colour are dependent on this data alone since the descriptions of the selected illuminant and observer are invariant. It is therefore essential that the spectrophotometer be maintained in good working condition, with regular performance checks, and that its calibration with white working standards is valid and stable. The repeatability of the measurements should depend only on the uniformity of the sample.

21.3.2 Reflectance measurements with textiles

Any textile fabric has considerable variations in texture and colour. These are an inherent consequence of the production process. For colour measurement on textiles, therefore, correct sampling is of the utmost importance. Several samples are usually taken from various parts of a batch of material and the reflection spectrum of each sample measured several times. In this way, an average reflection spectrum is obtained. For the reflectance measurements, it is important that the sample is opaque and that no light transmits through the material and reflects back from the face of the sample holder. Reflection from several layers of a fabric avoids this problem. Sometimes fabric reflectance is measured using a black felt backing to absorb any transmitted light. Sample presentation is often a problem for loose fibre and yarn because the reflectance depends on the degree of packing that must therefore be reproducible from sample to sample. Yarn is often wound onto a piece of flat card at uniform tension. Loose fibre may be formed into a compact
pad or compressed into a glass container. A different method of sample presentation will give a somewhat different colour specification but is often satisfactory for comparison of similar samples handled in the same way.

Almost all textile materials have a characteristic texture that influences the diffuse reflection of the incident light and thus the appearance when viewed from different angles. Rotation of the sample by 90° between recordings of four spectra, which will then be averaged, minimises any directional effects caused by the texture. Many textiles have different textures on the back and face of the material. Sometimes reflectance measurements must always be carried out on the same face of the material or with any pile always brushed in the same direction. Carpets represent an extreme case of this.

Reflection spectra of dyed textiles are often quite sensitive to environmental conditions in the laboratory. Frequently, reflectance values change when the humidity or temperature of the sample changes. For the best reproducibility, careful conditioning of the samples at constant temperature and relative humidity is recommended before the spectrum measurement. Obviously, this is not possible under production conditions so a rapid compromise method of sample treatment must be established. It is critical that this gives reproducible results.

White light sources for polychromatic illumination usually generate a small proportion of ultraviolet light with wavelengths below 400 nm. Ultraviolet light is necessary for exciting the fluorescence of the optical whiteners used in textiles (Section 5.4.5). With polychromatic illumination, light with a wavelength below 400 nm can excite the blue fluorescence of these compounds. The emitted fluorescence is detected as reflected light and apparent reflectance values of greater than 100% are possible in the wavelength range for fluorescence emission (Figure 5.5). A number of textile dyes are also fluorescent, their fluorescence being activated by absorption of near ultraviolet or visible light. Their fluorescence is included in the reflectance measurement in abridged spectrophotometers where all wavelengths are sampled simultaneously. The reflection spectrum, and therefore the final calculated colour coordinates, will depend on the particular light source used for illumination of the sample in the spectrophotometer. Inclusion of the fluorescence emission can be avoided using monochromatic illumination of the sample, dispersion of the reflected light into its component wavelengths and measurement of the reflected intensity at the same wavelength as the illuminating ray. The equipment for this is more expensive.
21.4 HUMAN COLOUR VISION

Colour perception depends on three factors: the light, the object and the observer. A complete colour specification also always requires three parameters. We usually describe colour using the terms hue, saturation and lightness. The hue refers to the actual colour sensation (red, blue, yellow), the saturation or chroma to the degree of differentiation from grey (dull or vivid), and the lightness to the amount of light reflected from the object (light or dark). In the Munsell colour system, these attributes are assigned alphabetic and numerical levels (Section 21.7).

The Young–Helmholtz trichromatic theory of colour vision postulated that there are three types of colour-sensitive receptor in the eye. The eye contains two different types of light-sensitive cells, called rods and cones after their characteristic shapes. They are both located in the retina in the last layer of nerve cells furthest from the cornea. The cones exclusively occupy the central region of the retina or fovea, close to the optical axis, their number decreasing away from the axis. They operate when the level of illumination is relatively high (photopic vision). There are three types of cones with wavelengths of maximum sensitivity in the red, green and blue regions of the visible spectrum, respectively, in agreement with the trichromatic theory. The rod cells are not colour-sensitive and detect light under conditions of weak illumination (scotopic or night vision). They predominate in the regions away from the central axis.

Under photopic conditions, the rods are light-saturated and ineffective. As the level of illumination gradually decreases, red colours are the first to lose their chromaticity (colourfulness) and become more grey, followed by the blues and then finally greens. At night, all cats are grey. The different characteristics of the cones and rods explain these changes in colour vision as the level of illumination drops and there is a switch from photopic to scotopic vision. This is not an abrupt change and there is a wide range of intermediate light levels where both photopic and scotopic vision operate.

The relative photopic luminous efficacy describes the observed brightness (luminance) of lights of different colours with the same total power. It has a bell-shaped variation with wavelength being at a maximum at 555 nm (green) (Figure 21.4). This means that red and blue lights must have much higher power to have the same luminance as a green light. The relative scotopic luminous efficacy curve has a similar shape but shifted to lower wavelengths. It is this shift that is responsible for reds being the first colours to lose chromaticity when the illumination power decreases and the eye switches from photopic to scotopic...
operation (compare the photopic and scotopic luminous efficacies at 650 nm in Figure 21.4).

What is the distinction between the power and luminance of a light source? As pointed out above, spectral lights of equal power are not perceived to have equal brightness. The power of a light source specifies how much radiant energy it emits, whereas the luminance gives its brightness as perceived by the observer. The luminance of a monochromatic light is directly proportional to the source power (strictly power per unit area per unit solid angle) multiplied by the value of the photopic luminous efficacy function, usually written as $V(\lambda)$ (Figure 21.4).

Another major colour vision theory is the opponent colours theory, originally proposed by Hering. It states that colour perception depends on a red–green response, a yellow–blue response, and on the total amount of light entering the eye. The name ‘opponent colour’ arises because the colour red may tend towards blue or yellow, but never towards green. Likewise, a yellow tends towards green or red, but not blue. Thus, red–green and yellow–blue represent opponent colour pairs. The light absorbed by the colour-sensitive cones initiates reversible photochemical reactions that result in the generation of nerve impulses. This involves the three types of cones, according to the trichromatic hypothesis.
Examination of the retina, however, has shown that nerve fibres interconnect many of the different types of cells found there. The initial trichromatic red, blue and green responses undergo considerable modification in the layers of interconnected retinal cells and the impulses leaving the eye through the optic nerve transmit colour information as red-green, yellow-blue and total luminance signals. Both of the major colour theories thus appear to be correct.

21.5 CHARACTERISATION OF THE CIE STANDARD OBSERVERS

21.5.1 Colour matching experiments by additive mixing of coloured lights

In the CIE colorimetric system, the specification of the colour of an object is based on the spectral power distribution (SPD) of the light source, the reflection or transmission spectrum of the object, and on the response of an average observer with normal colour vision (standard observer). The latter is characterised by data from colour matching experiments in which beams of light from three primary sources, usually red, blue and green, are mixed to reproduce the colour of another source of light. This type of colour matching involves additive mixing in which light directly enters the eye of the observer without modification by absorption. This is different from the more common subtractive mixing with dyes and pigments, where the colour arises from the selective absorption of certain wavelengths of the light and reflection of the others. In additive mixing, approximately equal proportions of the three primary red, blue and green lights produce white light. In subtractive mixing, the primary colours are red, blue and yellow and their combination produces black.

In the colour matching experiment defining the human colour response, a mixture of superimposed red, blue and green primary lights illuminates one part of a reflecting white screen. A succession of monochromatic spectral lights of known wavelength, all with the same constant power, illuminate the adjacent field (Figure 21.5). The proportions of the three primary sources are adjusted until their mixture has a colour identical to that of the spectral light of given wavelength in the neighbouring field. At this point, the demarcation line between the two fields disappears. The eye is an excellent null detector and readily recognises any mismatch of the colours in the two fields. The observer records the proportions of the red, green and blue primaries that, when combined together, reproduce the colour of each particular wavelength of the visible spectrum, each having the same constant power. These quantities are called the spectral tristimulus values. Despite
some small variations in the values obtained by different observers, the average
spectral tristimulus values define the colour vision characteristics of a standard
observer.

There are strict experimental requirements:

1. the overall light intensity corresponds to that for photopic vision, or colour
vision using the cone cells in the retina;

2. the field of vision subtends an angle of either 2° or 10°, the smaller angle
ensuring exclusive use of the cone receptors without any participation of the
rod cells;

3. the observer has normal colour vision. Neither fatigue, adaptation nor the
background influences the observations;

4. the colour of any of the three primary sources cannot be matched by a
combination of the other two lights;

5. the relative luminances of the three primaries are adjusted so that a mixture
of equal proportions of the three lights matches a standard white such as the
equal energy white light. The SPD of this light is a horizontal line at constant
power for all wavelengths.
At any given wavelength, the observer determines the values of the three spectral
tristimulus values \( r(\lambda) \), \( g(\lambda) \) and \( b(\lambda) \). The symbol \( (\lambda) \) after each tristimulus value
indicates that the values vary with wavelength. The colour matching conditions
for any spectral light of given wavelength and constant power may be represented
by an equation in terms of these tristimulus values:

\[
C(\lambda) = r(\lambda) + g(\lambda) + b(\lambda)
\]

This simply states that the spectral light of colour \( C \) and wavelength \( \lambda \), at the
given constant power, can be matched by additive mixing of amounts \( r(\lambda) \), \( g(\lambda) \)
and \( b(\lambda) \) of the three respective primary lights \([R]\), \([G]\) and \([B]\). These spectral
tristimulus values are also called colour matching functions. To avoid confusion
among symbols, a letter inside square brackets always designates a primary light.
Thus, \([R]\) means the red primary light. The above equation is not an algebraic
equation, the symbol \( = \) signifying only the equivalence of two matching colours.

The high purity of the spectral lights prevents direct colour matching by
additive mixtures of three primaries. The observer involved in this type of colour
matching finds that the colour of the spectral lights can only be reproduced if they
are first desaturated somewhat. This is done by illuminating the field of the
spectral colour with a small amount of one of the primary lights, and then
matching this resulting colour by illumination of the adjacent field with a
combination of the other two primaries. Thus, the equation for matching a green
spectral light might be:

\[
C(\lambda) = r(\lambda) + g(\lambda) + b(\lambda)
\]

Alternatively, this may be written as:

\[
C(\lambda) = r(\lambda) + g(\lambda) + b(\lambda)
\]

giving a negative \( r(\lambda) \) tristimulus value, in this case.

The specification of the colour of any spectral light requires three tristimulus
values. These give the coordinates for each colour in a three-dimensional colour
space. This is, however, very difficult to illustrate and therefore the tristimulus
values are often normalised by dividing each value by the total of the three. This gives the chromaticity coordinates, whose sum is unity.

\[
\begin{align*}
    r &= \frac{\tau}{\tau + \beta + \kappa} \\
    g &= \frac{\pi}{\tau + \beta + \kappa} \\
    b &= \frac{\kappa}{\tau + \beta + \kappa} \\
    r + g + b &= 1
\end{align*}
\]  

(4)

To distinguish the spectral chromaticity coordinates from the tristimulus values, only the latter have a bar above the symbol. The chromaticity coordinates allow a simple two-dimensional graph with one value plotted against a second. The third value is automatically known by difference. Such a graph is called a chromaticity figure.

In the colour matching experiment, doubling the luminance of a spectral light doubles the values of the tristimulus values for matching it. The tristimulus values would, however, still be in the same ratio, since only the luminance changes. Doubling the values of \( \tau(\lambda) \), \( \pi(\lambda) \) and \( \kappa(\lambda) \) does not therefore change the values of the chromaticity coordinates \( r(\lambda) \), \( g(\lambda) \) and \( b(\lambda) \). In fact, each colour matching function is proportional to the luminance of the respective primary light required for matching the spectral light of a given wavelength. Luminance values are additive, so the spectral lights of varying wavelength and constant power used in the matching experiment will have variable luminances proportional to the sum of their tristimulus values. Thus, the chromaticity coordinates of the spectral colours correspond to those for colours of constant luminance since their sum is always unity. A chromaticity figure, therefore, gives no information about the luminance of a colour. It defines only the chromaticity or 'colourfulness'. Lights of the same hue, say a bright and a dull orange differing in luminance, will have different tristimulus values but can have identical chromaticity coordinates.

The spectral tristimulus values or colour matching functions characterise the colour vision of an average observer. The experimental values of \( \tau(\lambda) \), \( \pi(\lambda) \) and \( \kappa(\lambda) \) showed good agreement, with only a little scatter, when different observers matched colours under the controlled conditions described above. Such data were first obtained in two independent studies for matching with a 2° visual angle. Later, the 2° observations were verified, and new studies were undertaken for a 10° visual field. These data were used to define the CIE 1931 standard colorimetric observer (2° visual field) and the CIE 1964 supplementary colorimetric observer (10° visual field).
21.5.2 The CIE colorimetric systems

In the next section, we will see how the data from the colour matching experiment is used to calculate the tristimulus values for the colour of an object by a summation technique. For matching any monochromatic spectral light of a given wavelength, there is always one negative tristimulus value. This makes calculation of the tristimulus values of an object colour by summation more time consuming. For this reason, and others, the CIE decided in 1931 to propose a series of colour matching functions having no negative numbers. These were obtained by transformation of the values of \( r', g', b' \) (2° visual field) into a set \( x, y, z \) based on alternative primaries called \([X]\), \([Y]\) and \([Z]\). These primaries correspond to virtual red, green and blue lights each with a purity exceeding that of the spectral lights themselves. There are no real sources corresponding to these new primaries. Figure 21.6 shows the positions of \([X]\), \([Y]\) and \([Z]\) relative to \([R]\), \([G]\) and \([B]\) in the \(rgb\) chromaticity figure. For the red primary, \( r = 1 \); for the green \( g = 1 \); and thus the blue primary is located at \( r = 0, g = 0 \). These form a right-angled colour triangle \([R]–[G]–[B]\). The line connecting

![Figure 21.6 The CIE rgb chromaticity figure showing the coordinates of the primaries and the locus of the spectral colours (2° visual field)](image-url)
the chromaticity coordinates of the spectral colours lies outside the triangle because of the negative values that occur in matching.

The appropriate equations (to three significant figures) for transformation of the rgb colour matching functions to the xyz set (2° visual field) are:

\[
\begin{align*}
\pi(\lambda) &= 2.77\pi(\lambda) + 1.75\pi(\lambda) + 1.13\pi(\lambda) \\
\gamma(\lambda) &= 1.00\gamma(\lambda) + 4.59\gamma(\lambda) + 0.0601\gamma(\lambda) \\
\zeta(\lambda) &= 0.0565\gamma(\lambda) + 5.59\gamma(\lambda)
\end{align*}
\]

These new colour matching functions are equally valid because one set can be transformed into another set based on different primaries. In fact, the original data for the CIE 1931 standard observer were obtained by Wright (1929, 10 observers) using monochromatic primaries of wavelengths of 460, 530 and 650 nm, and also by Guild (1930, 7 observers) whose primary lights were lamps fitted with red, blue and green filters. The two sets of data did not appear at all identical. Guild, however, transformed his spectral tristimulus values, as well as those of Wright, into values based on a common set of spectral primaries with wavelengths of 700, 546 and 436 nm and demonstrated the equivalence of the two sets of data. The tristimulus values for colour matching using a 10° visual field, \( x_{10}(\lambda) \), \( y_{10}(\lambda) \) and \( z_{10}(\lambda) \) were similarly transformed into a new set \( x_{10}(\lambda) \), \( y_{10}(\lambda) \) and \( z_{10}(\lambda) \) based on another set of imaginary primaries \([X_{10}], [Y_{10}]\) and \([Z_{10}]\). This again avoided negative values of the colour matching functions. The values defined the 1964 supplementary standard observer. Note that the primaries \([X_{10}], [Y_{10}]\) and \([Z_{10}]\) are not the same as \([X], [Y]\) and \([Z]\) used for the 1931 standard observer.

The three colour matching functions for a spectral light define the coordinates of its colour in a three-dimensional colour space. Again, it is more convenient to calculate and graph the corresponding chromaticity coordinates.

\[
\begin{align*}
x &= \frac{\pi}{\pi + \gamma + \zeta} \\
y &= \frac{\gamma}{\pi + \gamma + \zeta} \\
z &= \frac{\zeta}{\pi + \gamma + \zeta} \\
x + y + z &= 1
\end{align*}
\]

The graph of \( y \) versus \( x \), showing the chromaticity coordinates of the spectral colours, is the well-known CIE chromaticity diagram shown in Figure 21.7. The right-angled colour triangle now has the chromaticity coordinates of the primaries \([X], [Y]\) and \([Z]\) at the apices. Note that all the colour matching functions are
positive and the locus of the chromaticity coordinates of the spectral colours lies within the boundaries of the triangle.

The method of transforming tristimulus values based on one set of primaries into values based on an alternative set involves a common mathematical technique called coordinate transformation. This is analogous to calculating the spherical coordinates of a point in space (one distance and two angles) from values of the more usual rectangular coordinates \( x, y \) and \( z \). The mathematics is somewhat lengthy and beyond the scope of this chapter. The technique involves the mathematics of converting Figure 21.6 to 21.7.

The CIE colorimetric system consists of recommendations for the SPDs of various illuminants (A, D_65, and so on), and of the colour matching functions \( x(\lambda) \), \( y(\lambda) \) and \( z(\lambda) \) or \( x_{v(\lambda)} \), \( y_{v(\lambda)} \) and \( z_{v(\lambda)} \) for standard observers matching spectral colours using visual fields subtending angles of 2° or 10°, respectively. The colour matching functions represent the relative proportions of the three virtual primaries \([X],[Y] \) and \([Z]\) (or \([X_{10}],[Y_{10}] \) and \([Z_{10}]\)) necessary for the reproduction of the colours of monochromatic spectral lights, at unit power, by an average observer with normal colour vision. In terms of the colour matching equation, at each wavelength:

\[
C(\lambda) = \tau(\lambda)[R] + \tau(\lambda)[G] + \tau(\lambda)[B] = \tau(\lambda)[X] + \tau(\lambda)[Y] + \tau(\lambda)[Z]
\]
Table 21.1 gives an abridged list of the approximate values of the colour matching functions ($\bar{x}_{10}$, $\bar{y}_{10}$ and $\bar{z}_{10}$) for the 10° standard observer.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$S(\lambda)$</th>
<th>$\bar{x}_{10}$</th>
<th>$\bar{y}_{10}$</th>
<th>$\bar{z}_{10}$</th>
<th>$S\bar{x}_{10}$</th>
<th>$S\bar{y}_{10}$</th>
<th>$S\bar{z}_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>82.8</td>
<td>0.019</td>
<td>0.002</td>
<td>0.086</td>
<td>1.58</td>
<td>0.17</td>
<td>7.12</td>
</tr>
<tr>
<td>420</td>
<td>93.4</td>
<td>0.241</td>
<td>0.021</td>
<td>0.973</td>
<td>22.46</td>
<td>2.00</td>
<td>90.83</td>
</tr>
<tr>
<td>440</td>
<td>104.9</td>
<td>0.384</td>
<td>0.062</td>
<td>1.967</td>
<td>40.25</td>
<td>6.51</td>
<td>206.37</td>
</tr>
<tr>
<td>460</td>
<td>117.8</td>
<td>0.302</td>
<td>0.128</td>
<td>1.745</td>
<td>35.61</td>
<td>15.10</td>
<td>205.61</td>
</tr>
<tr>
<td>480</td>
<td>115.9</td>
<td>0.081</td>
<td>0.254</td>
<td>0.772</td>
<td>9.33</td>
<td>29.39</td>
<td>89.49</td>
</tr>
<tr>
<td>500</td>
<td>109.4</td>
<td>0.004</td>
<td>0.461</td>
<td>0.219</td>
<td>0.42</td>
<td>50.41</td>
<td>23.90</td>
</tr>
<tr>
<td>520</td>
<td>104.8</td>
<td>0.118</td>
<td>0.762</td>
<td>0.061</td>
<td>12.33</td>
<td>79.84</td>
<td>6.36</td>
</tr>
<tr>
<td>540</td>
<td>104.4</td>
<td>0.377</td>
<td>0.962</td>
<td>0.014</td>
<td>39.34</td>
<td>100.43</td>
<td>1.43</td>
</tr>
<tr>
<td>560</td>
<td>100.0</td>
<td>0.705</td>
<td>0.997</td>
<td>0</td>
<td>70.52</td>
<td>99.73</td>
<td>0</td>
</tr>
<tr>
<td>580</td>
<td>95.8</td>
<td>1.014</td>
<td>0.869</td>
<td>0</td>
<td>97.16</td>
<td>83.24</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>90.0</td>
<td>1.124</td>
<td>0.658</td>
<td>0</td>
<td>101.16</td>
<td>59.25</td>
<td>0</td>
</tr>
<tr>
<td>620</td>
<td>87.7</td>
<td>0.856</td>
<td>0.398</td>
<td>0</td>
<td>75.10</td>
<td>34.91</td>
<td>0</td>
</tr>
<tr>
<td>640</td>
<td>83.7</td>
<td>0.432</td>
<td>0.180</td>
<td>0</td>
<td>36.12</td>
<td>15.05</td>
<td>0</td>
</tr>
<tr>
<td>660</td>
<td>80.2</td>
<td>0.153</td>
<td>0.060</td>
<td>0</td>
<td>12.24</td>
<td>4.84</td>
<td>0</td>
</tr>
<tr>
<td>680</td>
<td>78.3</td>
<td>0.041</td>
<td>0.016</td>
<td>0</td>
<td>3.20</td>
<td>1.24</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>71.6</td>
<td>0.010</td>
<td>0.004</td>
<td>0</td>
<td>0.69</td>
<td>0.26</td>
<td>0</td>
</tr>
<tr>
<td><strong>Sums</strong></td>
<td><strong>5.86</strong></td>
<td><strong>5.83</strong></td>
<td><strong>5.84</strong></td>
<td><strong>554.1</strong></td>
<td><strong>582.4</strong></td>
<td><strong>631.1</strong></td>
<td></td>
</tr>
</tbody>
</table>

$Y = 100 = k \sum (S\bar{y}_{10})k = \sum_{i=1}^{100} \frac{S\bar{y}_{10}}{582.4} = 0.172$

$X = k \sum (S\bar{x}_{10}) = 0.172 \times 554.1 = 95.2$

$Z = k \sum (S\bar{z}_{10}) = 0.172 \times 631.1 = 108.4$

The major differences between the two standard observers are:

1. the correspondence of the $\bar{y}(\lambda)$ colour matching function for the 1931 observer (2°) with the photopic luminous efficacy $V(\lambda)$, which is not the case for the $\bar{y}_{10}$ colour matching function (10° observer);
2. the better correlation of the results for the 10° observer with actual colour matching observations, where some involvement of the observer’s rod receptors influences colour perception.

Figure 21.8 compares the colour matching functions for the 1931 and 1964 standard observers.
21.6 Determination of the tristimulus values of a colour

21.6.1 Calculation of the tristimulus values of lights and illuminants

The definition of the standard observer, in terms of colour matching with imaginary primary lights and the mathematics of coordinate transformations, is a difficult concept. The simple principle of the colour matching experiment, however, provides an explanation of the calculation the tristimulus values of the colour of a light source or of a real object. The discussion will be limited to calculations for the 1964 CIE supplementary standard observer (10° visual field) as this is most widely used in textile colour measurement. The method applies equally well to the alternative 2° observer.

First, let us look at the colour matching functions \( x_{10}(\lambda) \), \( y_{10}(\lambda) \) and \( z_{10}(\lambda) \) given in Table 21.1. The colours of the spectral lights of known wavelength and each with the same total power were matched by mixing appropriate proportions of the three primaries \( [X_{10}] \), \( [Y_{10}] \) and \( [Z_{10}] \). The matching condition for any spectral light is given by:

\[
C(\lambda) = n_{10}(\lambda)X_{10} + n_{10}(\lambda)Y_{10} + n_{10}(\lambda)Z_{10} \quad (8)
\]
The subscript 10, and the indication of wavelength dependence, will now be omitted to simplify the symbols. If these spectral lights with wavelengths in the 400 to 700 nm range were combined, the equal energy white light would result because each component wavelength has the same power. Because of the principle of additivity, this white light would be matched by an amount of the [X] primary corresponding to the sum of the \( x \) tristimulus values for all the wavelengths, and by the corresponding sums of \( y \) and \( z \) for the [Y] and [Z] primaries, as shown by the equation:

\[
\text{White} = \sum \left( \frac{\text{C}\lambda}{\text{G}108} \right) = \sum \left( \frac{\text{C}\lambda}{\text{G}159} \right) \text{[X]} + \sum \left( \frac{\text{C}\lambda}{\text{G}43} \right) \text{[Y]} + \sum \left( \frac{\text{C}\lambda}{\text{G}43} \right) \text{[Z]} \tag{9}
\]

where the symbol \( \sum \) denotes the summation of the values over the wavelength range for visible light from, say, 400 to 700 nm. Recall that Eqn 9 states that the equal-energy white light will be reproduced by a mixture of \( \sum \lambda \) parts of the primary [X], \( \sum \lambda \) parts of the primary [Y] and \( \sum \lambda \) parts of the primary [Z]. The summations of the respective colour matching functions for the 10° observer give essentially three equal values of about 5.84 (see Table 21.1). Thus, the equal energy white light would have three identical tristimulus values of 5.84 (or 100 each after the normalisation procedure to be described) and thus three equal chromaticity coordinates of 0.33.

The equation:

\[
\text{C}\lambda \text{[unit power]} = \frac{1}{\text{G}108} \text{[X]} \text{[Y]} \text{[Z]} \tag{10}
\]

states that a match of a spectral light of wavelength \( \lambda \) at unit power is possible by mixing the three primary lights [X], [Y] and [Z] in the proportions \( x \), \( y \) and \( z \), respectively. If we had to match the same spectral light, but at a total power of \( S \text{[G}108\text{]} \), the matching condition would be described by the above equation multiplied by \( S \), giving:

\[
\text{C}\lambda \text{[power S[\lambda]]} = \frac{S}{\text{G}108} \text{[X]} \frac{S}{\text{G}108} \text{[Y]} + \frac{S}{\text{G}108} \text{[Z]} \tag{11}
\]

where the tristimulus values are now \( Sx \), \( Sy \) and \( Sz \).

It is now possible to see how the tristimulus values for a continuous polychromatic light of known SPD can be calculated. The SPD gives the power from the source at each wavelength, with variable values of \( S[\lambda] \). Its colour arises
from the combined effects of all these wavelengths. Using the principle of additivity, we can write a summation for the combination of the wavelengths responsible for the observed colour:

\[
\text{Colour of light} = \sum [\text{CIA} \times \text{power (\text{SIA})}] = \sum [\lambda X] + \sum [\lambda Y] + \sum [\lambda Z]
\]  

(12)

In this equation for the summations over all the wavelengths, the values of \( S_x, S_y \) and \( S_z \) all vary from one wavelength to the next. Thus, the colour of this particular light of known SPD would be matched by mixing the three primaries \( X \), \( Y \) and \( Z \) in the proportions \( X, Y \) and \( Z \) given by:

\[
X = \sum (S \lambda) \quad Y = \sum (S \lambda) \quad Z = \sum (S \lambda)
\]  

(13)

The values of \( X, Y \) and \( Z \) give the tristimulus values of this light of given SPD. In the CIE system, however, the tristimulus values are normalised so that the light representing an illuminant always has a \( Y \) tristimulus value equal to 100. This is done using a normalisation constant \( k \), defined in such a way that:

\[
k = \frac{100}{\sum (S \lambda)}
\]  

(14)

The tristimulus values for an illuminant have the usual symbols with a subscript \( n \). If the \( Y \) tristimulus value of the illuminant is 100, then:

\[
k = \frac{100}{\sum (S \lambda)}
\]  

(15)

Table 21.1 illustrates this type of calculation. It shows that Illuminant D65 has \( X_n = 95.2, \ Y_n = 100.0, \) as required by the normalisation, and \( Z_n = 108.4. \) The calculation procedure recommended by the CIE involves summation over a wavelength range from 360 to 830 nm at 5 nm intervals. This gives \( X_n = 94.8, \ Y_n = 100.0 \) and \( Z_n = 107.3, \) the correct tristimulus values for Illuminant D65. The slightly larger values of \( X \) and \( Z \) obtained in the approximate example above arose
from the use of less precise summations over fewer wavelengths and neglecting the wavelengths below 400 and above 700 nm.

The most accurate CIE procedure for calculation of the tristimulus values of a colour recommends measurements of the reflectance factors from 360 to 830 nm with a wavelength increment of 1 nm. This is not possible with many abridged spectrophotometers that only have a range from 400 to 700 nm, with a measurement interval of 10 or even 20 nm. This minimizes measurement and calculation times and gives satisfactory results for industrial use. To avoid disparity of the calculated tristimulus values when using different wavelength intervals over a truncated range, tristimulus values should preferably be computed using pre-calculated weighting functions, \( W_{k} \). These are defined by:

\[
W_{x}(\lambda) = kS(\lambda) \pi_{x}(\lambda) \quad W_{y}(\lambda) = kS(\lambda) \pi_{y}(\lambda) \quad W_{z}(\lambda) = kS(\lambda) \pi_{z}(\lambda)
\]

Tables of values of the weighting functions are available for different wavelength intervals using different illuminants and standard observers [1]. The values are adjusted so that the sums give the same tristimulus values for an illuminant irrespective of the wavelength interval used in the calculation. Table 21.2 illustrates this for Illuminant D65 and the 10° standard observer, for a wavelength interval of 20 nm (note that the summation gives the correct tristimulus values for Illuminant D65). For a truncated wavelength range of 400 to 700 nm, as often found in abridged spectrophotometers, the weighting factors for wavelengths below 400 and above 700 nm are added to the values at the beginning and end of the wavelength range, respectively.

21.6.2 Calculation of the tristimulus values of the colour of an object

The method for calculating the tristimulus values of the colour of an object is based on the measurements of the reflectance factor \( R(\lambda) \) at a number of equally spaced wavelengths in the visible region of the spectrum. We must first recall again the three factors influencing the perceived colour of an object – the light source, the way light is reflected from the object, and the observer. The light source that illuminates the object has a given SPD. When light reflects from the surface of a coloured object, the relative power of each wavelength of the illuminating light is reduced by the varying degrees of reflection. Thus, the reflected light has a different SPD for which the power at each wavelength is that of the incident light \( S(\lambda) \) multiplied by the reflection factor \( R(\lambda) \). The condition
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for matching the colour of a spectral component of wavelength \( \lambda \) with a power of \( S(\lambda) \times R(\lambda) \), is:

\[
C(\lambda) \text{ [power } S \times R] = (SR^x \{X\}) + (SR^y \{Y\}) + (SR^z \{Z\})
\]  

(17)

The colour of the object is that produced from the combined effects of the colours of all the component wavelengths entering the eye of the observer:

\[
\text{Object colour} = \sum \{C(\lambda) \text{ [power } S \times R]\}
\]  

\[
= \sum \{SR^x \{X\} + \sum \{SR^y \{Y\} + \sum \{SR^z \{Z\}\}
\]

(18)

The tristimulus values of the colour of the object are given by the summations of the SRx, SRY and SRz values over all the wavelengths, each multiplied by the normalisation constant \( k \), calculated for the illuminant:

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( W_{\lambda x} )</th>
<th>( W_{\lambda y} )</th>
<th>( W_{\lambda z} )</th>
<th>( R \text{ sample} )</th>
<th>( R \cdot W_{\lambda x} )</th>
<th>( R \cdot W_{\lambda y} )</th>
<th>( R \cdot W_{\lambda z} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.008</td>
<td>0.012</td>
<td>0.222</td>
<td>0.002</td>
<td>0.000</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>420</td>
<td>2.951</td>
<td>0.280</td>
<td>13.768</td>
<td>0.031</td>
<td>0.091</td>
<td>0.009</td>
<td>0.0427</td>
</tr>
<tr>
<td>440</td>
<td>7.227</td>
<td>1.042</td>
<td>36.808</td>
<td>0.038</td>
<td>0.275</td>
<td>0.040</td>
<td>1.399</td>
</tr>
<tr>
<td>460</td>
<td>6.578</td>
<td>2.534</td>
<td>37.827</td>
<td>0.043</td>
<td>0.283</td>
<td>0.109</td>
<td>1.627</td>
</tr>
<tr>
<td>480</td>
<td>1.278</td>
<td>4.872</td>
<td>14.226</td>
<td>0.056</td>
<td>0.072</td>
<td>0.273</td>
<td>0.797</td>
</tr>
<tr>
<td>500</td>
<td>-0.259</td>
<td>8.38</td>
<td>3.254</td>
<td>0.027</td>
<td>-0.007</td>
<td>0.228</td>
<td>0.088</td>
</tr>
<tr>
<td>520</td>
<td>1.951</td>
<td>14.030</td>
<td>1.025</td>
<td>0.071</td>
<td>0.139</td>
<td>0.996</td>
<td>0.073</td>
</tr>
<tr>
<td>540</td>
<td>6.751</td>
<td>17.715</td>
<td>0.184</td>
<td>0.084</td>
<td>0.567</td>
<td>1.488</td>
<td>0.015</td>
</tr>
<tr>
<td>560</td>
<td>12.223</td>
<td>17.407</td>
<td>-0.013</td>
<td>0.093</td>
<td>1.137</td>
<td>1.619</td>
<td>-0.001</td>
</tr>
<tr>
<td>580</td>
<td>16.779</td>
<td>14.210</td>
<td>0.004</td>
<td>0.069</td>
<td>1.661</td>
<td>1.407</td>
<td>0.000</td>
</tr>
<tr>
<td>600</td>
<td>17.739</td>
<td>10.121</td>
<td>-0.001</td>
<td>0.111</td>
<td>1.975</td>
<td>1.123</td>
<td>0.000</td>
</tr>
<tr>
<td>620</td>
<td>13.135</td>
<td>5.971</td>
<td>0.000</td>
<td>0.253</td>
<td>3.323</td>
<td>1.511</td>
<td>0.000</td>
</tr>
<tr>
<td>640</td>
<td>5.859</td>
<td>2.399</td>
<td>0.000</td>
<td>0.460</td>
<td>2.995</td>
<td>1.104</td>
<td>0.000</td>
</tr>
<tr>
<td>660</td>
<td>1.901</td>
<td>0.741</td>
<td>0.000</td>
<td>0.662</td>
<td>1.258</td>
<td>0.491</td>
<td>0.000</td>
</tr>
<tr>
<td>680</td>
<td>0.469</td>
<td>0.184</td>
<td>0.000</td>
<td>0.816</td>
<td>0.383</td>
<td>0.150</td>
<td>0.000</td>
</tr>
<tr>
<td>700</td>
<td>0.117</td>
<td>0.044</td>
<td>0.000</td>
<td>0.873</td>
<td>0.102</td>
<td>0.038</td>
<td>0.000</td>
</tr>
<tr>
<td>Sums</td>
<td>94.811</td>
<td>100.000</td>
<td>107.304</td>
<td>13.960</td>
<td>10.580</td>
<td>4.430</td>
<td></td>
</tr>
</tbody>
</table>

The procedures used to give the best values of the weighting functions lead to some small negative values. These are real and must be used in the calculations to ensure accurate tristimulus values. \( R \) is the fractional reflectance of the sample’s surface.
The key parameters in the calculations are those for the three factors that determine the perceived colour of an object, namely:

1. the various values of $S(\lambda)$ for the relative SPD of the selected illuminant;
2. the values of $R(\lambda)$, the reflectance factors of the object at the different wavelengths;
3. the colour matching functions $x(\lambda)$, $y(\lambda)$ and $z(\lambda)$ of the chosen standard observer, all of which vary with wavelength.

The normalisation constant $k$ ensures that $Y = 100.0$ for the illuminant. This normalisation allows calculation of an object’s tristimulus values using:

1. the relative rather than the absolute SPD of the illuminant;
2. the percentage reflectance rather than the fractional reflectance factor (provided the value of the normalisation constant $k$ is divided by 100);
3. the spectral tristimulus values (colour matching functions), or the spectral chromaticity coordinates.

Table 21.2 shows a typical calculation for an object with a given reflectance spectrum.

21.6.3 Colour specification using the CIE XYZ colorimetric system

What do the values of the tristimulus values $X$, $Y$ and $Z$ mean? The colour of the object in question could be matched by additive mixing of $X$, $Y$ and $Z$ units of the respective primaries $[X]$, $[Y]$ and $[Z]$, or:

$$\text{Colour} = X[X] + Y[Y] + Z[Z]$$

Since $[X]$, $[Y]$ and $[Z]$ correspond to virtual red, green and blue primaries, the highest of the three tristimulus values of a colour will be $X$ for red, $Y$ for green and $Z$ for blue, respectively. In general, dark samples have low tristimulus values, particularly the value of $Y$, and light colours have high values. Thus, it is usually possible to predict the approximate colour of an unseen sample just from its
Although the tristimulus values do provide an approximate guide to an object’s colour, this is not the intended function of the CIE colorimetric system. Its sole purpose is to establish whether two objects have identical perceived colours, when viewed under conditions corresponding to those of the selected illuminant and standard observer. If the respective tristimulus values of the colours for two samples 1 and 2 are equal \((X_1 = X_2, Y_1 = Y_2 \text{ and } Z_1 = Z_2)\) then the samples will have identical colours under the given viewing conditions. Otherwise, the colours will appear different.

The CIE XYZ system provides a very powerful colour communication tool. The numerical description of a colour always requires three parameters, such as the three values \(X, Y\) and \(Z\). For the 1931 standard colorimetric observer, the \(Y\) tristimulus value gives a direct measure of the lightness or darkness of a sample. This is so because the \(Y\) colour matching function was selected to have its values equal to those of the photopic luminous efficacy. This is only approximately true for the 1964 supplementary observer. All illuminants and the perfect diffuse reflector have \(Y = 100\), and for a perfect black surface \(X = Y = Z = 0\).

The tristimulus values of a colour are psychophysical quantities but have no quantitative relation to the usual terms that we use to describe colours. These are:

<table>
<thead>
<tr>
<th>Fabric colour</th>
<th>(X_{10})</th>
<th>(Y_{10})</th>
<th>(Z_{10})</th>
<th>(X_{10})</th>
<th>(Y_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>20.80</td>
<td>12.28</td>
<td>5.21</td>
<td>0.543</td>
<td>0.321</td>
</tr>
<tr>
<td>Blushy-red</td>
<td>19.49</td>
<td>12.40</td>
<td>13.55</td>
<td>0.429</td>
<td>0.273</td>
</tr>
<tr>
<td>Orange</td>
<td>41.35</td>
<td>27.60</td>
<td>10.34</td>
<td>0.522</td>
<td>0.348</td>
</tr>
<tr>
<td>Deep reddish-brown</td>
<td>12.45</td>
<td>8.20</td>
<td>3.28</td>
<td>0.520</td>
<td>0.343</td>
</tr>
<tr>
<td>Pale yellow</td>
<td>68.66</td>
<td>74.83</td>
<td>36.42</td>
<td>0.382</td>
<td>0.416</td>
</tr>
<tr>
<td>Deep yellow</td>
<td>53.26</td>
<td>47.96</td>
<td>7.34</td>
<td>0.491</td>
<td>0.442</td>
</tr>
<tr>
<td>Green</td>
<td>21.69</td>
<td>35.45</td>
<td>36.36</td>
<td>0.237</td>
<td>0.366</td>
</tr>
<tr>
<td>Dark green</td>
<td>11.18</td>
<td>17.07</td>
<td>18.24</td>
<td>0.240</td>
<td>0.367</td>
</tr>
<tr>
<td>Blue</td>
<td>14.78</td>
<td>16.69</td>
<td>36.34</td>
<td>0.221</td>
<td>0.235</td>
</tr>
<tr>
<td>Dark blue</td>
<td>6.07</td>
<td>6.73</td>
<td>13.37</td>
<td>0.232</td>
<td>0.257</td>
</tr>
<tr>
<td>Pale violet</td>
<td>52.03</td>
<td>51.58</td>
<td>72.46</td>
<td>0.296</td>
<td>0.293</td>
</tr>
</tbody>
</table>

Table 21.3 Tristimulus values and corresponding chromaticity co-ordinates for typical dyed textile fabrics.
(1) the hue, which defines the colour (red, blue and so on);
(2) the saturation or chroma, which tells whether the colour is dull or bright
(degree of difference from grey);
(3) the lightness, which indicates how light or dark the colour is.

Tristimulus values serve only to demonstrate whether two colours are identical or not; they give no reliable information on the degree of perceived colour difference between two samples. What other information do the tristimulus values of the colour of an object provide?

21.6.4 Illuminant metamerism

Illuminant metamerism occurs when two objects, which have matching colours when examined under one source of light, say daylight (Illuminant D65), have different perceived colours under another source, such as tungsten light (Illuminant A). This type of metamerism arises in the following way. The two objects contain different colorants and have different reflection spectra. Under the first source, say daylight, the lights reflected from the respective samples that enter the eye have different SPDs, given by the values of $S(\lambda)/G(\lambda)$. However, both SPDs generate the same colour sensation. The respective values of $R(\lambda)$ for the two samples, used in the summation calculation of $X$, $Y$ and $Z$, are different, but in combination with the $S(\lambda)$ values for, say, Illuminant D65, they give identical sets of tristimulus values for the two samples:

$$X_1 = X_2, \quad Y_1 = Y_2, \quad Z_1 = Z_2$$

This is always possible because there are far fewer colour sensations than the infinite number of SPDs. If the two coloured samples that match in daylight are then viewed under a different source, such as tungsten light, the combinations of $R(\lambda)$ with the alternative values of $S(\lambda)$ give non-identical tristimulus values and thus a mismatch of the perceived colours.

Metamerism therefore involves two objects with different reflection spectra, giving identical colours and tristimulus values under one source, but different colours and tristimulus values when the illumination changes. The only way illuminant metamerism can be avoided is when the two samples contain identical amounts of the same colorants and thus have matching colours with identical reflection spectra. Even for such non-metameric samples, the perceived colours
change when the illumination changes, but they change in exactly the same way. The colours thus remain matched. The change of the perceived colour on changing the illumination often goes unnoticed because of the rapid adaptation of the eye. An example of tristimulus data for metameric and non-metameric samples is found in Table 21.4. In addition, the reflection spectra in Figure 21.9 also

Table 21.4 Tristimulus values of metameric and non-metameric colours of dyed fabrics (samples 1 and 2 were matched using identical dyes; samples 1 and 3 were dyed with different dyes)

<table>
<thead>
<tr>
<th>ILLUMINANT</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILLUMINANT</td>
<td>D65</td>
<td></td>
<td></td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Y</td>
<td>Z</td>
<td>X</td>
<td>Y</td>
<td>Z</td>
<td></td>
</tr>
<tr>
<td>NON-METAMERIC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>10.22</td>
<td>9.82</td>
<td>6.39</td>
<td>13.97</td>
<td>10.89</td>
<td>2.26</td>
</tr>
<tr>
<td>Sample 2</td>
<td>10.20</td>
<td>9.91</td>
<td>6.38</td>
<td>13.96</td>
<td>10.79</td>
<td>2.24</td>
</tr>
<tr>
<td>Match</td>
<td>Match</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>METAMERIC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>10.22</td>
<td>9.82</td>
<td>6.39</td>
<td>13.97</td>
<td>10.79</td>
<td>2.24</td>
</tr>
<tr>
<td>Sample 3</td>
<td>10.19</td>
<td>9.90</td>
<td>6.41</td>
<td>14.45</td>
<td>11.01</td>
<td>2.05</td>
</tr>
<tr>
<td>Match</td>
<td>Mis-match</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 21.9 Reflection spectra of metameric textile samples
illustrate illuminant metamerism for two grey samples. Calculation of the tristimulus values for both spectra (curves A and B) give $X_{10} = 5.87$, $Y_{10} = 5.72$ and $Z_{10} = 4.92$ when using CIE Illuminant D$_{65}$ and the samples do appear identical in daylight. The values are $X_{10} = 7.55$, $Y_{10} = 6.10$ and $Z_{10} = 1.63$ for curve A (dotted line), and $X_{10} = 7.34$, $Y_{10} = 6.11$ and $Z_{10} = 1.60$ for curve B (solid line) when calculated using CIE Illuminant A and the samples do not match under tungsten light, sample A being visibly redder.

**21.6.5 The CIE chromaticity diagram**

Once the tristimulus values of a colour are known, the corresponding chromaticity coordinates can be calculated:

$$X = \frac{X}{X+Y+Z}, \quad Y = \frac{Y}{X+Y+Z}, \quad Z = \frac{Z}{X+Y+Z}$$

The well-known CIE chromaticity diagram is a graph of the chromaticity coordinates of the spectral colours, usually $y$ versus $x$ as in Figure 21.8. All real colours have chromaticity coordinates inside the curve of the coordinates of the spectral lights. The line joining the two ends of the curve corresponds to the chromaticity coordinates of the non-spectral purples obtained by mixing a red spectral light ($\lambda = 750 \text{ nm}$) with a violet spectral light ($\lambda = 380 \text{ nm}$).

This chromaticity diagram gives no indication of how much light reflects off the sample and thus of whether the colour appears light or dark. Two colours may have identical chromaticity coordinates (identical values of $y$ and $x$) but quite different degrees of lightness (different values of $Y$). Note that the orange and dark red-brown samples in Table 21.3 have quite different tristimulus values but almost identical chromaticity coordinates. This is also true for the green and dark green samples. The complete specification of a colour in terms of its chromaticity coordinates must therefore include $Y$ as well as $x$ and $y$. Again, complete description of a colour requires three parameters. Two colours with the same set of values of $x$, $y$ and $Y$ for a given illuminant and standard observer, are identical in colour for the given conditions. This is the key result of the CIE colorimetric system, the equivalence or difference of two colours. The CIE chromaticity diagram provides no quantitative information on the appearance of colours. It is, however, useful to know where certain colours are placed in the diagram.

One advantage of the CIE chromaticity diagram is that the chromaticity
coordinates of coloured lights, produced by additive mixing of two primary sources, lie on the line joining the chromaticity coordinates of the two primaries. This has important implications in illumination engineering and colour television.

For real colours, the greater the Y tristimulus values, the more restricted are the values of their chromaticity coordinates x and y. The chromaticity diagram is the base of a three-dimensional figure with a lightness axis (Y axis) at right angles to the plane of the diagram starting at the point for the illuminant. The boundaries of this figure define a three-dimensional colour space within which the points corresponding to the coordinates of all real colours (x, y and Y) are situated. For high values of Y (light colours), there is a strong trend towards yellow, while light blues, reds and greens become much less probable. Only saturated colours of low lightness have coordinates close to the spectral locus well away from the vertical Y axis. Figure 21.10 illustrates this in the form of a contour diagram.

Another difficulty with the CIE chromaticity diagram is the problem of the positions of points for blacks, greys and whites. A white surface will usually have chromaticity coordinates close to those of the illuminant, somewhere in the centre of the diagram. Blacks, however, have very low reflectance and their chromaticity coordinates tend to be scattered around the white point depending on the tint. Neutral blacks, greys and whites are essentially achromatic (without colour) and
have about the same chromaticity coordinates. Black and white give low and high values of $Y$ respectively, at the two extremes of the lightness axis, while the $Y$ values for neutral greys lie in between.

21.6.6 Whiteness

White objects have high reflectance at all wavelengths in the visible region of the spectrum. Individuals differ widely in their preferences for and evaluations of whiteness, pronounced cultural preferences being common. The preferred white in Western society, for non-fluorescent samples, has chromaticity coordinates $x = 0.31$ and $y = 0.31$. This white is thus shaded somewhat towards blue ($z = 0.38$ by difference).

Colorimetry is valuable for evaluating the degree of whiteness of materials, particularly when they have a tendency to yellow. None of the various whiteness equations has proved to be superior to others. The CIE recommends a whiteness index defined by:

$$W = Y + 800(x_n - x) + 1700(y_n - y)$$ (23)

where $Y$ is the sample’s $Y$ tristimulus value, $x$ and $y$ are its chromaticity coordinates, and $x_n$ and $y_n$ the chromaticity coordinates of the illuminant, for either of the standard observers using Illuminant D65. The higher the value of $W$, the greater the degree of whiteness. Do not confuse the whiteness index $W$ with the weighting factors in Table 21.2. To establish the tint of a white object, the following equation is recommended:

$$T_W = K(x_n - x) - 650(y_n - y)$$ (24)

where $K = 1000$ or 900, for the 2° and 10° standard observers respectively. Positive values of $T_W$ correspond to a green tint, whereas negative values correspond to a red tint. These equations serve for the comparison of similar whites only.

21.7 THE MUNSELL COLOUR SYSTEM

Specification and communication of colours require a number of different colour organisation systems to serve different colour using groups. Some systems are
based on coloured samples that may be randomly arranged or organised according to some guiding principle. The CIE system gives a numerical description of a colour and has no samples.

The Munsell Book of Colours is one of the best-known sample-based systems. It is used in both the graphic arts as well as in industry. In this system, each colour is described in terms of its hue, value (lightness) and chroma (saturation). These are the usual terms that we use to describe colours and colour differences. Note again that three variables are used.

The hue is defined by the colours red, yellow, blue and so on. The ten basic hues in the Munsell system are arranged around a circular axis from red (R), through yellow (Y), green (G) and blue (B), to purple (P) (Figure 21.11). They are designated R, YR, Y, GY, G, BG, B, PB, P and RP. Each of the ten hues has ten subdivisions for a total of 100 hues. For example, the series of hues around yellow are designated ... 8YR, 9YR, 10YR, 1Y, 2Y, 3Y, ... 8Y, 9Y, 10Y, 1GY, 2GY, ... and so on.

The value gives the lightness of a colour on a vertical scale with 11 divisions. Samples with no hue (greys) lie along the central axis going from black to white. Real samples for pure white and black, with a value of 10 and 0 respectively, do not exist and the practical scale goes from 9 to 1. Colours with identical perceived lightness all lie in the same horizontal plane at the appropriate height along the value axis.

Figure 21.11 Illustration of the mutually perpendicular hue, value and chroma axes in the Munsell system
The chroma of a given hue increases moving away from grey on a radial scale with up to 14 divisions and corresponds to the saturation or vividness of the colour. A grey sample of given value (lightness) is surrounded by a circle of different hues. Samples of the same hue with the same lightness become more vivid and have greater chroma as they become more colourful and less grey. The samples in the Munsell system have an alphanumeric specification. Thus, 5Y8/10 indicates a light yellow of fairly high saturation, hue = 5Y, value = 8, chroma = 10.

In the Munsell Book of Colours, each page presents a series of samples of constant hue but varying value (vertically) and chroma (horizontally). If the pages of the book fan out in a circle, one can recognise the three-dimensional colour space in terms of hue, chroma and value (Figure 21.11). This space is irregular as the number of chroma steps for each hue, at each value level, varies considerably because of the lack of high chroma paint pigments in some hues.

The coloured paint chips in the book are prepared to high tolerances and are available in a glossy or matte finish. The chips are selected and arranged in such a way that the perceived colour difference between any pair of neighbouring samples along the radial chroma axis is always the same independent of the hue or value. This is also true of neighbouring samples that lie along the vertical value scale, or around the circular hue axis. Unfortunately, samples differing by one value step have about the same degree of colour difference as neighbouring samples differing by two chroma steps, or three hue steps (at chroma = 5). Nevertheless, the Munsell system represents a well-organised, three-dimensional colour space. Its major disadvantage is that the colour differences between adjacent pairs of samples are quite large, greatly exceeding typical commercial colour tolerances.

Measurements of the CIE tristimulus values of the colours of Munsell samples have been carried out and recommendations made ensuring the equality of the colour differences between neighbouring chips in any given direction, despite the differences in the visual steps in the hue, value and chroma directions. These improvements are called the Munsell Renotations. They are important because they directly relate visual colour differences to colorimetric measurements.

21.8 VISUAL UNIFORMITY OF COLOUR SPACES

21.8.1 Differences in the tristimulus values of two colours

A major problem with the CIE XYZ colorimetric system is its non-uniformity in terms of visual assessment. This means simply that equal differences in perceived colour between pairs of samples do not correspond to equal differences in the
COLOUR MEASUREMENT

tristimulus values. Any colour can be specified by its three tristimulus values X, Y and Z. If these are plotted on a three-dimensional graph with mutually perpendicular axes, a single point represents the coordinates of each colour. All real colours would have their coordinates (X, Y and Z) within the boundary defining this XYZ colour space. The difference in colour between two samples would correspond to the distance between the two points for their respective coordinates.

What are the consequences of the visual non-uniformity of the XYZ colour space? In general, two greens that are just perceptibly different in colour will give a considerably larger difference in tristimulus values than a pair of two red or blue samples that have been judged to have the same colour difference as the pair of greens. This means that a single colour tolerance for all shades is impossible. The colourist therefore needs to establish different colour tolerances in terms of X, Y and Z for each shade produced. This rather defeats the objective of having a colour measurement system for colour assessment.

This problem prompted an extensive search for a more uniform colour space. Those that have been recommended are based on modifications of the XYZ system. The ideal colour space is one for which identical spacings between the points corresponding to the coordinates of similar colours would always correspond exactly to the same observed colour differences, independent of the actual colours of the samples. Despite many attempts, the ideal colour space having this characteristic has proved to be very elusive. The CIE has recommended other types of colour space that are more visually uniform than the XYZ space but none have yet proved to be completely satisfactory.

21.8.2 The CIELAB colour space

The Hunter Lab colorimeter was the first instrument allowing colour measurement readings in terms of opponent colours, red-green or a* and blue-yellow or b*, and of the colour’s lightness (L*), as described in Hering’s colour vision theory. The CIELAB colour space was developed from earlier attempts to transform the X, Y and Z tristimulus values into coordinates that would provide better uniformity. Nickerson and Stultz modified the initial work by Adams and developed what became known as the ANLAB (Adams–Nickerson LAB) system. The ANLAB colour space involved complex calculations but proved very popular because it permitted specification of the colour difference between two coloured samples. It has essentially the same axes as the Munsell system.
The current CIELAB colour space was a further development of the ANLAB system, originally suggested by MacAdam (1973) and based on non-linear cube root transformations of the CIE tristimulus values. The CIELAB system, recommended by the CIE in 1976, is a very popular one for colour and colour difference specification. The three parameters calculated are $L^*$, $a^*$ and $b^*$. The value of $L^*$ for a given colour varies between 0 (perfect black) and 100 (perfect white), and gives a measure of the lightness of the colour. The value of $a^*$ is a measure of the red–green character of the colour, with positive values for red shades and negative values for green. The value of $b^*$ gives the yellow–blue character with positive values for yellow shades and negative for blues (Figure 21.12).

![Diagram of CIELAB colour space](image)

**Figure 21.12** The mutually perpendicular $L^*$, $a^*$ and $b^*$ axes of the CIELAB colour space

The values of $L^*$, $a^*$ and $b^*$ are calculated from the tristimulus values of the colour ($X$, $Y$ and $Z$), each value being first divided by the corresponding tristimulus value of the appropriate illuminant ($X_n$, $Y_n$ and $Z_n$). The psychometric lightness $L^*$ is calculated from:

$$L^* = 116 \left( \frac{Y}{Y_n} \right)^{1/3} - 16$$

(25)
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$a^*$ and $b^*$ are given by:

$$a^* = 500 \left( \frac{X}{X_n} \right)^{1/3} - \left( \frac{Y}{Y_n} \right)^{1/3}$$  (26)

$$b^* = 200 \left( \frac{Y}{Y_n} \right)^{1/3} - \left( \frac{Z}{Z_n} \right)^{1/3}$$  (27)

For very dark colours, other mathematical forms replace the cube root functions for $(X/X_n)$, $(Y/Y_n)$ and $(Z/Z_n)$ if their values are equal to or less than 0.008856. Note that the red–green response is a function of the difference between $X$ and $Y$, and the blue–yellow response a function of that between $Y$ and $Z$.

The CIELAB colour space has rectangular axes as shown in Figure 21.12. The position of the point representing a colour can also be in cylindrical coordinates as in the Munsell system with axes corresponding to the value (height), chroma (radius) and hue (angle). Using such coordinates for the CIELAB space, the exact position of a point will be defined by a height above $L^* = 0$, a radial distance $C^*_{ab}$ from the central vertical grey axis where $a^* = b^* = 0$, and by an angle $h_{ab}$ relative to some initial chroma radius. The hue angle is measured from the positive $a^*$ axis. Note again, three parameters are required to completely specify a colour, either $L^*$, $a^*$ and $b^*$, or $L^*$, $C^*_{ab}$ and $h_{ab}$.

A human observer invariably characterises colour differences in terms of hue, saturation and lightness. The cylindrical coordinates $L^*$, $C^*_{ab}$ and $h_{ab}$ thus correspond more closely to the way in which we describe colours. Figure 21.13 illustrates the relationships between $C^*_{ab}$ and $h_{ab}$, and $a^*$ and $b^*$, given below. The calculation of $C^*_{ab}$ and $h_{ab}$ is based on the trigonometry of a right-angled triangle:

$$C^*_{ab} = \sqrt{(a^*)^2 + (b^*)^2}$$

$$\tan(h_{ab}) = \frac{b^*}{a^*}$$  (28)

The range of values of $a^*$ is from +60 (vivid red) to −50 (vivid green), whereas for $b^*$ the values vary from +90 (vivid yellow) to −50 (vivid blue). The corresponding values of $C^*_{ab}$ are therefore from 0 up to 90. The hue angle $h_{ab}$ varies from $0^\circ$ ($a^*$
axis, red) through 90° (positive b* axis, yellow), 180° (negative a* axis, green), 270° (negative b* axis, blue), up to 360 or 0° (a* axis). In calculating the hue angle, it is necessary to know in which quadrant the colour point is located. For example, for a* = -20 and b* = -20, b*/a* = 1. Therefore, h_ab could be 45 or 225°. The latter value is the correct one for these values of a* and b*. Table 21.5 gives some typical values of CIELAB coordinates for dyed fabrics.

Table 21.5 CIELAB data for the dyed fabrics samples in Table 21.3

<table>
<thead>
<tr>
<th>Fabric colour</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C_ab*</th>
<th>h_ab</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>41.66</td>
<td>62.50</td>
<td>8.10</td>
<td>63.02</td>
<td>7.40</td>
</tr>
<tr>
<td>Bluish-red</td>
<td>41.84</td>
<td>45.76</td>
<td>-7.52</td>
<td>46.37</td>
<td>350.70</td>
</tr>
<tr>
<td>Orange</td>
<td>59.53</td>
<td>53.64</td>
<td>44.86</td>
<td>69.93</td>
<td>39.90</td>
</tr>
<tr>
<td>Deep reddish-brown</td>
<td>29.91</td>
<td>33.93</td>
<td>25.43</td>
<td>42.30</td>
<td>36.90</td>
</tr>
<tr>
<td>Pale yellow</td>
<td>89.83</td>
<td>-4.93</td>
<td>70.36</td>
<td>70.53</td>
<td>94.00</td>
</tr>
<tr>
<td>Deep yellow</td>
<td>58.00</td>
<td>-5.95</td>
<td>64.11</td>
<td>64.39</td>
<td>95.30</td>
</tr>
<tr>
<td>Green</td>
<td>64.52</td>
<td>-41.29</td>
<td>15.18</td>
<td>43.99</td>
<td>159.80</td>
</tr>
<tr>
<td>Dark green</td>
<td>45.18</td>
<td>-42.77</td>
<td>7.86</td>
<td>43.48</td>
<td>169.60</td>
</tr>
<tr>
<td>Blue</td>
<td>46.57</td>
<td>-13.31</td>
<td>-4.21</td>
<td>44.26</td>
<td>252.50</td>
</tr>
<tr>
<td>Dark blue</td>
<td>31.18</td>
<td>-3.36</td>
<td>-38.98</td>
<td>39.12</td>
<td>265.10</td>
</tr>
<tr>
<td>Pale violet</td>
<td>73.25</td>
<td>49.38</td>
<td>-21.59</td>
<td>53.89</td>
<td>336.40</td>
</tr>
</tbody>
</table>

Figure 21.13 The CIELAB colour space showing the chroma and hue angle of a colour
The CIELAB colour space is much more uniform in terms of numerical versus visual colour differences than the XYZ system. When the coordinates of a number of Munsell colours of constant hue and value, but varying chroma, are plotted on the CIE x-y chromaticity diagram, a series of smooth curves is obtained. If the XYZ colour space were visually uniform, this series of Munsell colours of increasing chroma or purity would give a series of straight lines with equally spaced points which is not the case in the left hand Figure 21.14. Similar x-y plots for Munsell colours of constant value and chroma, but varying hue, do not give circles, as would be required for a uniform XYZ colour space, but deformed ellipses. Along any axis of the Munsell system, the samples have constant differences of hue, chroma or value. Similar plots of the $L^*$, $a^*$ and $b^*$ values of Munsell samples demonstrate the improved uniformity of the CIELAB colour space (Figure 21.14).

![Graphs of y versus x, and of b* versus a* at constant L*, for a series of Munsell paint chips](image)

**REFERENCES**

CHAPTER 22

Colour differences and colorant formulation

22.1 COLOUR DIFFERENCE EQUATIONS

22.1.1 Quantitative colour differences using CIELAB

Visual evaluation of colour differences involves both the description of the colour difference and consideration of the viewing conditions. Even when two observers examine a pair of samples under identical conditions, they may not agree on whether the samples match, or on the colour difference between them. Instrumental colour difference measurements eliminate colour assessment disagreements arising from variations in the colour vision of the observers and in the viewing conditions. In commercial colour matching, a product’s colour may not be identical with that of the target but it may still be acceptable. Colour matchers therefore distinguish between colour difference perceptibility and acceptability. A colour difference evaluation system should ideally allow the specification of the maximum permissible colour difference for acceptability as well as the much more stringent tolerance for perceptibility.

Colours that do not match have different sets of the tristimulus values X, Y and Z. The major criticism of the CIE XYZ colour space is that equal differences in perceived colour between pairs of samples do not correspond to equal differences in the tristimulus values (Section 21.8.1). The XYZ colour space is thus not particularly useful for colour difference evaluation.

The values of \( L^*, a^* \) and \( b^* \) for a given colour locate its position in the three-dimensional CIELAB space. The colour difference between two similar non-matching colours is the distance between the points for their respective coordinates in the CIELAB colour space. This is calculated using the law of Pythagoras (Figure 22.1).

The colour difference \( \Delta E^*_{ab} \) is:

\[
\Delta E^*_{ab} = \sqrt{\Delta L^*^2 + \Delta a^*^2 + \Delta b^*^2}
\]

(1)
where:

\[ \Delta L^* = L^*_\text{sam} - L^*_\text{std} \]
\[ \Delta a^* = a^*_\text{sam} - a^*_\text{std} \]
\[ \Delta b^* = b^*_\text{sam} - b^*_\text{std} \] (2)

and where the subscripts ‘sam’ and ‘std’ refer to the sample and standard colour, respectively.

Such a measurement of colour difference is very useful for establishing whether a coloured sample is an acceptable match to the target, or for evaluating the degree of metamerism of a single sample when the illuminant changes. This system of colour difference specification is now widely used. Many colour matchers consider that a value of \( \Delta E^*_{ab} \) less than 1.0 unit corresponds to an acceptable colour match. Examination of Figure 21.13, however, shows that the CIELAB colour space, although considerably more uniform than the XYZ space, is not perfect. The coordinates of Munsell colours of constant value and chroma do not give perfect circles in an \( a^*-b^* \) figure, nor do colours of constant hue and value but increasing chroma give exactly straight lines. In addition, the value of \( \Delta E^*_{ab} \) does not always correspond to the colour difference evaluated by visual examination of the samples. Thus, a single colour tolerance for all shades is again an elusive goal.

Figure 22.1 Differences in lightness, chroma, hue and colour in the CIELAB colour space
22.1.2 The CIELAB hue and chroma differences

A human observer invariably characterises colour differences in terms of differences in hue, saturation and lightness. The human eye is, however, much more sensitive to small differences in hue than to small differences in saturation or lightness. Two slightly different pale coloured samples may give a value of $\Delta E_{ab}$ of 2.0 units mainly because of differences in saturation and lightness, with little difference in hue. The samples would most likely be an acceptable match. A second pair of samples, with the same colour difference of $\Delta E_{ab} = 2.0$, would not be acceptable if this was mainly from a difference of hue. If one plots the values of $a^*$ against $b^*$ for a series of colours with the same value of $L^*$, that are slightly different from a standard colour, the samples that are just perceptibly different from the standard colour have coordinates lying around a flattened ellipsoid oriented towards the origin ($a^* = b^* = 0$) with the coordinates of the standard at its centre. These ellipses are quite narrow in the direction of hue angle, but elongated in the chroma direction ($C^*$), as well as in the lightness direction. The values of $\Delta E_{ab}$ for just visible differences in hue are therefore much smaller than those for just visible differences in lightness or saturation (Figure 22.2).

![Figure 22.2 Values of $L^*$ and $C^*$, for colours of constant hue, and of $a^*$ and $b^*$ for colours of constant $L^*$, that are just perceptibly different from a colour standard](image)

For similar colours, whose coordinates are close together in the colour space, it is possible to define a difference in chroma $\Delta C^*$ and a difference in hue $\Delta H^*$. The value of $C^*$ is given by:

$$C^*_{ab} = \sqrt{a^{*2} + b^{*2}}$$  \hspace{1cm} (3)

and:

$$\Delta C^*_{ab} = C^*_{sam} - C^*_{std}$$  \hspace{1cm} (4)
Figure 22.1 shows how the law of Pythagoras gives:

$$\Delta E_{ab}^* = \Delta L^* + \Delta C_{ab}^* + \Delta H_{ab}^*$$  \hspace{1cm} (5)

Since $\Delta L^*$, $\Delta E_{ab}^*$, and $\Delta C_{ab}^*$ are known, the value of $\Delta H_{ab}^*$ is calculated by difference:

$$\Delta H_{ab}^* = \sqrt{\Delta E_{ab}^* - \Delta L^* - \Delta C_{ab}^*}^2$$  \hspace{1cm} (6)

The values of $\Delta L^*$, $\Delta C_{ab}^*$, and $\Delta H_{ab}^*$ give a more useful indication of the colour difference between a sample and a standard than a simple measure of $\Delta E_{ab}^*$ because they define the colour difference in terms of characteristics used by a human observer. In colour matching, the value of $\Delta H_{ab}^*$ will have stricter tolerances than those for $\Delta L^*$ and $\Delta C_{ab}^*$.

The objective of CIELAB was a more uniform colour space in which instrumental colour differences such as $\Delta E_{ab}^*$ would always correlate with visually perceived colour differences. Over twenty years of experience have shown that the CIELAB colour space is not perfect. Figures 21.13 and 22.2 illustrate this conclusion. A single value of the CIELAB colour difference is not a completely reliable colour tolerance. The non-uniformity of the CIELAB colour space gives different values of $\Delta E_{ab}^*$ in different regions of the space for identical differences in perceived colour. Table 22.1 shows some CIELAB colour difference data for two yellow and two blue fabrics. For each hue, there is a slight difference in colour between the pairs of samples, but this was within the commercial acceptability tolerance. Note that for the yellow pair, $\Delta E_{ab}^*$ is double the value for the blue pair, and that, in each case, $\Delta H_{ab}^*$ is less than both $\Delta L^*$ and $\Delta C_{ab}^*$.

<table>
<thead>
<tr>
<th>Colour</th>
<th>$\Delta L^*$</th>
<th>$\Delta C_{ab}^*$</th>
<th>$\Delta H_{ab}^*$</th>
<th>$\Delta E_{ab}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brilliant Yellow</td>
<td>0.99</td>
<td>1.20</td>
<td>0.76</td>
<td>1.73</td>
</tr>
<tr>
<td>Deep Blue</td>
<td>0.60</td>
<td>0.52</td>
<td>0.30</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 22.1 Comparison of colour differences found for acceptable matching of yellow and blue dyings
22.1.3 The CMC system

The correlation of instrumentally determined colour differences with visual evaluations is a serious fundamental and practical problem. The continued introduction of new colour difference equations, the most recent in 1994, shows that this problem still persists. The majority of colour difference equations are merely of historical interest and we will examine only the CMC and CIE-1994 systems. Both of these convert CIELAB data for a pair of similar colours into a colour difference value and allow specification of a single colour tolerance for all hues. This is an advantage in commercial colour matching.

The CMC system was originally developed by R. McDonald and later recommended by the Colour Matching Committee of the SDC with only minor modifications. The initial work involved 55 target shades with colour coordinates all around the CIELAB colour space. For each target colour, a series of dyeings with colours close to the target were obtained and examined by a number of competent colour matchers. They evaluated the acceptability or unacceptability of each dyeing relative to its target shade. This pass/fail evaluation involved comparison of the colour difference of the dyed samples, with the contrast between a pair of almost identical grey samples. For each set of samples, the values of $L^*$, $C^*_{ab}$ and $H^*_{ab}$ were plotted using rectangular coordinates. This gave a series of points close to the coordinates for the target shade but scattered around it in all directions. An ellipsoid was then drawn through these points, with the coordinates for the target at its centre, and whose surface enclosed the points for those samples judged to be acceptable matches with the target by at least 50% of the observers. Points lying outside the surface of this ellipsoid represented coordinates of shades that were unacceptable to more than 50% of the colour matchers. The size of this acceptability ellipsoid is defined by the lengths of its three semi-axes $S_L$, $S_C$ and $S_H$ in the $L^*$, $C^*_{ab}$ and $H^*_{ab}$ directions, respectively. This type of study was later repeated for a much larger number of standard shades, the evaluation being carried out by a single observer.

The sizes of the acceptability ellipsoids vary depending upon the location of the coordinates of the standard shade in the CIELAB colour space. This is a consequence of its visual non-uniformity. The equations describing the variations of $S_L$, $S_C$ and $S_H$ were subsequently accepted by the CMC. They allow calculation of the lengths of the three mutually perpendicular semi-axes of the ellipsoids (Figure 22.3). The values of these are related to the acceptable tolerances for lightness, chroma and hue.
The values of $S_L$, $S_C$ and $S_H$ vary as the coordinates of the standard shade change. Electronic computation easily handles the rather complex equations:

$$S_L = \frac{0.040975 \times L^*}{1 + 0.01765 \times L^*} \quad \text{for} \quad L^* > 16, \quad S_L = 0.511 \quad \text{for} \quad L^* < 16$$

$$S_C = \frac{0.0638C_{ab}^*}{1 + 0.0113C_{ab}^*} + 0.638$$

$$S_H = S_C \left[ (T,f) + 1 - f \right]$$

In the equation for $S_{xy}$, the values of the parameters $f$ and $T$ are given by:

$$f = \frac{C_{ab}^4}{1900 + C_{ab}^4}$$

$$T = 0.36 + 0.4 \cos(h_{ab} + 35) \quad \text{for} \quad h_{ab} < 164^\circ \text{ but } > 345^\circ$$

$$T = 0.56 + 0.2 \cos(h_{ab} + 168) \quad \text{for} \quad h_{ab} > 164^\circ \text{ but } < 345^\circ$$

Figure 22.3 Illustration of a CMC acceptability ellipsoid showing the three semi-axes.
In the equations for $T$, the values between the vertical lines are absolute values. Even though the cosine of an angle may be positive or negative, the absolute value is always positive.

The value of $S_L$ increases with increase in the value $L^*$ of the sample-target pair ranging from the minimum value of 0.511 up to about 1.4, whereas $S_C$ increases from about 1 to 3 with increasing $C^*_{ab}$. This means that a difference in lightness is more visually acceptable to an observer for light rather than dark colours, and a difference in chroma more acceptable for saturated than for dull colours. The variations of $S_H$ are more complex, increasing with increasing $C^*_{ab}$ but always oscillating as the hue angle increases. Figure 22.4 illustrates these variations of $S_H$ with hue angle. A human observer is more sensitive to hue differences for colours of low chroma with hue angles around 55° (orange) and 280° (reddish-blue), particularly the former. Hue differences in the range 135°–210° (greens) and around 345° (bluish-red) are more readily accepted. The values of $S_H$ are lower than those of $S_C$ and $S_L$ because of the lower tolerance to hue differences. The observed variations in the ellipsoid semi-axes reflect the visual non-uniformity of the CIELAB colour space.

The CMC colour difference is defined by:

$$ (\Delta E_{CMC})^2 = \left( \frac{\Delta L}{1 \times S_L} \right)^2 + \left( \frac{\Delta C^*}{c \times S_C} \right)^2 + \left( \frac{\Delta H^*}{S_H} \right)^2 $$  (13)

Figure 22.4  Variation of $S_H$ with hue angle at two chroma values
This equation gives the coordinates of points lying on the surface of a three-dimensional ellipsoid, with semi-axes with lengths of $S_L$, $S_C$ and $S_H$ and with $\Delta E_{\text{CMC}} = 1.0$. The weighting factors $l$ and $c$ for $S_L$ and $S_C$ in the respective denominators of the CMC colour difference equation indicate the lesser importance of the tolerances $S_L$ and $S_C$ relative to $S_H$. This allows variations of these weighting factors for different situations and different substrates. The CMC recommend $l = 1$ and $c = 1$ when evaluating perceptibility differences, but $l = 2$ and $c = 1$ for differences in acceptability. This is in line with the greater visual tolerance of lightness differences in colour matching. The values $l = 2$ and $c = 1$ are those usually recommended for use in evaluating the colours of textile samples.

The CMC acceptability ellipsoids are longer in the lightness and chroma directions than in the hue direction. They become larger the greater the lightness and chroma of the colour. If the CIELAB colour space were uniform, the acceptability volumes would all be spherical and of equal size throughout the colour space. In the CMC system, the varying size of the acceptability ellipsoids around the CIELAB colour space corrects for its visual non-uniformity. In any region of the colour space, pairs of samples having a value of $\Delta E_{\text{CMC}}$ less than 1.00 will be an acceptable match ($l = 2$), or indistinguishable ($l = 1$), to greater than 50% of the observers. A value of $\Delta E_{\text{CMC}} = 1.0$ thus becomes the sole colour acceptability tolerance for all colours. A pass/fail evaluation based on a single colour difference value has obvious advantages in commercial colour matching.

The CMC system has become an international standard in many countries.

### Other colour difference equations

In addition to the CMC colour difference equation, three other advanced formulas merit some attention. There are no published details of the Marks and Spencer colour difference equation but it is used by their suppliers. The BFD (University of Bradford) and CIE-94 formulas are similar to the CMC formula. The CIE-94 colour difference equation \[1,2\] is identical to the CMC equation but the values of $S_L$, $S_C$ and $S_H$ are calculated using simpler linear equations. For CIE-94, $S_L$ is constant, and $S_H$ depends only on the chroma and not on the hue angle. The CIE-94 equations are:

$$
S_L = 1 \quad S_C = 1 + 0.045C_{ab}^* \quad S_H = 1 + 0.015H_{ab}^* \quad (14)
$$

The BFD colour difference equation is similar to that of the CMC system, but has an additional term depending on $\Delta C_{ab}^*$ and $\Delta H_{ab}^*$. In addition, the lightness
difference ($A_{LDEB}$) is calculated differently from the CIELAB value while the other equations are even more complex than those of the CMC system.

All these methods of quantifying colour difference are relatively new and current experience is insufficient to establish which is superior. The present situation is that neither the BFD nor the CIE-94 formulas seem to be any better than the CMC formula [3] and are not likely to replace it as a national standard.

22.2 SHADE SORTING

For the assembly of an article composed of a number of identical fabric panels, these must have the same colour, particularly when joined at a seam. This is often a problem when different rolls of fabric exhibit the slight colour variations typical of batch dyeing. Textile manufacture involves many multi-variable processes, all of which should be quite reproducible if each roll of fabric is to have the same colour. Each slight variation in yarn characteristics or fabric construction, in the preparation and bleaching processes, in the weighing of the fabric and dyes or in the actual dyeing conditions, can cause slight batch-to-batch colour differences. Therefore, if a client has ordered a large number of rolls of the same fabric, it is common for these to exhibit slight but visible colour differences. These variations prevent cutting of any particular panel from any roll of fabric at random since it would be a matter of luck if two adjacent panels of fabric had exactly the same shade.

The objective of shade sorting is to identify and group together rolls of fabric with a negligible colour difference from which panels can be cut and assembled into the required article without any objectionable colour differences between adjacent panels. This, of course, requires setting appropriate colour tolerances, usually in consultation with the client. Visual colour sorting is not particularly reliable. The same person often produces different sorting results from day to day for the same set of samples.

A number of shade sorting systems help to minimise this problem. They depend on colorimetric measurements, colour difference tolerances and powerful software. In measuring small colour differences, it is essential that the data are reproducible and that the colorimeter or spectrophotometer measures true colour differences and not differences caused by variations in the presentation of the sample or in the operation of the instrument. The colourist must be constantly aware of the factors that influence the colour coordinates of a sample. These include fabric texture, sample orientation, lustre, metamerism and viewing conditions. Particular
attention to sampling technique, sample manipulation and instrument operation is essential to ensure reproducible colorimetric measurements. Shade sorting is only reliable if the colorimetric data are precise.

The 555 shade sorting system [4] has gained wide acceptance despite some limitations. The following illustrates some of the principles of shade sorting using the 555 system as an example. A region of the CIELAB colour space around the standard shade is divided into a series of rectangular boxes oriented along the three perpendicular \( L^* \), \( C^*_{ab} \) and \( H^*_{ab} \) directions. The three dimensions of each box are equal to twice the values of the desired tolerances for \( L^* \), \( C^*_{ab} \) and \( H^*_{ab} \), respectively. All colours with \( L^* \), \( C^*_{ab} \) and \( H^*_{ab} \) coordinates within any box have an acceptable colour difference relative to the colour whose coordinates would locate it at the geometric centre of the box. Two types of colour tolerances must be considered:

1. somewhat large tolerances for \( L^* \), \( C^*_{ab} \) and \( H^*_{ab} \) defining a relatively large colour difference from the target shade. Samples having a larger colour difference than this are unacceptable and indicate a possible problem in production;

2. tolerances for \( L^* \), \( C^*_{ab} \) and \( H^*_{ab} \) that are much more stringent and represent a small acceptable colour difference from the colour having coordinates at a box centre.

Even though a group of samples may have a visibly different shade than the target colour, they may all be sufficiently close in colour that the points for their coordinates are all inside the same box. The coordinates of the target shade are at the centre of the box labelled 555. All samples having values of \( \Delta L^* \), \( \Delta C^*_{ab} \) and \( \Delta H^*_{ab} \) relative to the target less than the established tolerances for \( L^* \), \( C^*_{ab} \) and \( H^*_{ab} \) have coordinates within the 555 box. These samples are not unacceptably different in colour from the target shade. The remaining boxes, all with the same dimensions, fill the space surrounding the 555 box in the three perpendicular directions. Their numerical designation depends upon the number of tolerance increments, along each of the three axes, from the central 555 box (Figure 22.5).

Table 22.2 shows the relation between box numbers and colour tolerances. The numbers in the box designation refer to the numbers of tolerance steps from the target colour at the centre of the 555 box in the \( \Delta L^* \), \( \Delta C^*_{ab} \) and \( \Delta H^*_{ab} \) directions, respectively. Thus, a sample whose coordinates place it the 627 box is lighter than the standard with a positive value of \( \Delta L^* \) from 1 to 3 times the established lightness tolerance (Table 22.2). Thus, 1 is added to the first five in 555. Scheme 22.1 shows that in any of the three coordinate directions, the
Figure 22.5 Illustration of the boxes lying along the three perpendicular axes in the 555 shade sorting system

Table 22.2 Shade assignment in the 555 shade sorting system of a blue fabric with \( L^* = 37.73, a^* = -2.45 \) and \( b^* = -39.04 \) with tolerances for \( L^* = 0.5, C_{L*} = 0.3 \) and \( H_{L*} = 0.2 \)

<table>
<thead>
<tr>
<th>( \Delta L^* ) darker</th>
<th>( \Delta C_{L*} ) duller</th>
<th>( \Delta H_{L*} ) greener</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  -4.50</td>
<td>1  -2.70</td>
<td>1  -1.80</td>
</tr>
<tr>
<td>2  -3.50</td>
<td>2  -2.10</td>
<td>2  -1.40</td>
</tr>
<tr>
<td>3  -2.50</td>
<td>3  -1.50</td>
<td>3  -1.00</td>
</tr>
<tr>
<td>4  -1.50</td>
<td>4  -0.90</td>
<td>4  -0.60</td>
</tr>
<tr>
<td></td>
<td>-0.51</td>
<td>-0.31</td>
</tr>
<tr>
<td></td>
<td>-0.50 standard</td>
<td>-0.30 standard</td>
</tr>
<tr>
<td></td>
<td>+0.50</td>
<td>+0.30</td>
</tr>
<tr>
<td>5  standard +0.50</td>
<td>5  standard +0.30</td>
<td>5  standard +0.20</td>
</tr>
<tr>
<td></td>
<td>+0.51</td>
<td>+0.31</td>
</tr>
<tr>
<td></td>
<td>+1.50</td>
<td>+0.90</td>
</tr>
<tr>
<td>6  +1.50</td>
<td>6  +0.91</td>
<td>6  +0.60</td>
</tr>
<tr>
<td>7  +1.50</td>
<td>7  +1.50</td>
<td>7  +1.00</td>
</tr>
<tr>
<td>8  +2.51</td>
<td>8  +1.51</td>
<td>8  +1.00</td>
</tr>
<tr>
<td>9  +3.50</td>
<td>9  +2.10</td>
<td>9  +1.40</td>
</tr>
<tr>
<td></td>
<td>+2.70</td>
<td>+1.80</td>
</tr>
</tbody>
</table>

\( \Delta L^* \) lighter \( \Delta C_{L*} \) brighter \( \Delta H_{L*} \) redder
COLOUR DIFFERENCES AND COLORANT FORMULATION

The dimension of a box in that direction is twice the tolerance. It also illustrates the relation between the tolerances for $L^*$, $C^*_{ab}$, and $H^*_{ab}$ and the box number specification. The sample corresponding to box 627 is less saturated than the standard. Its $C^*_{ab}$ value is negative and 5 to 7 times the chroma tolerance. Thus in this case, 3 is subtracted from the second 5 in 555. The third digit, 7, shows that the hue of the sample has a value of $H^*_{ab}$ that is positive and at 3 to 5 times the hue tolerance. Since $H^*_{ab}$ is calculated by taking a square root, the actual positive or negative sign is not certain. It is usual to give it the sign of the hue angle difference of the sample relative to the standard:

$$\Delta h_{ab} = h_{ab,\text{sam}} - h_{ab,\text{std}} \quad \Delta H_{ab} = +ve \text{ if } \Delta h_{ab} = +ve$$ (15)

Although the colours of samples designated 627 differ from the standard shade, they are sufficiently close that adjacent panels from them would match. This, of course, assumes that all the samples contain the same dyes and that there are no metamerism samples. The tolerances for $L^*$, $C^*_{ab}$, and $H^*_{ab}$ tend to have different values for different shades and their establishment requires a considerable amount of preliminary work. The most efficient manner of defining colour tolerances is in terms of $S_L$, $S_C$, and $S_H$ of the CMC system.

The 555 shade sorting system is not without problems. Colours whose coordinates place them at opposite corners of a cubic box will have a 73% greater colour difference than for those located at two opposite faces. This may be more or less exaggerated for a box with unequal dimensions. It is thus possible, during shade sorting, to increase the dimensions of the boxes, in an attempt to decrease the number of sorted colour groups, and then to find that the number of groups
increases. There is also the problem of colours with coordinates in the box corners that might be better grouped with colours having coordinates in the corner of an adjacent box. For example, the boxes 555, 556, 565, 566, 655, 656, 665 and 666 all share a common corner. Colours having coordinates around that point could be sorted into as many as eight boxes. Improved sorting is possible by dividing the colour space around the standard shade into boxes with more complex close-packed geometric forms such as octahedra or dodecahedra. In this case, the mathematics is more complex but some shade sorting software uses such shapes.

It is also possible to sort colours into acceptable groups without a grid dividing the colour space. The Clemson Color Clustering (CCC) system [5] groups together colours having similar colour coordinates. The calculation starts by considering the point for the coordinates of each colour as one group and then combines points in proximity into a smaller number of groups. The choice of points to include in a given group depends on the colour difference between the points that are the furthest apart in that group. The procedure gives either the minimum number of colour groups within which there is a specified maximum colour difference, or the maximum colour difference within a group for a pre-selected number of groups. The actual sphere including the points for all the colours in one group may overlap with spheres for other colour groups but each point belongs to only one sphere. This system invariably sorts samples into a smaller number of groups than the 555 system but the significance of the target shade (555) is lost in CCC sorting.

22.3 COLORANT FORMULATION

22.3.1 Spectrophotometric matching

The objective of colorant formulation in the textile context is to calculate the amounts of dyes required to colour a given material with exactly the required shade. Before 1970, this was done in the laboratory by adjusting the dyeing formula and visually comparing the colours of dyed samples with that of the target shade. Thus, if a sample of a green dyeing was a little too blue and slightly paler than the standard, the amounts of both the blue and yellow dyes in the formula were increased, with a slightly greater increase for the yellow dye to correct the shade. The skill was in knowing by how much to change the amounts of the dyes. This type of adjustment depended on experience, but was often a matter of trial and error. Obviously, a skilled colour matcher was a major asset of a dyehouse.

Today, match prediction depends on instrumental colour measurement.
For a given CIE Illuminant and standard observer, the reflection spectrum of a sample determines the coordinates for its colour in any colour space. One method of matching the colour of a sample is to reproduce its reflection spectrum with an appropriate mixture of colorants. The colour coordinates of the sample and target must then be identical. This is called spectrophotometric matching.

Many formulation procedures for spectrophotometric matching use a simplified form of the Kubelka–Munk equation relating the absorption and scattering coefficients and the concentrations of the colorants in the sample with its overall reflectance. For a mixture of a number of colorants in a sample, the global Kubelka–Munk K/S value at a given wavelength is:

\[
\frac{K}{S} = \frac{k_i + \sum (k_i C_i)}{s_i + \sum (s_i C_i)} \left(1 - \frac{R_g}{R_g} \right) \frac{1}{2R_g} \tag{16}
\]

where \(K\) and \(S\) are the respective values of the absorption and scattering coefficients of the various dyes (i) and of the undyed textile material (t). \(C_i\) is the concentration of each colorant. \(R_g\) is the reflectance of a sample of fabric that is sufficiently thick to prevent light transmission through it. \(\Sigma(C_i K_i)\) represents the sum of the products of \(C_i\) and \(K_i\) for the various dyes, with a similar definition for \(\Sigma(C_i S_i)\).

In dyed textiles, most dyes are molecularly dispersed in the fibres and do not contribute significantly to light scattering. Their values of \(S_i\) are negligible. The global value of \(K/S\) for the dyed textile then becomes a linear function of the amounts of colorants present in the sample. Thus, the above equation with \(S_i = 0\) becomes:

\[
\frac{K}{S} = \frac{k_i + \sum (k_i C_i)}{s_i + \sum (s_i C_i)} \left(1 - \frac{R_g}{R_g} \right) \frac{1}{2R_g} \tag{17}
\]

The value of \(K/S\) for the undyed material is the value \(\langle K/S \rangle_0\) when all the \(C_i\) values are zero. The values of \(a_i\) in this equation depend on the wavelength. They are calculated from the reflectance spectra of a series of dyeings prepared with known amounts of individual dyes. For the moment, we will assume that these calibration dyeings give 100% exhaustion. Thus, the amount of dye in the fibre equals the amount added to the dyebath. For the dyeing at each dye concentration, the global K/S value is obtained from the measured reflectance at
each wavelength. The values of $a_i$ are the slopes of the linear graph of $K/S$ versus $C_i$ (Figure 22.6). For a single dye, the preceding equation at any wavelength has the form:

$$\frac{K}{S} = \left(\frac{K}{S}\right)_i + a_i C_i$$

(18)

For the typical case, where the reflection spectrum of a standard sample will match that of a dyeing using a mixture of three dyes, the value of $K/S$ for the standard sample (std) at any wavelength must equal that for the matching dyeing (m) at that wavelength:

$$\left(\frac{K}{S}\right)_{std} = \left(\frac{K}{S}\right)_i + a_1 C_1 + a_2 C_2 + a_3 C_3$$

(19)

Since the values of $(K/S)_{std}$ for the standard, $(K/S)_i$ for the undyed fabric and the values $a_1$, $a_2$ and $a_3$ can all be calculated from reflectance measurements, the solution for the unknown values of $C_1$, $C_2$ and $C_3$ in the above equation requires three simultaneous equations. We can write three forms of the above equation, one for each of three different wavelengths.
Table 22.3 K/S values for 0.20% owf calibration dyeings, undyed fabric and the standard to be matched plus values of $a_i$ for the dyes

<table>
<thead>
<tr>
<th>Values of reflectance, $R$ (%)</th>
<th>Values of $a_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>440 nm</td>
</tr>
<tr>
<td>Yellow 5GL</td>
<td>8.56 (4.88)</td>
</tr>
<tr>
<td>Blue 5GL</td>
<td>38.53 (0.49)</td>
</tr>
<tr>
<td>Red FFN</td>
<td>26.93 (0.99)</td>
</tr>
<tr>
<td>Red BF</td>
<td>36.76 (0.54)</td>
</tr>
<tr>
<td>Undyed fabric</td>
<td>78.67 (0.03)</td>
</tr>
<tr>
<td>Target shade</td>
<td>4.44 (10.28)</td>
</tr>
</tbody>
</table>

Table 22.3 gives the reflectances and corresponding K/S values at three wavelengths for dyed samples of 100% textured polyester fabric. Each was dyed with 0.20% owf of a disperse dye at 130 °C by the same procedure. The table also includes the corresponding $a_i$ values, plus (K/S)$_t$ values for polyester fabric that has been through the dyeing process without added dyes, and for the target dark brown colour to be matched.

The values of $a_i$ are calculated as follows. At a wavelength of 440 nm, the 0.20% dyeing with the dye Yellow 5GL, and the undyed polyester, have reflectance values of 8.56% and 78.67%, respectively. For the polyester dyed with Yellow 5GL at 440 nm:

$$R = 0.0856, \quad \frac{K}{S} = \frac{(1 - 0.0856)^2}{2 \times 0.0856} = 4.88$$  \hspace{1cm} (20)

For the undyed polyester, the reflectance at 440 nm is 78.67% and:

$$R = 0.7867, \quad \left(\frac{K}{S}\right)_t = \frac{(1 - 0.7867)^2}{2 \times 0.7867} = 0.029$$  \hspace{1cm} (21)

For the dyeing with 0.20% Yellow 5GL at 440 nm:

$$\frac{K}{S} = \left(\frac{K}{S}\right)_t + C_i a_i, \quad 4.88 = 0.029 + 0.20 \times a_i, \quad a_i = 24.28$$  \hspace{1cm} (22)
To calculate the formula for a dyeing to match the dark brown target colour using the blue and yellow dyes along with the dye Red FFN, the equation for the overall K/S value is written for wavelengths of 440, 520 and 620 nm, respectively. From the data in Table 22.3:

At 440 nm, \(10.28 = 0.03 + 24.28C_1 + 2.31C_2 + 4.81C_3\)
At 520 nm, \(10.36 = 0.02 + 0.24C_1 + 4.34C_2 + 0.11C_3\)
At 620 nm, \(7.06 = 0.01 + 0.10C_1 + 21.13C_2 + 0.11C_3\)  

The solution to this set of three simultaneous equations in three unknowns, by the usual substitution method, gives \(C_1 = 0.306\%\) (Yellow 5GL), \(C_2 = 0.331\%\) (Blue 5GL) and \(C_3 = 0.429\%\) (Red FFN).

For the calibration dyeings and undyed fabric, the spectrophotometer provided reflectance values at 16 different, equally spaced wavelengths from 400 to 700 nm. Values of \(a_1, a_2\) and \(a_3\) for the individual dyes can thus be calculated at each wavelength using Eqn 24. Using the calculated values of \(C_1, C_2\) and \(C_3\) for the anticipated matching dyeing, the anticipated \((K/S)_m\) values can be calculated. These provide the predicted reflectance values at each wavelength (Eqn 25). To simplify the equations, \((K/S)_m\) is replaced by \(F_m\).

\[
\left(\frac{K}{S}\right)_m = \frac{F_m}{C_1a_1 + C_2a_2 + C_3a_3} \quad (24)
\]
\[
F_m = \frac{(1 - R_m)^2}{2R_m} \quad \text{or} \quad R_m = \frac{(1 + F_m)^2}{2F_m} \quad (25)
\]

Figure 22.7 shows that the calculated 16-point reflection spectrum for the match is almost identical to that of the target and, for CIE Illuminant D65 and the 1964 supplementary standard observer, the CIELAB colour difference \((\Delta E^{*ab})\) of the anticipated match from the standard is only 0.14. Thus, an almost exact spectrophotometric match has been possible using calculations at only three wavelengths. This is therefore a non-metameric match. This was deliberate in this case because the three dyes chosen for the match were identical to those in the target and the experimental dyeing using the predicted formula matched the standard in daylight.
This type of calculation can be repeated using the same yellow and blue dyes, but replacing the Red FFN by Red BF. The predicted match formula based on Eqs 23 to 25 then becomes $C_1 = 0.332\%$ (Yellow 5GL), $C_2 = 0.332\%$ (Blue 5GL) and $C_3 = 0.553\%$ (Red BF). Figure 22.7 also shows the calculated reflection spectrum of this anticipated match. It differs considerably from that of the target although the reflectance values are identical at the three wavelengths used for the calculation, as required. In this case, the colour difference of the predicted match relative to the standard is $\Delta E^*_{ab} = 3.40$. This represents a significant colour difference, which was clearly visible in the test dyeing using the predicted formula.

After some mathematics to show how handling simultaneous equation can be simplified, we will see how this poor formula can be improved.

22.3.2 Solution of simultaneous equations using simple matrix algebra

Simultaneous equations are conveniently set out in matrix form and solved using matrix algebra. From Table 22.3, the three simultaneous equations corresponding to wavelengths 440, 520 and 620 nm for the dyeing formula incorporating the dye Red BF are given below, with (K/S), placed on the left hand side.
Table 22.4 gives this information in matrix format. This shows that Matrix A multiplied by Concentration Matrix C gives Matrix B.

Table 22.4 Matrix format for the three simultaneous equations for calculation of a dyebath formula

<table>
<thead>
<tr>
<th>Matrix A</th>
<th>Matrix C</th>
<th>Matrix B</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.28 2.31 2.58</td>
<td>C₁</td>
<td>10.28 (-0.03 = 10.25)</td>
</tr>
<tr>
<td>0.24 4.34 15.94 (\times)</td>
<td>C₂</td>
<td>10.36 (-0.02 = 10.34)</td>
</tr>
<tr>
<td>0.01 21.13 0.03</td>
<td>C₃</td>
<td>7.06 (-0.01 = 7.05)</td>
</tr>
</tbody>
</table>

\[ A \times C = B \]  

(27)

The interpretation of this is quite simple. Each of the three terms across the top row of Matrix A is multiplied by the corresponding term down Matrix C. The sum of the three products is the value of the top term in Matrix B. Thus, 10.25, is equal to \((24.28 \times C₁) + (2.31 \times C₂) + (2.58 \times C₃)\). This is the first of the previous simultaneous equations. The second term down Matrix B is obtained similarly, by summation of the products of the values across the second row in Matrix A and the corresponding values down Matrix C, and so on. In matrix algebra, certain rules apply. To multiply Matrix A by Matrix C, the former must have the same number of vertical columns as the number of horizontal rows in the latter.

The inverse of Matrix A (Matrix $A^{-1}$) is a $3 \times 3$ matrix of numbers that when multiplied by Matrix A gives the Identity Matrix. The latter is a square matrix.
with a diagonal of ‘ones’ and all the remaining values as ‘zero’. Matrix inversion is only possible in the case of a square matrix such as Matrix A (3 columns x 3 rows). In the usual algebraic notation:

\[
\frac{\text{Matrix } A}{\text{Identity matrix,}} = \frac{\text{Matrix } A^{-1}}{(A \times A^{-1})}
\]

Table 22.5: Illustration of matrix multiplication to give the Identity matrix

<table>
<thead>
<tr>
<th>Matrix A</th>
<th>Matrix A^{-1}</th>
<th>Identity matrix, ((A \times A^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.28, 2.31, 2.58</td>
<td>0.0413, -0.0067, -0.0031</td>
<td>1, 0, 0</td>
</tr>
<tr>
<td>0.24, 4.34, 15.94</td>
<td>0.0000, -0.0001, 0.0473</td>
<td>0, 1, 0</td>
</tr>
<tr>
<td>0.01, 21.13, 0.03</td>
<td>-0.0006, 0.0629, -0.0128</td>
<td>0, 0, 1</td>
</tr>
</tbody>
</table>

Table 22.6: Dyebath formulation by matrix multiplication

<table>
<thead>
<tr>
<th>Matrix A^{-1}</th>
<th>Matrix B</th>
<th>Matrix C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0413, -0.0067, -0.0031</td>
<td>10.25, 0.332</td>
<td>0.0000, -0.0001, 0.0473</td>
</tr>
<tr>
<td>-0.0006, 0.0629, -0.0128</td>
<td>7.05, 0.553</td>
<td></td>
</tr>
</tbody>
</table>

Tables 22.4–22.6 give the complete matrices for the formulation problem. The calculation of the values for an inverted matrix requires manipulation of many simultaneous equations. Fortunately, most computer spreadsheets quickly calculate inverted matrices. How does this work? A 3 x 3 Identity Matrix represents the solution of nine simultaneous equations, which allows calculation of the values in the required inverted matrix. Each number in the Identity Matrix is a sum of the products of numbers across a row of Matrix A and a corresponding number down a column of its inverse Matrix A^{-1} and has a value of zero or unity.

The numbers in the top row of Matrix A and those down the left column of Matrix A^{-1} give the top left value of the Identity Matrix \((A \times A^{-1})\):

\[
(24.28 \times 0.0413) + (2.31 \times 0) + (2.58 \times -0.0006) = 1.00
\]

\[(29)\]
The second value down the left column of the identity matrix \((A \times A^{-1})\) is given by:

\[
(0.24 \times 0.0413) + (4.34 \times 0) + (15.94 \times -0.0006) = 0
\]

and so on.

Matrix \(A^{-1}\), the inverse of Matrix A, multiplied by Matrix B, gives the values of Matrix C. This is shown in Table 22.6. The result gives values of \(C_1\), \(C_2\) and \(C_3\) identical to those given earlier for the recipe including the dye Red BF. Matrix inversion and multiplication are quite tedious when done manually. They are accurately and rapidly performed by computer, using for example a spreadsheet. This is essential for precise spectrophotometric matching at 16 equally spaced wavelengths from 400 to 700 nm. In this case, there are 16 simultaneous equations in terms of the three or more unknown dye concentrations.

### 22.3.3 Tristimulus matching

Section 22.3.1 illustrated colorant formulation calculations for matching a target dark brown shade. The three-dye combination including the dye Red FFN gave a spectrophotometric match. When this dye was replaced with Red BF matching was not possible. Another technique called tristimulus matching attempts to correct the formula so that a colour match can be achieved. The objective of tristimulus matching is to generate a dye formula that will result in a dyeing whose tristimulus values match those of the target colour for the chosen CIE illuminant and standard observer. Such a match will invariably only be acceptable for the given viewing conditions. It will be a metamer match since the reflection spectra of the match and target will not usually be identical as different colorants are present. After measurement of the reflection spectrum of a dyed sample with a given dye formula, this technique is used to modify the formula and even to calculate any shading additions to correct the final colour of the dyeing. The basic procedure is as follows.

From arbitrary or pre-estimated values of \(C_1\), \(C_2\), \(C_3\) and the known values of \(a_i\), first calculate the values of \(F_m\) and then \(R_m\) at, say, the 16 equally spaced wavelengths from 400 to 700 nm. The appropriate equations are those given previously. At each wavelength:

\[
\left(\frac{K}{S}\right)_m = \frac{K}{S_i} + C_1a_1 + C_2a_2 + C_3a_3 + ...
\]
The predicted reflection spectrum then allows calculation of the tristimulus values of the anticipated match \( X_m, Y_m \) and \( Z_m \) for the selected illuminant and standard observer. These are compared with the tristimulus values of the target colour to be matched \( X_{std}, Y_{std} \) and \( Z_{std} \). This gives the differences \( dX = X_{std} - X_m \), \( dY = Y_{std} - Y_m \) and \( dZ = Z_{std} - Z_m \).

If \( dX, dY \) and \( dZ \) are larger than acceptable, then it is necessary to calculate the concentration changes \( dC_1, dC_2 \) and \( dC_3 \) that will eliminate the tristimulus value differences between the target and match. A change in the concentration of any of the dyes will change the tristimulus values of the dyeing. We need to know the effect of changing the concentration of each of the three dyes on each tristimulus value. How does the tristimulus value \( X \) vary with change in the concentration of a single dye \( C_i \)? This comes from the slope of the graph of \( X \) versus \( C \) for the given dye obtained under conditions where all the other dye concentrations are constant \((6X/6C)\). It is called a partial derivative and written \( \partial X/\partial C \) rather than \( dX/dC \).

Changing the concentration of a dye by an amount \( dC \) will change the value of the tristimulus value \( X \) by an amount \( dX \) given by:

\[
\Delta X = \text{slope}(\partial X/\partial C) \times dC
\]

Similarly:

\[
\Delta Y = \left(\frac{\partial Y}{\partial C}\right) dC
\]

\[
\Delta Z = \left(\frac{\partial Z}{\partial C}\right) dC
\]

The total change of each tristimulus value can be written with a term for the effect of each dye concentration:

\[
\Delta X = \left(\frac{\partial X}{\partial C_1}\right) dC_1 + \left(\frac{\partial X}{\partial C_2}\right) dC_2 + \left(\frac{\partial X}{\partial C_3}\right) dC_3
\]

\[
\Delta Y = \left(\frac{\partial Y}{\partial C_1}\right) dC_1 + \left(\frac{\partial Y}{\partial C_2}\right) dC_2 + \left(\frac{\partial Y}{\partial C_3}\right) dC_3
\]

\[
\Delta Z = \left(\frac{\partial Z}{\partial C_1}\right) dC_1 + \left(\frac{\partial Z}{\partial C_2}\right) dC_2 + \left(\frac{\partial Z}{\partial C_3}\right) dC_3
\]

\[
R_m = (1 + F_m) - \sqrt{F_m^2 + 2F_m}
\]
This is expressed as the usual matrix multiplication:

\[
\begin{bmatrix}
\frac{\partial X}{\partial C_1} & \frac{\partial X}{\partial C_2} & \frac{\partial X}{\partial C_3} \\
\frac{\partial Y}{\partial C_1} & \frac{\partial Y}{\partial C_2} & \frac{\partial Y}{\partial C_3} \\
\frac{\partial Z}{\partial C_1} & \frac{\partial Z}{\partial C_2} & \frac{\partial Z}{\partial C_3}
\end{bmatrix}
\times
\begin{bmatrix}
\delta C_1 \\
\delta C_2 \\
\delta C_3
\end{bmatrix}
= 
\begin{bmatrix}
\delta X \\
\delta Y \\
\delta Z
\end{bmatrix}
\]

Influence Matrix \(I\) × Matrix \(C\) = Matrix \(T\)

or:

\[I \times C = T\]  \hfill (37)

The differences of the predicted match tristimulus values from those of the target (\(dX, dY\) and \(dZ\) in the Tristimulus Matrix \(T\)) can be calculated from measurements but the nine values in the Influence Matrix \(I\) are required in order to calculate the changes in the dye concentrations. How do we calculate values such as \(\delta X/\delta C_1\)?

We have already seen that:

\[X = \sum W_S R\]  \hfill (39)

calculated over 16 equally spaced wavelengths, where \(W_S\) is the appropriate weighting function for the given colour matching function and illuminant (Section 21.6.1), and \(R\) is the reflectance of the sample. Differentiation of this equation with respect to \(C_1\) gives:

\[
\frac{dX}{dc_1} = \sum W_S \left( \frac{dR}{dc_1} \right) - \sum W_S \left( \frac{dR}{df} \right) \left( \frac{df}{dc_1} \right)
\]

Since \(F\) in this equation is \(K/S\), \(df/dc_1\) is the value of \(a_1\). Differentiation of:

\[P = \frac{(1 - R)^2}{2R}\]  \hfill (41)

gives:

\[
\frac{dF}{dR} = \frac{(R^2 - 1)}{2R^3} \quad \frac{dR}{dF} = \frac{2R^3}{(R^2 - 1)}
\]

\hfill (42)
The values of \( R \) used in the calculation are usually those of the target sample. Thus, the equation for \( \frac{\partial \mathbf{X}}{\partial \mathbf{C}_1} \) becomes:

\[
\frac{\partial \mathbf{X}}{\partial \mathbf{C}_1} = \sum W_x \left( \frac{\partial R}{\partial \mathbf{C}_1} \right) + \sum \left( W_x \times \frac{2R_1^2}{(R_1^2 - 1)} \right) \times \mathbf{C}_1
\]

for which all the values are known at each wavelength. The other eight values in the Influence Matrix \( \mathbf{I} \) are calculated similarly.

It is now possible to calculate the values of the Concentration Matrix \( \mathbf{C} \). To do this, the Tristimulus Matrix \( \mathbf{T} \) is multiplied by the inverse of the Influence Matrix. The latter \((\mathbf{I}^{-1})\) is called the Correction Matrix:

\[
\mathbf{C} = \mathbf{T} \times \mathbf{I}^{-1}
\]

Once the required concentration changes have been calculated, the new more appropriate values are given by:

- \( \text{New } \mathbf{C}_1 = \text{Old } \mathbf{C}_1 + \mathbf{dC}_1 \)
- \( \text{New } \mathbf{C}_2 = \text{Old } \mathbf{C}_2 + \mathbf{dC}_2 \)
- \( \text{New } \mathbf{C}_3 = \text{Old } \mathbf{C}_3 + \mathbf{dC}_3 \)

where the \( \mathbf{dC} \) values may be positive or negative.

Going back to the first step (Eqn 32), the new values of the concentrations are then used to calculate the new anticipated reflection spectrum and the new values of \( X_m, Y_m \) and \( Z_m \) and then of \( \Delta X, \Delta Y \) and \( \Delta Z \).

This calculation sequence is repeated until values of \( \Delta X, \Delta Y \) and \( \Delta Z \) are within acceptable limits, such as less than 0.02, or until \( \Delta E^*_{ab} \) or \( \Delta E^*_{CMC} \) is an acceptably low value. It should now be obvious why this type of calculation using repeated matrix algebra requires a computer programme or a spreadsheet operating with a macro.

The formula for matching the dark brown target that included the dye Red BF gave a poor spectrophotometric match of the standard when using only three equations. The above iterative technique for a tristimulus match will calculate a new formula starting from the earlier calculated concentration values. The formula converges to \( \mathbf{C}_1 = 0.361\% \) (Yellow 5GL), \( \mathbf{C}_2 = 0.285\% \) (Blue 5GL) and \( \mathbf{C}_3 = 0.497\% \) (Red BF). Figure 22.7 includes the spectrum for this dyeing. Although it does not match that of the standard, it does reproduce the correct
tristimulus values for the 1964 supplementary standard observer and Illuminant D_65 and gives a negligible CIELAB \( \Delta E^*_{ab} \) colour difference value. Table 22.7 illustrates the development of the four iterations, using the tristimulus and correction matrices to calculate the formula corrections.

### 22.3.4 Some problems with colorant formulation calculations

The above calculation procedures, based on spectrophotometric or tristimulus matching, serve to illustrate some of the basic principles of colorant formulation. The method used to prepare the calibration dyeings, which provides the values of \( a_i \) for the dyes, and that used in actual production must be reproducible and give the same colour with the same dye formula. This point is critical. Computer colorant formulation is highly dependent upon the colorimetric data for the target, for the calibration dyeings with individual dyes and for the sample dyed with the predicted formula. Such measurements must be reliable and reproducible. Sample preparation and presentation, and the effects of texture, lustre, humidity and temperature all influence the values of the recorded reflection spectra. If the colorimetric system is not under complete control, accurate colorant formulation is impossible. This should be a constant preoccupation of the technician involved in such procedures.

<table>
<thead>
<tr>
<th>Iteration</th>
<th>1 initial</th>
<th>2</th>
<th>3</th>
<th>4 final</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 ) Yellow 5GL</td>
<td>0.332</td>
<td>0.357</td>
<td>0.361</td>
<td>0.361</td>
</tr>
<tr>
<td>( C_2 ) Blue 5GL</td>
<td>0.332</td>
<td>0.289</td>
<td>0.265</td>
<td>0.265</td>
</tr>
<tr>
<td>( C_3 ) Red BF</td>
<td>0.553</td>
<td>0.509</td>
<td>0.498</td>
<td>0.497</td>
</tr>
<tr>
<td>( X )</td>
<td>5.31</td>
<td>5.80</td>
<td>5.87</td>
<td>5.88</td>
</tr>
<tr>
<td>( Y )</td>
<td>5.15</td>
<td>5.63</td>
<td>5.72</td>
<td>5.72</td>
</tr>
<tr>
<td>( Z )</td>
<td>5.07</td>
<td>4.99</td>
<td>4.99</td>
<td>4.99</td>
</tr>
<tr>
<td>( dX )</td>
<td>0.57</td>
<td>0.08</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>( dY )</td>
<td>0.57</td>
<td>0.09</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( dZ )</td>
<td>-0.09</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( \Delta E^*_{ab} )</td>
<td>3.40</td>
<td>0.55</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>( dC_1 )</td>
<td>0.025</td>
<td>0.004</td>
<td>0.0006</td>
<td>( 4.9 \times 10^{-5} )</td>
</tr>
<tr>
<td>( dC_2 )</td>
<td>-0.043</td>
<td>-0.004</td>
<td>-0.0004</td>
<td>( -6.0 \times 10^{-5} )</td>
</tr>
<tr>
<td>( dC_3 )</td>
<td>-0.044</td>
<td>-0.110</td>
<td>-0.0007</td>
<td>( -7.0 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
A variety of more complex mathematical techniques for colour matching are known and used in commercial software for this purpose. Computer assisted colorant formulation, however, is occasionally unsatisfactory, even when the dyeing process and all the data are reliable. Sometimes in tristimulus matching, the computer will carry out successive calculation loops without providing a satisfactory formula. Occasionally, the iterative calculation results in a negative dye concentration or a gradually increasing match-standard colour difference. At this point, the calculation is useless. Some of the problems come from the invalidity of the assumptions made in the calculation procedures.

In our example calculations, the dye present in the fibre was the amount initially added to the dyebath. Many dyeings, however, do not give 100% dyebath exhaustion. Therefore, the relationship between $K/S$ of the dyeing and the amount of dye in the fibre is not easy to determine. In the preparation of calibration dyeings, $K/S$ is usually established as a function of the amount of dye added to the dyebath (% dye owf). Since the bath exhaustion will usually decrease with increasing dye concentration in the bath, the graph of $K/S$ versus % dye owf will not be linear but of gradually decreasing slope. Thus $a_i$ is concentration- as well as wavelength-dependent. There are a number of mathematical interpolation techniques that calculate the value of $a_i$ at any dye concentration provided the changes in slope are regular and not too exaggerated. Many colorant formulation programmes use these techniques to generate a series of concentration dependent values of $a_i$.

The global value of $K/S$ for the dyed sample may not be a linear combination of the $K/S$ values for the colorants present in it. The additivity of $a_iC_i$ terms to calculate the overall $K/S$ value of a dyeing may be invalid if the dyes in the material interact with each other or if the dyes have non-zero scattering coefficients. In some cases, dyes that interact with each other in the dyebath, or in the fibre, cause the exhaustion of a given dye in a mixture to differ from the value it would give alone at the same concentration, as in a calibration dyeing. In some cases, one adsorbed dye is able to exclude adsorption of another; for example, if the number of dye-binding sites in a fibre is limited. All these effects introduce errors into the formulation procedure.

The majority of dyes that fibres absorb directly (direct, acid, cationic and disperse dyes) usually give satisfactory dyebath formula predictions. The results are often less satisfactory for dyes where the final development of the colour requires a chemical process such as the reaction between a reactive dye and alkaline cellulose, or the oxidation and soaping of a vat dye. The actual colour of pigmented cotton, obtained using vat or azoic dyes, is dependent on the crystalline...
form of the particles present in the fibres and thus on the actual conditions of dyeing aftertreatments. These types of dyes may not have negligible scattering coefficients.

Modern computers allow rapid calculations of dyeing formulas using as many as 40 simultaneous equations based on reflectance measurements at equally spaced wavelengths from 380 to 780 nm. The software can manipulate non-linear relationships of $K/S$ as a function of initial dye concentration in the dyebath. The speed of the computer calculations allows derivation of a number of possible formulations. These involve different combinations of colorants, and other information aiding a final choice of formula, such as dye costs, colour fastness, degree of metamerism and inventory.

The software should be capable of predicting acceptable formulas with different combinations of three or more dyes. This can require considerable time unless the technician pre-selects from a limited number of suitable dyes. The number of combinations of three different dyes from a list of $m$ dyes is given by:

$$N = \frac{m!}{3!(m-3)!}$$

A number such as 3! is called a factorial, and represents all the whole numbers up to the one indicated multiplied together. Thus, $3! = 3 \times 2 \times 1$. For a set of six dyes, there are 20 possible combinations of three dyes, and for a set of 20 dyes the number increases to 1140. Ideally, a formula should be calculated for each possible combination, along with either a predicted reflection spectrum or colour coordinates. Calculations that do not lead to a formula within a given time are interrupted and formulas that predict too large a colour difference from the target are discarded. Some pre-selection of dyes saves considerable time. For example, a combination of three red dyes is useless for matching a blue shade.

Finally, unless an exact spectrophotometric match has been obtained, the colour of the sample will only match that of the target for a given CIE standard observer and illuminant. The sample and target colours will be metameric. The degree of metamerism can be evaluated in terms of a $\Delta E_{ab}^*$ colour difference from values of $L^*$, $a^*$ and $b^*$ calculated for, say, CIE Illuminant D65 and Illuminant A.

The availability of high speed computers has provided a powerful technology for match prediction. Further developments involving neural networks and artificial intelligence will be even more beneficial provided that they are accompanied by advances in dyeing and colorimetric reproducibility.
REFERENCES

CHAPTER 23

Printing

23.1 INTRODUCTION

Printing involves localised coloration. This is usually achieved by applying thickened pastes containing dyes or pigments onto a fabric surface according to a given colour design. In particular, the viscosity of a print paste is critical. It determines the volume of paste transferred to the fabric and the degree to which it spreads on and into the surface yarns. The paste must colour all the visible fibres on the printed surface, so it must penetrate somewhat into the yarn structure. If the paste is too 'thin', it will spread, giving poor print definition, and penetrate too far into the yarns decreasing the colour yield.

Printing was originally done by hand using wooden blocks with a raised printing surface, much as children do potato printing. The two main techniques used for transferring paste onto fabrics involve engraved rollers carrying paste in the recesses corresponding to the colour pattern, or screens with the open mesh in the pattern areas. There will be one roller or screen contacting the fabric surface for each colour to be printed.

The most important printing method today is pigment printing. This involves printing the coloured pattern onto the fabric surface and curing the printed areas by heating in air. The print paste contains coloured pigments and a binding agent. On curing in hot air, the binder forms a solid film of transparent polymer that holds the pigments in place on the yarn surfaces. The great advantage of pigment printing is that the fabric does not require washing after the fixation process.

Soluble dyes used in printing a fabric are of the same types as those normally used to dye it a solid colour. Apart from in pigment printing, the usual sequence of operations is printing, drying, steaming and washing. Dyes for printing must have high solubility because there is only a limited amount of water in a thickened print paste and after drying the dyes must re-dissolve in a limited amount of condensed steam. The paste must dissolve the dyes to allow their diffusion into the fibres. It will also contain all the other required chemicals for fibre wetting and dye fixation. The final washing removes the thickening agent, unfixed dyes and other auxiliary chemicals from the printed surface. During washing, it is critical that the dyes
removed do not stain any white ground or other printed areas. For this reason, dyes for printing often have relatively low molecular weights so that their substantivity is not very high. When a manufacturer sells the same dye for both dyeing and printing, the two product formulations will invariably be different.

Pigment and dye printing are both direct printing methods. Two other important indirect printing methods called discharge and resist printing also give coloured designs. In discharge printing, a uniformly dyed fabric is printed with a paste containing chemicals that destroy the colour leaving a white pattern. If the paste contains other dyes, stable to the chemical that discharges the ground colour, they can dye the treated area. In this way, multi-colour effects are also possible. In resist printing, the fabric is dyed after printing. The printed areas resist dye absorption so that these design areas are reserved. After removal of the resist agent, the design may be white or coloured if other dyes and appropriate chemicals were present in the original paste.

The rapid development of CAD computer systems for print design has had a significant impact on this activity. The development of digitised textile printing using, for example, ink jet printers is well underway. Such computer assisted manufacturing will considerably influence the textile printing industry in the near future. Its other preoccupation, as for the dyeing industry in general, is that of reducing the amounts of biodegradable and potentially harmful chemicals in the effluent leaving the works so that its environmental impact is limited.

23.2 FLAT SCREEN PRINTING

23.2.1 Printing techniques

Screen printing is an extension of the technique of stencilling in which a coloured image arises from the transfer of colour through open areas in the sheet placed upon the fabric surface. In flat screen printing, the screen consists of a woven polyester material, tightly stretched across the underside of a light, rectangular frame. During printing, the screen usually lies across the fabric width. The polyester fabric only allows the printing paste to pass through the mesh in those areas corresponding to the design being printed. A suitable coating blocks the remaining areas. There is a screen for printing each colour and each successive screen sits on the fabric in the exact position for accurate registration of the multi-colour design.

In manual screen printing, the fabric lays on a long table on top of the printing
blanket. This blanket is typically a cotton/polyester cloth, water-proofed by a coating of neoprene rubber. If the fabric slips or deforms during printing, there is a loss of print definition. The fabric is therefore usually pinned to the printing blanket, or stuck onto it with a water-based gum or thermoplastic adhesive. The latter type coats the blanket surface but only becomes sticky when heat softens the polymer. After printing, the fabric and printing blanket separate. Washing the blanket removes any gum and dye paste transferred through the cloth or beyond its edges. Thermoplastic adhesives are resistant to repeated washing and very durable when using water-based printing pastes. Beneath the printing blanket are several layers of cloth forming a uniform cushion called a 'lapping'. In some cases, a 'back-grey' cloth is inserted between the fabric and blanket. This grey cotton fabric absorbs any paste that transfers through the fabric and thus avoids smudging of colour on the back of the printed fabric. If used, it too must be washed and dried for re-use.

The printing paste is poured into the screen that sits on the fabric surface. Drawing a flexible rubber blade called a squeegee across the inner surface of the screen spreads the viscous dye paste and forces it through the open areas to print the fabric beneath. Two or four strokes across the screen are usual, the number depending on the porosity of the screen and the paste viscosity. Each passage of the squeegee should transfer the same amount of paste to the fabric in any given print. The angle, speed and pressure of the squeegee must therefore be the same for each print.

In semi-automated screen printing, a mechanically driven squeegee transfers the colour. This often has a pair of parallel rubber blades, with the paste held between them. When passing across the screen during printing, only the trailing blade is in contact with the screen surface. At the end of the stroke, the leading blade drops and the trailing blade rises ready for the back stroke. This eliminates the need to lift the squeegee over the residual paste at the end of each stroke. The Zimmer rolling rod applicator moves across the printing screen along the length of the fabric, driven by an electromagnet under the blanket. The roller is small enough that paste can flow over it so that lifting is not necessary. This type of roller gives less screen wear.

In manual and semi-automated screen printing, the end of each screen rests against a guide rail running along the table edge. The screen fits against a 'stop' that defines its position relative to the fabric. The screen for a particular colour gradually moves down the fabric length, fitting against the appropriate 'stop' as each repeat is printed. 'Pitch marks' printed on the fabric selvages will verify the
alignment of the screen for the next colour. Printing the entire length of fabric on
the table with one colour design allows some intermediate drying before
application of the next colour. The next screen does not then crush or mark the
paste layer already present so that the images are sharper.

In fully automated flat screen printing, productivity is higher. The screens for
each of the colours have the correct positions on the guide rail for exact
registration of their patterns. After printing all colours simultaneously, the screens
are lifted, and the printing blanket moves the fabric stuck to it so that a printed
pattern has the correct position for printing the next colour. Clamps securely hold
the sides of the blanket and they move the fabric by the exact required distance
after each print. The spacing between individual screens is usually one pattern
repeat. Thus, if a screen has two pattern repeats, and screens are spaced one
pattern repeat apart, the blanket must move the fabric two pattern repeats down
the table (Figure 23.1). In this way, gaps are avoided. Correct fabric placement is
vital for accurate registration of the different coloured patterns. In general, a slight
pattern overlap prevents a white gap between two printed colours.

At the end of the printing table, the fabric separates from the blanket and
passes into the dryer, while the blanket is washed, dried and recycled beneath the
printing table. Various mechanical devices compensate for the intermittent
movement of the fabric during printing but allow uniform movement of the fabric
during drying, and of the blanket during washing.

Figure 23.1 Screen placement and fabric movement as a function of repeat size in
automated flat screen printing

The main fault in screen printing is poor pattern registration. This arises from
inaccurate screen placement or fabric movement, from the fabric slipping on the
blanket because of poor adhesion, or from distortion of the screen mesh by the
drag of the squeegee. Marks on areas already printed are caused by the frame
crushing the paste beneath it while the paste is still moist. This is more of a
problem in fully automated screen printing where colours are printed one after the
other with little time for drying of the deposited paste. For this reason, printing of large areas of colour (blotches) is usually done last.

Off-contact printing minimises squeegee drag and frame marks. For this, the frame is not quite in contact with the fabric. The pressure of the squeegee forces the screen material to stretch slightly so that it touches the fabric and the paste transfers. ‘Splashing’ of colour is caused when the paste beneath the screen initially sticks the screen to the fabric. When the screen is lifted quickly, colour is splashed outside the printed zone as the paste on the fabric separates from that on the screen. Gently lifting the screen from one end and then the other avoids this, although it slows down the process.

Flat screen printing with large screens allows much greater print repeat sizes than is possible using engraved copper rollers (Section 23.4) or rotary screens (Section 23.3). Forcing the paste through the screen openings involves much lower applied pressures than in roller printing, so there is less penetration of paste into the fabric. This results in higher colour strength and less crushing of any fabric texture. Flat screen printing is, however, relatively slow and is now only used for materials such as high quality furnishing and fashion fabrics.

23.2.2 Flat screen production

Screen production for printing is the culminating step in a process involving many important aesthetic and technical decisions. These include:

1. the selection of the fabric and the printed design;
2. the choice of the size and arrangement of the design’s repeat rectangle;
3. the necessary colour separation of the design.

These steps are common to all printing methods. Colour separation involves reproduction of the pattern for each colour on separate clear films (diapositives). Much of the design work is now computerised. The designer must ensure printing of colours with a slight overlap to avoid white gaps between them. In some cases, printing of one colour on top of another produces a particular colour effect. This is known as a fall-on.

The same technique of screen production is used for both flat and rotary screens. The flat screen, mounted on its frame, is coated with a solution of a photo-sensitive polymer that will crosslink and harden on exposure to ultraviolet light. It will then be insoluble. A typical polymer is polyvinyl alcohol, its crosslinking sensitised by ammonium dichromate. The coated screen is dried and
then exposed beneath the diapositive for the given colour. All operations take
place in a darkroom. The inked zones, corresponding to the particular colour
pattern, do not transmit the ultraviolet light. The layer of polymer on the screen
beneath the pattern is thus not exposed and does not crosslink while the rest
hardens. The non-exposed polymer remains soluble and can be washed out,
leaving the screen open in those areas. The print paste will pass through the
screen where the unexposed polymer washed away but not through the regions
where the polymer has hardened and become insoluble. Any small pin holes in the
hardened areas on the screen are painted over. A coating of cellulose or
polyurethane lacquer reinforces the screen, the excess being sucked out of the
open areas. In some cases, thermal or radiative curing of the polymer makes it
harder and more resistant.

A flat screen may be produced in a single coating and exposure operation.
Alternatively, in the step-and-repeat process, one repeat design is produced per
exposure, the remainder of the screen being protected by dark paper. The pattern
or the screen is then moved by one repeat distance and the process repeated.

The screen mesh varies from about 60 up to 150 holes per linear inch
depending upon the type of pattern and the fabric. There is always a tendency for
the edges of printed areas to have a serrated appearance. This comes from the
arrangement of the spaces between the threads along the edge of an open area of
the screen. The spreading of the paste below the screen threads reduces this, aided
by using fine screens and lower viscosity pastes.

23.3 ROTARY SCREEN PRINTING

In rotary screen printing, coloured paste is forced through the open areas of a
cylindrical printing screen that rotates as the fabric moves beneath it. In contrast
to intermittent flat screen printing, rotary screen printing is fully continuous with
fabric speeds up to 50 m min⁻¹, if adequate drying capacity is available. Rotary
screen printing is now by far the major printing method for textile fabrics.

The printing blanket is shorter than in flat screen printing because cylindrical
screens occupy less fabric length. Their diameter is π or 3.14 times less than their
circumference. The use of a thermoplastic adhesive on a neoprene coated blanket
is common since this simplifies washing. A pump delivers paste from a container
into a central pipe that runs inside the full length of the screen. This pipe also
supports the squeegee. The paste runs down onto the rotating screen from holes in
the pipe. These are larger towards the far end to give even paste distribution
(Figure 23.2). The paste collects under the stationary squeegee, which forces it out through the holes in the rotating screen. This is the opposite of flat screen printing where the movement of the squeegee forces the paste onto the fabric. The squeegee is a flexible stainless steel blade, since rubber squeegees wear away too quickly. The blade curvature depends on the applied pressure and can be varied by adjustment of the side bearings. Uniform blade pressure across the width of the screen is essential to ensure even transfer of the paste to the fabric. Printing machines from Zimmer use an electromagnetic roller squeegee.

The screens are strong enough for rotation provided they are under tension along the cylindrical axis. They fit onto light aluminium end rings that can be driven from either one or both sides. The blanket and screen drives are usually linked. Once the screens are in place the paste delivery tubes and squeegee assemblies are fitted. On starting to print, the screen height can be adjusted and the screens can be advanced or retarded to give correct registration of the pattern.

Direct rotary screen printing does not allow the large repeats of flat screens. Large repeats can, however, be printed by automated intermittent raising and lowering of the rotating screens. In this way, two or three different rotating screens print the same colour to give a large repeat. Only a portion of the screen surface is

![Diagram of rotary screen printing process](image-url)
open so that when the screens are raised the paste is held in a closed area and does not drip onto the fabric.

Lacquered rotary screens, originally from Stork, usually have a pattern of hexagonal holes. The holes have sloping walls, being larger on the outside of the screen than on the inside. They are manufactured by electrodeposition of nickel onto an engraved mandrel. The mandrel is the cathode and the anodes are pieces of nickel submerged in the plating bath of a nickel salt. Hexagonal recesses are first carved into the thin copper layer on the mandrel surface and filled with an insulating polymer. The exposed copper is then lightly nickel plated and the recesses again filled in with insulating polymer. The nickel layer may then be oxidised with chromic acid to produce an oxide layer. This avoids adhesion of the nickel deposit to the mandrel in the final plating step that follows (Figure 23.3). No nickel deposits in the areas around the insulating polymer. This is where the hexagonal holes will be. The 0.1 mm thick screen of nickel can then be removed from the mandrel and rinsed. Very fine mesh screens cannot be produced because of the problem of bridging across the insulating polymer zones and filling-in of the holes as the nickel layer becomes thicker. Typical screens are 60 mesh (holes per linear inch) for blotches and 80 mesh for outlines.

Photopatterns are produced similarly to those for flat screens but using a single full-scale positive film for each colour. The colour positives are prepared by the step-and-repeat process using multiple exposures from a negative of the original repeat. Screens may be hand-coated with several layers of light-sensitive polymer or single coated with a special annular coating machine. The types of polymers used, such as melamine-formaldehyde condensates, are also different from those
used for flat screens since good adhesion to the nickel surface is essential. The polymer-coated screen is placed on an inflatable rubber tube and wrapped with the diapositive film, great care being taken to place it in exactly the correct position. The seam is usually helical to avoid sideways slippage. The inflated rubber tube holds the screen onto the film and the whole rotates during exposure to ultraviolet light. Washing then removes unexposed soluble polymer from what will be the open areas. After drying, any pin holes are touched up with lacquer and the residual polymer is heat cured to completely harden it. Finally the end rings are carefully fitted.

Galvano screens from Zimmer have solid electrodeposited nickel layers in the filled zones in place of lacquer and are therefore much stronger and less susceptible to pin holes. A thin inflatable nickel tube is coated with photosensitive polymer solution and dried. A full-size negative of the colour separation is wrapped around this followed by a negative of the mesh pattern (Figure 23.4). Inflation of the mandrel provides good contact between the layers during exposure to the ultraviolet light. After washing and drying, only the non-pattern areas and the areas corresponding to the supporting mesh in the pattern areas have no

*Figure 23.4* Arrangement of films for producing a galvano nickel screen (from *Textile Printing*, 2nd Edn, L. W. C. Miles (Ed), SDC, 1994 – Chapter 2, Figure 21, p. 50)
coating of hardened polymer. The latter acts as an insulator when the mandrel is subsequently nickel plated. The nickel builds up in those areas where there is no hardened polymer. The result is a thin nickel sheet with screen holes only in the areas of the design. Bridging across the tiny insulated zones is a problem with this type of screen and they do not have a mesh as fine as lacquered screens. The limit is about 80 mesh, in contrast to 100 mesh for lacquered screens. Lacquered screens are preferred for finer work and narrow fabrics. The stronger galvano screens are better for wider fabrics and for the more mechanically rigorous printing of carpets where more robust, thicker screens (0.4 mm) are needed.

23.4 ENGRAVED ROLLER PRINTING

Engraved roller printing is over 200 years old and the technique has changed little during this period. Figure 23.5 illustrates the essential details of the process. Printing takes place around a large rotating roller or bowl. The outer layer on the bowl is the fabric being printed by the transfer of coloured paste from the recesses in the engraved rollers pressing against it. The fabric covers about 50% of the circumference of the bowl. It is on top of and in contact with the continuous
printing blanket. This is typically a cotton/polyester cloth water-proofed by a coating of neoprene rubber. The blanket and printed cloth separate after printing and the blanket is washed and recycled. Beneath the printing blanket, the entire bowl has up to a dozen layers of a wool or wool/linen ‘lapping’. A continuous ‘back-grey’ of unbleached cotton may be inserted between the printing blanket and the fabric. It too must be washed, dried and returned to the printing bowl.

For a multi-colour print, there is a colour box and engraved roller for each colour, placed around the lower part of the bowl. The supporting framework must be robust since pressures as high as 22 000 lb in-2 (140 kg cm-2) push the engraved rollers onto the moving fabric on the bowl. This causes each engraved roller to rotate at the same linear speed and forces the fabric into the grooved recesses carrying the printing paste. Exact placement of the engraved rollers is essential to ensure accurate registration of the different coloured patterns in the correct position on the fabric. This is referred to as pitching.

A cloth- or brush-covered furnishing roller transfers the dye paste from a small colour box onto the engraved roller. A steel doctor blade (colour doctor in Figure 23.5), in contact with the engraved roller, scrapes the smooth copper surface clean, leaving paste only in the engravings. This blade moves to and fro across the print roller face to give even wear. After transfer of the paste from the roller to the fabric, a brass lint doctor cleans the engraved roller. This blade removes any loose fibres picked up from the cloth, and any differently coloured paste lifted from previously printed regions of the fabric. The lint doctor thus minimises contamination of the colour box.

Engraved printing rollers come in various diameters depending upon the repeat distance for the print design. The iron rollers have a layer of electrochemically deposited copper. Photo-gravure engraving is the most widely used technique. It is highly specialised and usually done outside the printworks. The roller is first coated with a thin layer of a photo-sensitive polymer. It is then wrapped with a diapositive film carrying the design for a given colour and rotated under a light source. Only the transparent areas of the film permit light passage and crosslinking of the polymer film. Washing removes the unreacted soluble polymer from the zones beneath the pattern, leaving the insoluble, crosslinked, acid-resistant polymer on the exposed surfaces. The exposed copper layer on the roller can then be etched with chemicals such as nitric acid or ferric chloride solution to form the recessed areas (Scheme 23.1). The polymer film protects the non-pattern areas from attack.

One major problem in roller printing is the effect of the pressure of the print rollers on wet paste already deposited on the fabric surface. As a printed area
passes under the next roller, some paste is pressed further into the fabric and some sticks onto the roller and is removed. Both effects leave less paste on the fabric surface, thus reducing the colour strength. For this reason, pale colours are printed first, followed by successively deeper ones. In one modern machine, the print rollers consist of a thin metal shell mounted on a mandrel and forced against the fabric by air pressure using an inflatable bag. This allows the use of lower pressures so that the crushing effect is reduced.

Other common printing faults include:

1. colour scratches parallel to the selvages caused by particles in the paste scratching the print roller;
2. strong, continuous lines of colour running up the cloth, called snaps. These arise from lifting of the doctor blade by a thread or particle of dried thickener, or a chipped blade;
3. smearing of unwanted colour over the fabric, called scumming. This comes from poor cleaning of the engraved roller surface and is a particular problem in discharge printing (Section 23.5.2);
4. colour depth variations because of fluctuations of the pressure applied to the print rollers.

Engraved roller printing of fabric more than 2 m wide is difficult because of the unlevel colours caused by bowing of the rollers under pressure. Copper is a soft metal and print rollers may be chromium plated after engraving to ensure adequate endurance. Rollers can also be re-plated for new designs. Nevertheless, engraved rollers are expensive. Once the dominant printing technique, engraved roller printing has been superseded by rotary screen printing.

23.5 PRINTING STYLES

23.5.1 Direct printing

Direct printing involves transfer of paste containing dyes to the appropriate areas of the fabric. After drying, the required localised dyeing of the fibres occurs during
steaming. Washing follows to remove the paste residue. In the case of pigment printing, the pigments adhere to the fabric surface with the cured binder film. No additional treatment is needed. Direct printing is the most important type of printing. It may even take place on a uniformly dyed fabric to produce particular colour effects. Such over-printing produces are called ‘fall-on’ effects. With roller printing machines, even the amount of paste transferred can be controlled to produce different depths of the same colour.

23.5.2 Discharge printing
In discharge printing, the fabric is first dyed to a solid shade and then printed with a paste containing chemicals capable of destroying the colour during the following steaming process. This allows printing of white designs on a ground colour of any depth with a pattern definition that is much higher than would be possible by direct colour printing. If the paste contains dyes resistant to the discharging agent, these dyes, called illuminating colours, will colour the printed areas.

For good discharge printing, dye selection is critical. A typical example of discharge printing involves printing a cotton fabric already dried with azo dyes with a paste containing a strong reducing agent. During steaming the reducing agent destroys the azo dye, reducing it to simpler amines. Washing removes these leaving a white design on the coloured fabric. Dye manufacturer’s shade cards give useful information on the ease of discharge of colour. Dyes are rated on a 1 to 5 scale, a grade of 5 indicating the most easily discharged. A dye with a rating of 5 would give a good white print, whereas a dye with a rating of 1 would be a suitable illuminating colour for a coloured discharge. Illuminating colours are often vat dyes. During steaming, the reducing agent generates the leuco compound that dyes the cotton. Air oxidation then regenerates the parent pigment.

The most common reducing agents are the various salts of formaldehyde-sulphoxylate (HOCH₂SO₂⁻). On heating, these decompose liberating formaldehyde and the sulphoxylate ion (HSO₂⁻), a powerful reducing agent (Scheme 23.2). The decomposition of thiourea dioxide also generates sulphoxylate. On heating, thiourea dioxide first rearranges to formamidine sulphonic acid, which then hydrolyses to urea and sulphoxylic acid (Scheme 23.3). The insoluble zinc and calcium formaldehyde-sulphoxylates and thiourea dioxide are useful in printing fabrics made of synthetic fibres. Their low water-solubility minimises capillary flow of reducing agent solution along the non-absorbent fibre surfaces. Such flow reduces print definition and can produce a coloured halo.
effect. Stannous chloride is also an effective reducing agent for azo dyes. It has the advantage of being a somewhat weaker reducing agent than the sulphoxylates so that it has less effect on illuminating dyes. These are often not completely inert towards strong reducing agents and their colour intensity will be greater when using a less powerful discharging agent.

\[
\text{HOCH}_2\text{SO}_2^- + \text{CH}_2\text{O} + \text{HSO}_2^- \\
\text{NH}_2\text{C} = \text{C} = \text{NH} + \text{SO}_2\text{H}
\]

\[
\text{NH}_2\text{C} = \text{NH}\text{SO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{C} = \text{C} = \text{O} + \text{H}_2\text{SO}_2
\]

Scheme 23.2

Scheme 23.3

It is vital that the paste consistency allows penetration of the reducing agent into the fabric to avoid any residual coloured surface fibres that might be visible. Water-retaining chemicals called humectants, such as glycerol, are therefore often present in the paste. The degree of penetration of the reducing agent into the yarns depends on the print paste viscosity, the amounts of solids and humectants present, and the printing and steaming conditions. If the paste is too thin, however, it will run laterally resulting in flushing, a loss of pattern definition from migration of the reducing agent. This often produces a visible ‘halo’ around the printed design, which may be coloured if an illuminating dye is present. In some cases, ‘haloing’ may be deliberate.

One problem in discharge printing is that the pattern printed onto the coloured ground is not usually visible. Printing mistakes are therefore not easily recognised. It is common to dope the paste with a small amount of white pigment or marker dye. Deliberate inclusion of titanium dioxide, or an optical whitener, makes the printed design visible and improves the white discharge.

‘Scumming’ occurs in roller printing (Section 23.4) when the roller picks up paste containing the reducing agent from an area already printed and later spreads it onto the dyed ground. Padding the fabric with a dilute solution of an oxidant often helps to eliminate this problem. The oxidising agent reacts with the ‘scum’ of
reducing agent and renders it ineffective. The amount of oxidant is insufficient to influence the high concentration of reducing agent in the printed areas.

The print paste includes a variety of other chemicals besides the reducing agent. The thickener must be stable to the reducing agent and non-ionic types are better, particularly if using stannous chloride. The latter coagulates many types of gums with anionic groups. Anthraquinone and some derivatives are “reduction catalysts”. The reducing agent first generates the anthrahydroquinone. This then reduces the dye, the anthraquinone being regenerated. Why this should be more effective than the reducing agent alone is not clear. A number of quaternary ammonium salts with a sulphonated benzyl group improve the discharge effect. An example is p-sulphobenzyl-dimethylanilinium-m-sulphonate (1, in Figure 23.6). This is an efficient benzylating agent and presumably reacts with the amines generated by the reduction of azo dyes. Washing readily removes the water-soluble benzylated amines produced (Scheme 23.4).

![Figure 23.6 p-Sulphobenzyl-dimethylanilinium-m-sulphonate](image)

**Scheme 23.4**

23.5.3 Resist printing

In resist printing, the fabric is first printed with an agent that resists either dye penetration or dye fixation. During subsequent dyeing, only the areas free of the resist agent are coloured. The advantage of this technique is that non-dischargeable dyes can be used for the ground colour.

Physical resisting agents prevent dye absorption by the fibres and include materials such as waxes, fats, pigments and resins. They provide a physical barrier to dye penetration. A simple example of resist printing is the painting of a beeswax
design on a fabric, followed by dyeing. This is the batik style, in which the wax prevents dye penetration into the fibres in the protected areas.

A chemical resisting agent prevents dye fixation. Examples include acids, alkalis, oxidising or reducing agents. These chemicals react with the dye, the fibre, or with the dyeing auxiliaries and prevent dye fixation.

The resist paste on the fabric surface must obviously be stable under the dyeing conditions. These are usually relatively mild. Nip-padding is one method of applying the ground colour without large amounts of water being present. The fabric does not pass through the pad bath but directly between the pad rollers. The lower roller dips into the bath, picks up a somewhat thickened solution of the dyes and transfers it uniformly to the fabric. Over-printing the entire surface with dye solution using an engraved roller is also common. Both techniques minimise the pick-up of liquid and intermediate drying of the printed fabric before steaming may not always be necessary.

Reactive dyes are useful for direct printing, and many of the azo reactive dyes also discharge to a good white. Anthraquinone and phthalocyanine reactive dyes, however, do not reduce to colourless products and are not suitable for discharge printing. They are, however, useful for dyeing after resist printing. The resist paste contains an acidic substance, such as citric acid or sodium dihydrogen phosphate. The fabric is printed with this and dried before nip-padding with a solution of sodium bicarbonate and the reactive dye. On steaming, the bicarbonate decomposes to give sodium carbonate, which induces fixation of the dye to the cellulose. The acid in the resist reacts with the bicarbonate so fixation does not occur in the printed areas.

Resist printing pastes usually have a high solids content. Because of this, they have a tendency to stick in fine engravings or block screens. It is common practice to strain the paste through a screen finer than the printing screen to avoid the latter problem.

Coloured resists are possible using appropriate dyes or pigments in the resist agent. For example, for a resist print with reactive dyes on cotton, the print paste includes an acid to prevent dye fixation, and a pigment along with a binder that will form a resistant film on steaming. The paste is printed, the reactive dye and sodium bicarbonate solution over-printed and the fabric steamed without drying. The ground colour comes from reaction of the reactive dye with the cotton, while the printed areas have the colour of the pigment held on the surface by the binder film.

Coloured resists are also possible using a combination of reactive halogen and vinyl sulphone dyes. The resist printing paste contains, for example, a
chlorotriazine reactive dye, sodium bicarbonate and sodium bisulphite. This is printed onto the fabric, which is then completely over-printed with an alkaline paste of the vinyl sulphone reactive dye. The fabric is dried and steamèd. The chlorotriazine dye reacts with the cotton aided by the sodium carbonate that is formed in the resist printed areas but the sodium bisulphite also present inhibits the reaction of the vinyl sulphone dye (Scheme 23.5). The latter only colours the ground where bisulphite is absent.

Scheme 23.5

23.6 PIGMENT PRINTING

Rotary screen resin-bonded pigment printing is by far the most important printing technique because of its simplicity and low cost. Coloured pigments have no substantivity for the fibre. They are held on the fabric surface in a film of a suitable polymeric binding agent. After printing, heating the fabric for a short period cures the binder. No additional processing is required, the main advantage of this printing method. There is no penetration of colour into the fibres. The binder holds the pigment on the fabric surface by adhesion to the fibres. It tends to stiffen the fabric in the printed areas. This effect is hardly noticeable for small designs since the large unprinted areas retain their flexibility. The pigments used have excellent fastness to light. The technique is applicable to all types of fibres but adhesion of the binder is usually best for hydrophilic fibres such as cotton. For dark colours on polyester and acrylic fibres, the fastness to washing, dry cleaning and rubbing may only be fair.

A typical pigment print paste contains a considerable number of chemicals each of which has a specific role to play. The paste may include coloured pigments, binder, binder crosslinking agent, thickener, flow moderator, weak acid curing catalyst, softener, defoaming agent, water absorbing chemicals or humectants such as urea or glycerol, and emulsifying agents. Chemical suppliers often market two separate partial mixtures of appropriate chemicals. These are stable and only require simple combination before printing.

Apart from carbon black and titanium dioxide for black and white respectively, and metal powders for special effects, the coloured pigments used are organic...
compounds synthesised by the dye manufacturers. They belong to the same chemical classes as soluble dyestuffs (azo, anthraquinone, phthalocyanine) but have no ionic groups.

The binder for a water-based print paste is typically a copolymer produced by emulsion polymerisation of a mixture of monomers such as butyl acrylate and acrylonitrile, or of styrene and 1,3-butadiene. During drying of the printed zones, the particles of swollen binder gel exudate on the fabric surface and coalesce into a coherent film. By regularising the monomer composition and the degree of polymer crosslinking the binder will give a film with the desired elasticity and solvent, light and washing fastness. One method of promoting crosslinking is to incorporate into the polymer a small amount of a comonomer with a residual reactive group such as N-methylolmethacrylamide. During curing, the N-methylol groups along the polymer chains undergo intermolecular condensation reactions producing a number of crosslinks (Figure 23.7). This is called internal crosslinking.

Since the condensation reaction generates water, and is reversible, dry air is used for curing rather than steam. The crosslinks are, however, reasonably stable to hydrolysis during mild washing and are not present in sufficient number to produce a rigid film. They ensure good film stability, little swelling of the film in dry cleaning solvents and improve the adhesion to the fibre surface.

Crosslinking can also occur by adding to the paste an agent capable of reacting with the binder polymer during curing. These are external crosslinking agents. N-methylolmelamines or their methyl ethers are typical examples. The N-methylol groups can react with groups in the binder polymer or with the fibre as well as with other chemicals in the paste such as thickeners (Figure 23.7). External crosslinking is better for printing on synthetic fibres because of the improved adhesion of the film produced.

The condensation of N-methylol compounds requires an acid medium and the pigment print paste will therefore have an added weak acid such ammonium dihydrogen phosphate. This compound causes reduction of the pH of the print film during curing, promoting crosslinking.

The print paste must contain a thickener to provide the correct viscosity and flow. Pigment printing pastes should have pseudoplastic flow (Section 23.10.3). The shear stress developed by the squeegee reduces the paste viscosity so that it flows easily through the screen. Once the shear decreases, however, it becomes viscous again and does not penetrate far into the fabric surface. This avoids sticking the yarns together with binder and hardening the fabric surface. Oil-in-water emulsions give good results. These consist of about 70% white spirit
hydrocarbons and 30% water with a small amount of non-ionic emulsifying agent (Section 23.10.1). After drying, there is no solid residue on the fabric surface as the emulsion thickener completely evaporates during curing. The hydrocarbons used in oil-in-water emulsions may be released to the environment, however, and their use is in forced decline. Carbohydrate gums are not usually suitable for use in pigment printing because of the ready reaction of their hydroxyl groups with N-methylol compounds. Fortunately, colloidal aqueous solutions of polymers such as polyacrylic acid have similar rheology to the oil-in-water emulsions provided that the carboxylic acid groups dissociate. Rheology is the science of the deformation and flow of materials. Addition of ammonia produces the ammonium salt of the polymer. The repulsion of the negatively charged carboxylate groups causes the polymer chain to open out and the polymer particles swell considerably because of
hydration of the anionic sites. A small degree of polymer chain crosslinking ensures that a true solution is not possible. These colloidal solutions exhibit the required pseudoplastic flow. This type of thickener leaves a solid residue on the fabric surface that can cause a harsh handle. Incorporation of a softening agent counteracts this.

23.7 PRINTING WITH SOLUBLE DYES

For water-soluble dyes, the sequence of operations is printing the fabric with a thickened paste containing the dyes, followed by drying and steaming. During steaming, the dyes re-dissolve in the water condensed on the paste films and diffuse into the fibres. Relatively long steaming times are typical. A final washing removes the thickener, unfixed dyes and other chemicals from the fabric, under conditions that avoid staining of white or coloured areas of the fabric by the extracted unfixed dyes.

23.7.1 Printing cotton fabrics

Printing cotton fabrics with reactive dyes offers many process options. Sodium alginate (2, in Figure 23.8) thickeners, derived from seaweed, show little tendency to react with the dyes despite the presence of many hydroxyl groups. The anionic carboxylate groups in the alginate presumably repel the similarly charged dye molecules and hinder their reaction with the hydroxyl groups. Alginates, however, readily precipitate in the presence of calcium and magnesium ions and this hardens the print paste. Soft water, or a sequestering agent, is essential for paste preparation and for washing-off after fixation otherwise the paste film will not dissolve. Other useful thickeners include those based on polyacrylic acid or oil-in-water emulsions.

The reactive dyes in the aqueous print paste must be stable. The preferred alkali is sodium bicarbonate. This gives a neutral, stable reactive dye paste and

Figure 23.8 Sodium alginate
storage without any risk of dye hydrolysis is possible. On steaming or baking, the bicarbonate decomposes into carbonate, a stronger alkali, which causes reaction with the cellulose. For dyes of lower reactivity, pastes containing sodium carbonate or even NaOH ensure better fixation by activating the cellulose more effectively.

After printing, a variety of dye fixation methods is possible. For some of the less reactive dyes, steaming for 5 to 15 min may be necessary depending upon the steam temperature. Superheated steam allows rapid fixation in less than 1 min. This is called flash ageing. The water that initially condenses onto the fabric quickly evaporates since the superheated steam is not saturated. Hydrolysis of the dye-fibre bond can occur on excessive steaming at high temperatures. Under the alkaline conditions required for dye fixation, some azo reactive dyes may undergo reduction by cellulose aldehyde groups. Adding a mild oxidant such as sodium m-nitrobenzenesulphonate to the paste minimises this.

Fixation of printed reactive dyes also occurs on baking at 160–180 °C for up to 3 min. Whether fixed using steam or dry heat, large amounts of urea in the print paste ensure that the paste retains enough water to re-dissolve the dyes. Urea is not necessary, or at least the amounts can be much smaller, if the fabric is printed with a neutral reactive dye paste containing no alkali. After printing, the fabric is padded with an alkali solution containing salt and then steamed. Alternatively, for dyes of higher reactivity, an alkali shock treatment gives effective fixation. The printed fabric passes through an alkaline solution containing salt at 100–105 °C. Fixation occurs within 20–30 s.

Washing out the unfixed and hydrolysed reactive dyes is a critical step. Dyes of low substantivity are preferred because they are easier to remove from the cotton and are less likely to re-absorb on other areas of the fabric.

In print pastes containing vat dyes, sodium formaldehyde-sulphoxylate (HOCH₂SO₂Na) is the preferred reducing agent. This is stable at room temperature. There is no loss of reactivity on storing pastes containing all the required chemicals or on drying the printed fabric. The formaldehyde-sulphoxylate decomposes on steaming liberating sulphoxylate ion, which reduces the vat dye to the leuco compound. Potassium carbonate is the preferred alkali in the paste since it is more soluble than sodium carbonate. Alternatively, the vat dye can be printed using a paste without reducing agent. After drying, the fabric is padded with an alkaline solution of hydros followed by steaming or flash ageing. The thickener used is of the polyacrylate type that coagulates on contact with the alkaline solution. This minimises bleeding and smudging during padding. Some azoic and ingrain dyes are still used in printing, much more so than in
dyeing. The print paste may contain a coupling component and a diazonium ion, the latter stabilised as a diazamino compound with an amino acid. On steaming the weakly alkaline paste, the liberated diazonium ion couples to form the azo pigment.

The phthalogen dyes (Section 19.5.2) are still important for printing turquoise to green shades. The paste contains the phthalocyanine precursor (aminoiminoisoindolene), the special emulsified glycol solvent, the copper complex, a small amount of ammonia and thickener. The phthalocyanine pigment is produced on baking or steaming.

23.7.2 Printing other fibres
Polyester fabrics can be printed with pastes containing disperse dyes. Specially formulated disperse dyes with non-ionic dispersants can be used. Since the fixation temperatures are relatively low, the paste contains a carrier (o-phenylphenol) or a fixation accelerator (polyethylene oxide condensate). All hydrophobic materials from preparation or from the printing process itself must be removed from the fibre surface. This avoids thermal migration of the dyes into the hydrophobic surface film if the fabric is subject to temperatures above about 140°C. Thickeners such as alginate or starch ethers give flexible films that are easily washed off after printing.

The paste may contain a weak acid such as sodium dihydrogen phosphate, and a weak oxidant such as sodium m-nitrobenzene sulphonate. These inhibit alkaline decomposition and reduction of sensitive disperse dyes, respectively. The preferred fixation method uses high temperature superheated steam, or dry heat as in the Thermosol process. The latter method allows much shorter fixation times but can result in a harsher fabric handle. On steaming with superheated steam, water first condenses on the fabric, swelling the thickener film on the surface. The water then re-evaporates as the temperature rises above 100°C. The fixation time depends upon the steam pressure and temperature. Dyes that readily sublime should be avoided. A reduction clearing aftertreatment is needed for deep shades.

Nylon materials are printed using acid dyes. The paste often contains solubilising agents such as thiourea (NH₂CSNH₂) and thiodiethyleneglycol (HOCH₂CH₂SCH₂CH₂OH) to ensure that the dyes re-dissolve during steaming. The weakly acid paste may contain ammonium sulphate or citric acid. Fixation by steaming at 100°C often requires long times, up to 30 min. This is shorter if using pressurised steam. Washing-off conditions must minimise staining of the
unprinted ground. An alkaline washing solution containing sodium carbonate gives the lowest dye substantivity. In addition, a cationic auxiliary in the wash liquor will complex any desorbed acid dyes and prevent their re-absorption.

23.7.3 Printing of cotton/polyester fabrics

Pigment printing is the major method used for cotton/polyester fabric because the colour application is superficial and independent of the two different fibres present. The usual limitations of lower fastness to dry cleaning and abrasion in deep shades, as well as the poor handle, have not limited the use of this method. Cotton/polyester can be printed with a single type of dye when using some azoic, vat or disperse dyes but none of these methods are of universal application.

The major direct printing method with dyes uses a combination of disperse and reactive dyes. In fact, ready-mixed dye combinations are available from some dye manufacturers for this purpose. Both types of dyes are fixed by treatment in hot air at 190–210 °C for 30–60 s, or in superheated steam at around 180 °C for several minutes. Washing under initially alkaline conditions assists in clearing the disperse dye.

23.8 TRANSFER PRINTING

Transfer printing in the textile industry usually means the sublimation of thermally stable dyes from a coloured design on paper at high temperature followed by absorption of the dye vapours by synthetic fibres in the fabric. The paper presses against the fabric and dye transfer occurs without any distortion of the pattern. This type of vapour transfer printing was developed in the 1960s for printing fabrics made of synthetic fibres. To date, there are no commercial methods for transfer printing fabrics made from natural fibres.

The printing of polyester fabrics with low molecular weight disperse and solvent dyes, which readily sublime at around 200 °C, is the most important vapour transfer printing method. The dyes used have only a limited number of polar substituents and are relatively free of dispersing agents and diluents. Dye selection is critical. The dyes must sublime on heating but must also have adequate fastness to washing and hot pressing. This is possible for printing polyester but is not usually the case with other types of synthetic fibres. When printing with dye mixtures, compatible dyes with comparable transfer properties are essential to
ensure colour constancy. Incompatible dyes may give width and length variations in colour because of differences in their rates of vaporisation and of absorption.

The fabric usually has a high proportion of hydrophobic fibres such as polyester since the vapourised dyes are not strongly absorbed by natural fibres. Cotton/polyester fabrics with up to 50% cotton can be transfer printed provided a resin finish has been applied. The vapourised dyes absorb into the polyester fibres and into the resin finish in the cotton. With melamine-formaldehyde precondensates, curing of the resin and vapour transfer printing can be combined into one operation.

The fabric must be dimensionally stable up to a temperature of 220 °C during the transfer period to ensure good pattern definition. Heat setting or relaxation by scouring prior to printing is therefore essential. The latter process also eliminates spinning and knitting oils.

A key step is production of the appropriate paper with the coloured design. The inks containing the volatile dyes are printed onto one surface of the paper. The paper has low permeability towards the printing ink solvent to ensure good pattern definition. Strong paper, resistant to heating to 220 °C, is necessary. At this temperature, the release of the dye vapour from the ink layer must be quite rapid. The paper is printed using a variety of techniques, the most popular being rotary screen printing. This technique allows more colour on the paper surface, and printing of wider papers than with other continuous printing methods. Resins in the ink bind the dyes to the paper and prevent marking-off onto the back of adjacent paper layers when the paper is rolled up. The resin, and any other additives such as thickeners, should not hinder dye vaporisation nor transfer onto the fabric themselves.

Even though the paper is in contact with the fabric during printing, there is a small air gap between them because of the uneven surface of the fabric. The dye vaporises when the back of the paper heats up and the vapour passes across this air gap. For vapour phase dying, the partition coefficients are much higher than for aqueous systems and the dye rapidly absorbs into the polyester fibres and builds up (Figure 23.9). There is an initial temperature gradient across the air gap but the fibre surface soon heats up and the dye can then diffuse into the fibres. In most respects, the printing mechanism is analogous to Thermosol dyeing in which disperse dyes are vapourised from cotton and absorbed by polyester fibres (Section 15.7.6).

In garment printing with flat bed printers, production rates are quite low. The paper and fabric are uniformly pressed face to face. The back of the paper contacts...
a uniformly heated plate at around 200 °C. The transfer takes from 20 to 60 s. Continuous fabric printers use heated calenders and give printing speeds around 20 m min $^{-1}$. A boiling liquid inside the calender condenses all over the inner metal surface and ensures uniform heating of the outer shell. The paper winds around the heated calender, its printed face in contact with the fabric. The two layers are held in place under slight pressure by an endless Nomex blanket (Figure 23.10). Nomex is a heat resistant aramid (aromatic polyamide) fibre manufactured by Du Pont. A backing paper inserted between the fabric and blanket prevents marking-off onto the latter. The pressure and high temperature required for vapour transfer printing can cause some compression and surface glazing of the thermoplastic fabrics.

Both flat bed and cylinder printing machines can operate with a partial vacuum to generate a flow of air through the paper and then the fabric. This greatly increases the dye transfer rate and the degree of dye penetration into the yarns.
The fabric winds around a partially evacuated perforated cylinder with the paper on the outside. No blanket is required as the air pressure holds the two layers in place. Infrared heaters placed around the cylinder increase the temperature to vaporise the dyes. Alternatively, a flexible metallic mesh holds the paper and fabric against a heated calender surface. A vacuum chamber with suitable seals covers the mesh around about three-quarters of the calender surface and pulls air through the paper and fabric layers. Vapour transfer printing with vacuum is possible using shorter heating times and allows effective dye transfer at temperatures around 160 °C.

The major restrictions of vapour transfer printing include the rather limited range of volatile but fast dyes, the difficulties of printing wide materials and the inability to print fabrics containing high proportions of natural fibres. Each length of material gives an equal length of used print paper. This is not usually suitable for recycling, nor would this be practicable. In some cases, the dye penetration into the yarns tends to be rather poor and fabrics often expose underlying white fibres when stretched. One major advantage of transfer printing is that no washing-off is needed, as there are no chemicals and very little surface dye to remove from the fabric.

23.9 CARPET PRINTING

The printing of tufted nylon carpets with acid dyes is an important sector of the textile coloration industry particularly in North America. A chapter on printing would be incomplete without some mention of it. Printing of carpets offers many
more complex colour designs than are possible by combination of differently coloured yarns by tufting alone. The different localised coloration techniques include regular printing using flat and rotary screens, space dyeing in which continuous filament yarn is printed with bands of colour before assembling the carpet, and spray dyeing.

Flat or rotary screen carpet printing is similar to printing fabrics. For rotary screen printing, the nickel galvano screens are considerably more robust than those used in fabric printing. Penetration of the print paste into the carpet pile without an undesirable loss of the pattern definition is the major problem. A slight vacuum, developed in a slot below the carpet and aligned with a double blade squeegee, assists this penetration. In another method, a hydrostatic head of print paste forces the paste further into the pile.

In one common space dyeing method, continuous multifilament nylon, either at full extension or in the form of a tubular weft-knitted sock, is padded with a ground colour and then printed with random bands of different acid dye pastes using engraved rollers, rollers with raised foam surfaces, or jets. The dye paste displaces the unfixed ground colour. Steaming of the printed nylon fixes the acid dyes and the yarn is well washed. The dried space-dyed continuous filament, after de-knitting in the case of the tubular sock, is then tufted into the carpet backing. The various coloured zones blend to give a characteristic random speckled design.

Large quantities of carpet are ‘printed’ by running fine streams of differently coloured dye solutions onto the carpet surface in an organised pattern. Passing the carpet through squeeze rollers helps the mixing of the dye solutions on the surface. The carpet may have already been padded with a solution of acid dyes to provide a ground colour. The streams of dye solution tend to displace the ground dye solution already present, since the dyes are not fixed at this stage. They thus generate their own particular colour effect. The presence of a gum thickener is also common to control the spread of the dye solutions. By controlling the viscosity of the dye solution and of the applied gum solution, if used, and the flow of the dye streams, the degree of spreading may be varied to produce sharp or diffuse colour patterns. The carpet is then steamed to fix the acid dyes and finally well washed (Section 13.12.1). Fixation in a horizontal steamer gives the best pattern definition. Rapid fixation of the acid dyes avoids any tendency for migration of dye either towards or away from the fibre tips. This minimises ‘haloing’ and ‘frosting’ effects. Haloing is a colour effect produced by lateral migration of dyes resulting in light and dark zones around the colour design. Migration of dyes away from the fibre tips leaving them paler in colour causes the frosting effect.
The possible colour designs are those from the limited number that the machine is capable of producing. The advantages of this type of spray coloration are the absence of pressure to cause flattening of the pile, as in screen printing, the rapidity of pattern change, and the very large repeat designs that are possible. The limited waste makes short runs economical.

The gum used in carpet coloration is a major component of the dyeing mixture. This is often a natural gum, such as xanthan or guar gum, or a modified derivative. It should be cheap, easily dispersed and dissolved, compatible with other chemicals in the mixture and easily removed from the carpet by washing in cold water. The gum aids the uniformity of wetting, limits the spread of the dye solution and helps to eliminate frostiness at the pile surface caused by the migration of the dye away from the fibre tips during steaming.

23.10 THICKENERS

23.10.1 Chemicals used as thickeners

Viscous pastes used for textile printing usually consist of either solutions of high molecular weight polymers or emulsions of immiscible liquids. The chemicals used belong to various chemical classes. Unbranched polymers give viscous solutions at low concentrations but the viscosity falls with increasing shear. Branched chain polymers require higher concentrations to give the required viscosity but are less sensitive to shear. The types of thickening agents used are:

1. naturally occurring carbohydrates such as guar and locust bean gum, cellulose and starch derivatives and alginates from seaweed. These dissolve or disperse in water to give viscous pastes. Their preparation from the solid carbohydrate requires considerable care. The powdered carbohydrate is rapidly dispersed in water before any significant swelling of the particles can occur. This avoids the formation of gummy lumps in the paste. This may then stand for some time before gradually heating, if required. As a precaution, the final paste is often strained;

2. emulsions of oil in water. These emulsions consist of small droplets of oil dispersed in water. The negative charges of the anionic emulsifier molecules adsorbed on the surfaces of the droplets prevent their coalescence. In textile printing, a typical emulsion thickener has about 70% white spirit (petroleum distillate boiling at 150–200 °C) in water. Both components are volatile and leave no residue after drying;
(3) solutions of synthetic polymers. Slightly crosslinked copolymers of acrylic acid derivatives and acrylic esters disperse in water but remain insoluble. On addition of an alkali such as ammonia, the carboxylic acid groups dissociate forming the carboxylate anion and the hydrophobic polymer chains uncoil because of the repulsion of the negative charges. A colloidal solution results with a substantial increase in viscosity. The polymer does not dissolve completely because of the crosslinks between the polymer chains. The resistance to flow is a consequence of the size of the polymer molecules and the large numbers of water molecules held on their surface solvating the carboxylate groups. The ammonia is lost during drying.

Mixtures of different thickening agents are often used to give printing pastes with the desired characteristics. For example, polyacrylic acid is sensitive to high concentrations of metal ions often found in many dyes. Its compatibility with such dyes is greater in the presence of other types of thickeners that do not precipitate with polyvalent metal ions. Emulsion thickeners are often mixed with carbohydrate pastes to give so-called ‘half emulsions’. The film of natural thickener left after drying ensures that the printed dyes do not rub off before fixation. In addition, less white spirit is needed, drying is faster and the lower amount of natural thickener results in a higher colour yield.

Many suppliers provide pre-prepared paste components. The final print paste is usually a blend of two pre-prepared components, the dyes having been mixed into one of them. The final paste invariably contains a considerable number of chemicals. Tables 23.1 and 23.2 gives some typical examples.

23.10.2 Characteristics of print pastes

The choice of thickener in a print paste determines not only the paste viscosity but also a number of other essential factors. These include:

(1) the print paste stability, particularly on storage. Compatibility of thickeners with respect to the added dyes and chemicals is critical. Thus, anionic polymers are rarely compatible with and readily coagulate in the presence of cationic dyes or multivalent metal ions from hard water or added chemicals. The hydroxyl groups in most carbohydrate gums react with reactive dyes. They are therefore excluded. Many print pastes contain naturally occurring thickening agents that provide nutrients for bacterial growth. Addition of some anti-bacterial preservative avoids bacterial contamination;
(2) the adhesion and flexibility of the printed paste film. The film of paste must not mark off onto a screen or roller printing another colour. A film of reasonable flexibility and adhesion ensures that it can withstand the mechanical handling required for drying and steaming without flaking off the fabric. In those cases where the thickener or binder remains on the printed fabric, the film must be completely transparent and not cause undue stiffness of the fabric;

(3) the colour yield of the printed area. During fixation, the dye must diffuse into the fibres from the film of paste that has swollen in the steam. This process depends on the thickener. Obviously, the dyes should have little or no substantivity for the polymeric thickening agent used. Dye diffusion into the fibres is easier from thin synthetic polymer films with low solids content. The colour yield also depends on the extent of penetration of the print paste into the fabric structure. This is partly determined by the paste viscosity;

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Amount (%)</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigments</td>
<td>15</td>
<td>Colorants</td>
</tr>
<tr>
<td>Trimethylolmelamine</td>
<td>14</td>
<td>Pigment binder</td>
</tr>
<tr>
<td>NH₃(H₂PO₄)₆ 16% aq</td>
<td>1</td>
<td>Catalyst for binder crosslinking</td>
</tr>
<tr>
<td>Water</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Gum tragacanth dispersion 6%</td>
<td>35</td>
<td>Thickener</td>
</tr>
</tbody>
</table>

Table 23.2 Approximate composition of a pigment-illuminated discharge print paste for a fabric already dyed with reactive dyes

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Amount (%)</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pigments</td>
<td></td>
<td>Colorants</td>
</tr>
<tr>
<td>Zinc formaldehyde-sulphoxylate</td>
<td>5</td>
<td>Discharge reducing agent</td>
</tr>
<tr>
<td>Reactive acrylic copolymer</td>
<td>10</td>
<td>Pigment binder</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>1</td>
<td>Catalyst for binder crosslinking</td>
</tr>
<tr>
<td>White spirit</td>
<td>60</td>
<td>Emulsion thickener</td>
</tr>
<tr>
<td>Carboxymethylcellulose</td>
<td>7</td>
<td>Natural thickener</td>
</tr>
<tr>
<td>Water</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>5</td>
<td>Humectant</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
(4) The ease of removal of the residual film of paste remaining on the fabric after fixation. After printing, the film of residual thickening agent is usually washed from the fabric;

(5) The cost of the thickening agent. The cost of the thickener and the costs associated with its removal from the fabric should be as low as possible;

(6) The environmental impact of thickeners in the effluent leaving the printworks. The large amounts of these chemicals in the effluent can significantly increase the BOD of the waste water.

23.10.3 Fundamentals of viscosity

In screen printing, the squeegee compresses the paste between the blade and the screen developing a hydrodynamic pressure. The flow of the paste through the open holes in the screen onto the fabric relaxes this pressure. The hydrodynamic pressure developed must be sufficient to fill the screen holes with paste and, aided by the capillary forces drawing the paste between and into the fibres, it must promote transfer of an adequate volume of paste onto the fabric. There must be no passage of paste through the screen before or after the actual printing transfer. The hydrodynamic pressure developed is a function of the squeegee blade angle, the paste viscosity, the screen hole size and the screen speed, rather than the pressure applied to the squeegee.

The Poiseuille equation gives the flow rate of liquid through cylindrical holes:

\[
Q = \frac{P \pi a^4}{8 \eta l}
\]  

where \(Q\) is the volumetric flow rate of the liquid transferred, \(l\) is the length of the hole, \(a\) is the hole radius, \(P\) is the constant pressure drop across the hole, and \(\eta\) is the liquid viscosity. This applies only to cylindrical holes and thus not to rotary screen holes. For the latter, \(P\) increases with increase in the hydrodynamic pressure. This is inversely proportional to the viscosity and proportional to the hole radius to a power greater than two. Thus, as in the Poiseuille equation, the volumetric flow rate of paste onto the fabric is more dependent on the hole radius than on the viscosity of the paste. The structure and absorbency of the fabric also influence \(Q\). Penetration of the paste into the fabric depends upon the pressure and the kinetic energy of the paste leaving the screen holes. The viscosity of the
paste restricts sideways spreading due to surface tension. As the fabric and screen separate, the layer of paste must split and separate into the film remaining on the fabric and the layer of paste left on the screen. This probably causes the formation and elongation of many threads of paste that then give small mounds of colour on the film surface leading to a spotty or 'mealy' appearance. Some flow is desirable at this point to give a level colour.

Viscosity is a measure of the resistance of a fluid to flow when subjected to a force. It is the ratio of the shearing stress to the rate of shear, as shown in Figure 23.11. This represents the flow of liquid below a rigid plate of area $A$ when a force $f$ moves it at a velocity $v$. Because of the liquid's viscosity, the lower layers of liquid move with decreasing values of $v$. The shear stress is $f/A$, and the rate of shear is the velocity gradient in the direction perpendicular to the plate, $dv/dx$. The viscosity is therefore:

$$
\eta = \frac{f/A}{dv/dx}
$$

Figure 23.11 Flow of liquid layers beneath a rigid plate illustrating the definition of viscosity

The greater the viscosity of the liquid, the greater the force required to make it flow at a given velocity, and the lower the velocity gradient or rate of shear. The units of viscosity are thus Pa s (Pascal seconds). This unit is ten times the older unit 'poise', after Poisseuille. Viscosity can be determined by measuring the flow of the liquid through a capillary tube but this is not suitable for print pastes. A cone and plate viscometer is used. A film of paste is wedged between two plates. The lower one is flat and the upper a flat cone tapering from the centre outwards at a
very small angle. The diameter of the cone selected depends on the viscosity of the paste. Driving the cone at a given velocity against the viscous drag of the liquid requires a measured force. The shear stress and the rate of shear can be calculated from the cone dimensions, the rate of rotation and the measured torque required to maintain it. A graph of the rate of shear as a function of the shear stress allows calculation of the viscosity.

Newtonian fluids such as water and oils have viscosities independent of the rate of shear. The graph of rate of shear versus shear stress is thus linear. A variety of other flow behaviours are possible where the viscosity depends upon the rate of shear (Figure 23.12). These are:

1. shear-thinning or pseudoplastic flow. At low shear stress, the paste remains quite viscous but then as the shear increases the viscosity decreases and flow becomes easier. This is typical of many print pastes;
2. plastic or Bingham flow. Some pastes do not begin to flow until a minimum shear stress or yield has been exceeded. Viscous pastes that do not fall off the stirring paddle are called ‘short’ and will exhibit a yield value. They are more useful for printing sharply defined patterns but not for blotches of colour where more spreading is desirable;
3. dilatant flow. This is a shear thickening behaviour in which the viscosity increases with increasing shear stress;
4. thixotropic flow. This is similar to shear thinning behaviour but the measured viscosity depends upon the duration of the applied shear stress.

Figure 23.12 Shear stress versus rate of shear for different types of liquids
Why does the viscosity of a dilute polymer solution or an oil-in-water emulsion decrease when the shear stress increases? Shear thinning occurs because the polymer molecules in the paste become oriented in the direction of flow and may shed water molecules solvating groups along the chains. In emulsions, the droplets adopt elongated shapes in the direction of flow rather than the initial spherical form when stationary. In addition, water molecules adhering to the layer of surfactant on an oil drop surface tear away reducing the size of the particle. These effects make flow easier. Thixotropic behaviour arises because of the time required for the reformation of the intermolecular bonds that have broken under the shear stress.

REFERENCES
CHAPTER 24

Testing of dyes and dyeings

This chapter provides an overview of the principles and procedures used to evaluate the properties of dyes and dyeings. An exhaustive treatment is not possible. There is, however, an extensive literature available and some references will be provided to help the reader delve further into the details of some of the testing methods.

24.1 SPECTROPHOTOMETRIC ANALYSIS OF DYE SOLUTIONS [1]

The colour of a dye solution shows that there is some transmission of light of wavelengths corresponding to that colour through the solution and extensive absorption of wavelengths of other colours. The transmission of monochromatic light (light at a single wavelength) through a solution is governed by the Beer-Lambert law, a combination of the laws determining how the concentration of the absorbing substance in solution and the path length of the light through the solution influence the extent of transmission:

\[
A(\lambda) = \log \left( \frac{I_0}{I_t} \right) = \varepsilon(\lambda)C_l = \log \left( \frac{100}{T(\lambda)} \right)
\]

where \( A \) is the absorbance or optical density at wavelength \( \lambda \), \( I_0 \) is the intensity of the incident light of fixed wavelength \( \lambda \), \( I_t \) is the intensity of the light transmitted through the absorbing medium (solution), \( C \) is the concentration of the absorbing substance in solution, \( l \) is the length of the light path through the solution, \( \varepsilon \) is the absorptivity or extinction coefficient at wavelength \( \lambda \), and \( T \) is the percentage transmission of the monochromatic light through the solution. The symbol \( \lambda \) in brackets after \( A \), \( T \) and \( \varepsilon \), indicates that these parameters vary with the wavelength of the light (Figure 24.1).

In this equation, the first logarithmic term is called the absorbance \( A \) or the optical density. It varies from 0 to infinity. The constant \( \varepsilon \) is a characteristic of the absorbing substance at a particular wavelength. Its units depend on those used to express the concentration and path length, the latter usually being in cm. For pure
substances, the solution concentration is usually expressed in mol l$^{-1}$ and $\epsilon$ has units of l mol$^{-1}$ cm$^{-1}$. Dye powders are always diluted forms of the dye and, in many cases, the molecular weight is not known. The dye concentration is thus expressed in, say, mg l$^{-1}$ of the dye powder or liquid and $\epsilon$ has units of l mg$^{-1}$ cm$^{-1}$.

![Figure 24.1](image)

Figure 24.1 A spectrophotometric cell holding a dye solution, its absorption spectra for three different dye concentrations, and the graph of absorbance as a function of concentration.

The Beer-Lambert law predicts a linear relationship between the solution absorbance at a given wavelength and the concentration of the absorbing substance for a given transmission path length. The latter is usually determined by the optical glass cell used to hold the solution and is often 1.00 cm. In most analytical work, the relation between absorbance and concentration is established at the wavelength of maximum absorbance of the dye solution to provide the greatest sensitivity (Figure 24.1).

Absorbance measurements are usually obtained using an absorption spectrophotometer. This has a source of white light that can be dispersed by a
diffraction grating into a spectrum of different colours, like a rainbow. By moving a slit across this spectrum, or by rotating the grating to move the spectrum across a slit, light of a given colour consisting of a narrow band of wavelengths – and therefore close to being monochromatic – can be isolated. This then passes through a solution of the absorbing compound held in a rectangular cell of known path length. The instrument is calibrated to give a light detector reading corresponding to 100% transmission or zero absorbance using the cell containing only the non-absorbing solvent, and to 0% transmission by blocking the light beam. When the solvent is replaced by the solution of the dye, the detector gives the transmission or absorbance reading for that solution (Figure 24.2).

![Figure 24.2 Schematic of a simple solution absorption spectrophotometer](image)

Dilute aqueous solutions of dyes usually follow the Beer–Lambert law and give a linear graph of absorbance versus concentration (Figure 24.1). The law is only valid for the transmission of monochromatic light and when the dye is in solution in a constant state. The absorbance of a dye solution at a particular wavelength is a direct function of the physical and chemical form of the molecules present. It is imperative that measurements are always carried out in solution at constant pH and at about the same temperature. Acid–base reactions can cause considerable changes in absorptivity and even in colour. The absorptivity of a dye invariably decreases if the dye begins to form aggregates or micelles in solutions at higher concentrations. This is often quite pronounced if the concentration of salts is also high and leads to a Beer–Lambert graph of gradually decreasing slope.

Spectrophotometric analysis is applicable to most types of dyes in solution and sometimes even in dilute dispersion. Once a calibration graph of absorbance versus concentration is available, unknown concentrations can be rapidly determined. The additivity of individual absorbances can be used in the analysis of
dye mixtures with two and three components but the precision depends on having dyes with well-separated spectral curves that do not interact with each other in the mixture.

### 24.2 THE EVALUATION OF THE COLOUR YIELD OF DYES

The colour yield of a dyeing is the depth of colour that a unit mass of dye is able to impart to the dyed substrate. It can be assessed visually but a more quantitative measurement is possible using the Kubelka-Munk $K/S$ value calculated from a reflectance measurement (Section 22.3.1). Dyes are sold in several different physical forms such as powdered or granular solids, or liquid solutions or dispersions. Since the colour of a dyeing obtained with a given amount of dye based on the weight of fibre (% owf) must be reproducible from one dye batch to the next, the dye manufacturers pay particular attention to the standardisation of their products. The colour strength of a dye is normally verified in the dyehouse laboratory before a new batch of dye is used in production. This may simply involve measurement of the absorbance of a solution of dye at a given wavelength and concentration and comparison of the result with similar measurements on previous dye batches.

Since many commercial dyes have more than one coloured component, plus shading dyes, the assessment of dye strength based on a solution absorbance measurement may not always agree with actual dyeing results. The results can be quite misleading in the case of reactive dyes since hydrolysis of the reactive group does not influence an absorbance measurement but greatly affects the colour yield of a dyeing. A more reliable method is therefore to carry out a dyeing trial and assess the colour yield of the dyeing. Instrumental measurements are more reliable than visual assessment. To obtain the best correlation between the measurements and visual observation, the reflectance spectrum of the dyeing is recorded and the Kubelka-Munk $K/S$ value calculated at each wavelength. These values are then integrated after weighting by multiplication by the sum of the appropriate CIE standard observer colour matching functions [2]:

$$\text{Colour strength} = \sum_{\lambda=380}^{780} \left( \frac{K}{S} \times (x_1 + y_2 + z_3) \right)$$

(2)

The colour yield is the value of the colour strength divided by the amount of dye.
used. It is most accurately determined from the graph of colour strength as a function of the amount of dye used (% owf).

Since different formulations of the same dye may contain different amounts of the dye and different additional chemicals, two products from different suppliers or even the same supplier may have different dyeing characteristics. The dyer needs to know what depth of colour is obtainable from a given weight of dye powder at a given cost. If one dye is to be substituted by another, it is also useful to know the relative fastness properties at the same depth of shade.

24.3  FASTNESS PROPERTIES OF DYEINGS AND THEIR ASSESSMENT [3]

24.3.1  Generalities

The stability of the colour of a dyeing, or its fastness, is one of its most important properties. A fast dyeing will not show significant visible fading during the useful life of the particular material. During use, a dyed material is exposed to a variety of agencies that can cause its colour to fade, and often in a complex manner. Fading may also be accompanied by changes in saturation and hue. In some cases, the colour may initially become deeper rather than paler. These changes occur because of decomposition of the dye molecules in the fibre (as in light fading), or because of their removal into the external medium (as in washing). In addition, in several fastness tests such as those for washing, colour may be transferred to adjacent white material. The degree of staining of adjacent material must then also be evaluated. In some cases, colour changes may be a consequence of the yellowing of the fibres by the particular treatment. The colour fastness of a material is a measure of its resistance to these types of changes and is a characteristic of the entire dye-fibre system. Despite this, it is common to refer to the fastness properties of a dye.

Few dyeings show uniformly high fastness to all agencies. It is quite common for certain of its fastness properties to be superior to others. The fastness properties of a dyeing are a characteristic of the particular dye-fibre combination. They are a complex function of many variables including:

1. the molecular structure of the dye;
2. the manner in which the dye is bound to the fibre, or the physical form present;
3. the amount of dye present in the fibre;
(4) the chemical nature of the fibre;
(5) the presence of other chemicals in the material;
(6) the actual conditions prevailing during exposure.

We have already seen many examples of the effects of the above variables on the fastness properties of dyeings for various types of dye–fibre combinations. In almost all cases, a given dye applied to different types of fibres will not give dyeings exhibiting the same fastness properties. Cationic dyes are a perfect example of this, their light fastness on acrylic fibres being much better than on wool or mordanted cotton.

The range of fastness tests is considerable because of the requirements for colour stability towards a large number of different agencies that arise during either production or use. For a specific end-use, some fastness properties of a dyed material will be critical and others of much less importance. For example, coloured window curtains should have good fastness to light but the fastness to chlorine water is irrelevant compared to that required for a swim suit material.

Fastness tests are described in detail in documents from professional organisations such as the Society of Dyers and Colourists (SDC), the American Association of Textile Chemists and Colorists (AATCC) and the American Society for Testing and Materials (ASTM). Many countries have established national colour fastness testing standards but, unfortunately, conditions for a given test still vary considerably. Most European countries adopt the fastness standards of the International Organisation for Standardisation (ISO) as their national standards. Hopefully, the continuing work of the ISO will lead to greater acceptance of such international standards. Because of the variability of fastness testing methods, the actual test method used should always be specified whenever a fastness property of a dyeing is determined. In addition, fastness testing methods are under constant revision and those involved in colour fastness evaluation must be aware of the latest developments.

24.3.2 Standard depths of shade

The fastness of a dyeing to a given agency such as washing or light normally depends on the depth of shade. We have already seen that light fastness is higher for deeper rather than paler shades. This is so because the effect on the colour of photochemical fading of a given number of dye molecules is more pronounced the fewer the initial number of molecules. On the other hand, washing fastness is
usually inferior for deeper shades since the concentration gradients driving diffusion between the fibre and the washing solution are much higher when more dye is present in the fibres.

Since dyeings vary in depth, it is common practice to determine a fastness property at a standard colour depth. Variations in the dye content of commercial dyes do not allow standardisation of colour depth of a dyeing on the basis of the % owf of the dye. The ISO recommends a series of reference colours in 20 different hues ranging from yellow to black. The standard depth is called the standard 1/1 depth. Black and navy are only available in two depths. For the other colours, other depths include the 2/1 standard depths, which are twice as deep as the 1/1 standards, or the 1/3, 1/6, 1/12 or 1/25 standard depths that are successively paler. For fastness testing, a dyeing is produced having a hue and strength matching as closely as possible one of the standard colours.

24.3.3 Methods of assessment

The visual assessment of colour change caused by a particular agency (apart from light fading) is assessed as the colour contrast between the original and tested sample using a Grey Scale. This consists of five pairs of carefully standardised, contrasting, non-glossy grey samples. One sample of each pair is always the same medium grey with a Y tristimulus value of 12 (10° standard observer, specular reflection included). The other halves vary from a pale grey (grade 1) to the same standard grey (grade 5). The CIELAB colour difference value (ΔEab*; Section 22.1.1) between the standard grey and the five greys in the scale varies from 0 (grade 5, standard grey) to 13.6 (grade 1, pale grey). The Grade 4 sample has a colour difference of 1.7 and the colour differences between the pairs of the following Grades 3, 2 and 1 form a geometric progression being two (3.4), four (6.8) and eight times (13.6) this value (Table 24.1).

After a fastness test, the original and tested samples are placed side by side along with the Grey Scale and the extent of colour loss evaluated. The fastness rating will be that of the pair of grey samples that show the same difference in contrast as the original and tested samples. Thus, grade 5 represents no visible change of contrast arising from the test and excellent fastness. The samples are compared in front of a uniform grey background that is midway between grade 1 and 2 of the Grey Scale and preferably exposed at 45° to light from the north (south in the southern hemisphere). The illumination and viewing conditions for this visual assessment are carefully standardised. It is possible to assign
intermediate grades for sample colour contrasts between those of two adjacent
Grey Scale pairs. These are expressed as 3\textendash}4, for example. This allows nine
fastness grades from 1 to 5, inclusive (Table 24.1). Because this is useful, some
Grey Scales have nine pairs of contrasting grey samples including those for the
intermediate grades. The report on the colour fastness must also note any change
of hue or saturation that occurs on testing since a variation in these on exposure
of the dyeing are quite common.

In addition to the Grey Scale for colour change, there is a similar scale for
staining of white fabric in fastness tests such as washing. This has five pairs of
samples. One is always white (Y > 85) and the other a grey of increasing depth
from white (grade 5) to medium grey (Grade 1) in steps of increasing contrast.
The CIELAB $\Delta E^*_{ab}$ value for the pairs varies from 0 (Grade 5, white) to 34.1
(grade 1) in steps that are about one, two, four or eight times a value of 4.3 (Table
24.1). For the assessment of staining, a piece of white material is stitched to the
dyed fabric being tested. Assessment of the degree of staining is again based on
matching the colour contrast between the original white material and the stained
fabric with that of the appropriate pair of grey\textendash}white samples of the Grey Scale for
staining. The examination conditions are those used for the assessment of colour
change, given above. Again, samples with intermediate contrasts can be
evaluated. A nine grade Grey Scale is also available with samples for the four
intermediate grades (4\textendash}5, 3\textendash}4, 2\textendash}3 and 1\textendash}2).

A chromatic transference scale is also available from the AATCC. This consists
of five rows of coloured samples in five different hues plus grey (corresponding to

### Table 24.1 Relation between CIELAB colour differences for fading and
staining and the Grey Scale fastness grade

<table>
<thead>
<tr>
<th>CIELAB colour difference for fading</th>
<th>Colour fastness grade</th>
<th>CIELAB colour difference for staining</th>
<th>Grey Scale fastness grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.40</td>
<td>5</td>
<td>&lt;1.10</td>
<td>1</td>
</tr>
<tr>
<td>0.40\textendash}1.25</td>
<td>4</td>
<td>1.10\textendash}3.25</td>
<td>2</td>
</tr>
<tr>
<td>1.25\textendash}(1.7)\textendash}2.10</td>
<td>4</td>
<td>3.25\textendash}(4.3)\textendash}5.15</td>
<td>3</td>
</tr>
<tr>
<td>2.10\textendash}2.95</td>
<td>3</td>
<td>5.15\textendash}7.25</td>
<td>4</td>
</tr>
<tr>
<td>2.95\textendash}(3.6)\textendash}4.10</td>
<td>3</td>
<td>7.25\textendash}(8.0)\textendash}10.25</td>
<td>5</td>
</tr>
<tr>
<td>4.10\textendash}5.80</td>
<td>2</td>
<td>10.25\textendash}14.45</td>
<td></td>
</tr>
<tr>
<td>5.80\textendash}(6.8)\textendash}8.20</td>
<td>2</td>
<td>14.45\textendash}(16.9)\textendash}20.45</td>
<td></td>
</tr>
<tr>
<td>8.20\textendash}11.60</td>
<td>1</td>
<td>20.45\textendash}29.05</td>
<td></td>
</tr>
<tr>
<td>&gt;11.60</td>
<td>1</td>
<td>&gt;29.05</td>
<td></td>
</tr>
</tbody>
</table>
the whole number grades of the Grey Scale for staining). The row of hues corresponding to grade 5 for staining show almost no colour, whereas the hues of row 1 are all relatively deep. The use of this kind of scale should give the same numerical assessment of staining as the Grey Scale. Tables 24.2 and 24.3 give verbal descriptions of the various fastness grades.

**Table 24.2 Description of the normal fastness grades**

<table>
<thead>
<tr>
<th>Fastness grade</th>
<th>Shade change of tested sample</th>
<th>Fastness</th>
<th>Staining of adjacent white sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 5</td>
<td>No change</td>
<td>Excellent</td>
<td>No staining</td>
</tr>
<tr>
<td>Grade 4</td>
<td>Slight loss in depth</td>
<td>Good</td>
<td>Very slight staining</td>
</tr>
<tr>
<td>Grade 3</td>
<td>Appreciable loss</td>
<td>Fair</td>
<td>Moderate staining</td>
</tr>
<tr>
<td>Grade 2</td>
<td>Significant loss</td>
<td>Poor</td>
<td>Significant staining</td>
</tr>
<tr>
<td>Grade 1</td>
<td>Great loss in depth</td>
<td>Very poor</td>
<td>Deep staining</td>
</tr>
</tbody>
</table>

**Table 24.3 Description of the light fastness grades**

<table>
<thead>
<tr>
<th>Fastness grade</th>
<th>Degree of fading</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 8</td>
<td>None</td>
<td>Outstanding</td>
</tr>
<tr>
<td>Grade 7</td>
<td>Very, very slight</td>
<td>Excellent</td>
</tr>
<tr>
<td>Grade 6</td>
<td>Slight</td>
<td>Very good</td>
</tr>
<tr>
<td>Grade 5</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>Grade 4</td>
<td>Appreciable</td>
<td>Moderate</td>
</tr>
<tr>
<td>Grade 3</td>
<td>Significant</td>
<td>Fair</td>
</tr>
<tr>
<td>Grade 2</td>
<td>Extensive</td>
<td>Poor</td>
</tr>
<tr>
<td>Grade 1</td>
<td>Very extensive</td>
<td>Very poor</td>
</tr>
</tbody>
</table>

With the general availability of computerised spectrophotometers, the determination of fastness properties can now be based on the quantitative measurement of colour change of the tested samples. This is desirable because visual examination based on comparison of the degree of contrast with a Grey Scale can result in variations in assessment among different observers. The problem is to find an acceptable method of converting the differences in the colour coordinates between the original and exposed samples into a fastness rating corresponding as closely as possible to the average visual rating obtained using the
Grey Scale for change in colour, or for staining. This is a field of active research and more than a half dozen systems have been proposed and evaluated.

One relatively simple approach is to measure the CIELAB or CMC colour difference (Section 22.1.3) and determine the fastness grade from the $\Delta E^*_{ab}$ values of the ISO colorimetric standardisation of the Grey Scale for colour change (Table 24.1). The current ISO standard for fastness determinations is somewhat different and is based on a Swiss standard. It was selected because it gives better prediction of the light fastness grades of the blue wool standards (Section 24.3.4). This method is based on measurement of CIELAB hue angle ($h_{ab}$), chroma ($C^*_{ab}$) and lightness ($L^*$) of the original and the tested samples, calculation of a modified colour difference, and from this determination of the fastness grade.

There are also two Japanese methods based on determination of brightness, colour depth and hue, defined in terms of Munsell (Section 21.7) or CIELAB coordinates. These methods compute the fastness grade directly without reference to the colour differences specifying the Grey Scale for colour change. Colorimetric methods for assessing the degree of staining have also been developed and tested. In the current ISO method, the staining grade is calculated from the colour difference between the original and stained white fabric ($\Delta E^*_{ab}$) and the lightness difference ($\Delta L^*$). Two key articles discussing these methods and their comparison have been published [4,5]. All of these calculation methods give fastness evaluations that are much less variable than visual assessments but there does not appear to be a great deal of difference between the methods.

The details of the many fastness tests are available from a variety of sources [6]. This section will concentrate only on the fastness of dyeings towards washing and exposure to light, outlining the various principles that apply.

24.3.4 Fastness to light

The evaluation of fastness to light exposure represents a special case, since eight rather than the usual five graduations are used. Fading from indoor light sources, which have negligible emission in the near ultraviolet, is much less of a problem and testing of light fastness usually refers to fastness to daylight or an equivalent artificial light source.

The rate of fading on exposure of a dyeing is sensitive to the spectral composition of the light from the source, especially the amount of ultraviolet light present, and also to the temperature and humidity of the air in contact with the samples. There are also problems with light fastness being affected by the presence
of any residual chemicals in the fibre and by chemicals in the surrounding air.
Exposure conditions are difficult to reproduce and evaluation of the degree of
fading using a standard Grey Scale is impractical. In particular, the variations in
daylight would lead to different results for successive tests on the same sample.
The evaluation of light fastness is based on the degree of fading of eight carefully
selected blue dyeings on wool whose light fastness is rated from 1 (very poor) to 8
(excellent). Each successive standard blue wool dyeing takes about twice as long
to fade to the same extent as the previous one in the series, except for the grade 7
standard, which is somewhat faster.

The samples and blue wool standards are partly covered with a card or metal
sheet and simultaneously and continuously exposed to daylight under glass but
allowing good ventilation. The frame holding the samples faces due south in the
northern hemisphere and is inclined at an angle to the horizontal about equal to
the latitude of the test location. The exposure is usually continued until the tested
and unexposed original samples show a colour contrast equivalent to Grade 4 on
the Grey Scale for colour loss. Part of the exposed portions of the dyeings may
then be covered and exposure continued until a colour contrast equivalent to
grade 3 on the Grey Scale is reached. For samples of very high light fastness,
testing is stopped if the Grade 7 blue standard has faded to a colour contrast of 4
before the sample exhibits obvious fading, in which case its fastness is graded as 8.
The light fastness of a dyed sample is the number of the blue wool standard that
has faded to the same extent as the exposed area of the sample. It is also common
practice to evaluate the light fastness relative to the blue wool standards for the
condition of a just perceivable colour difference between the exposed and original
dyed samples.

Daylight testing is slow for dyes with good light fastness. Accelerated test
methods in which artificial light sources promote fading are widely used,
particularly using xenon arc lamps. The results obtained often differ from those
obtained on exposure to daylight since the spectral distribution of the light from
the artificial source will be quite different from that of daylight, depending upon
the type of light source used and its operating conditions. The rate of fading by
daylight and artificial sources also depends upon the temperature and particularly
on the effective humidity of the air in contact with the exposed samples and the
effects of these variables are different for different dyes. The measurement of the
humidity of the air in contact with the samples is difficult to determine because
the temperature at the sample surface is higher than that of the ambient air
because of the absorption of the radiation. Fading lamps have high emission

...
intensities to give fairly rapid fading relative to normal daylight. The fabric samples are protected from excessive ultraviolet and infrared radiation. The effective air humidity can be evaluated using an azoic combination on cotton fabric produced from CI Azoic Diazo Component 13 and CI Azoic Coupling Component 4. Its light fastness grades range from 6–7 down to 3 as the relative humidity of the air varies from 0 to 100%. In a light fading machine, the air humidity is usually controlled so that the above standard azoic dyeing has a light fastness of 5 (40% relative humidity).

The standard method for light fastness recommended by the AATCC involves nine blue wool standards called ‘L2’ to ‘L9’. These nine standards consist of blue wool yarn dyed with CI Mordant Blue 1 (Grade L2, very poor light fastness) or CI Solubilised Vat Blue 8 (Grade L9, excellent fastness). The intermediate blue standards from L3 to L8 are mixtures of blue yarns dyed with these two dyes, the higher grades having a greater proportion of the vat dyed yarn so that each grade is about twice as fast as the previous one. The test procedure involves determination of the extent of exposure to light required to produce fading to Grade 4 on the Grey Scale for colour loss of their ‘L4’ blue wool standard dyeing. This exposure is designated as 20 AATCC fading units ($\Delta E_{ab} = 1.7$). To fade successive blue wool standards to a Grade 4 level on the Grey Scale for colour loss requires doubling the exposure in terms of the number of AATCC fading units. The results correlate fairly well with those of the ISO light fastness method.

24.3.5 Fastness to washing

Fastness to washing is one of the properties of a dyeing of importance to the consumer. Most washing tests are carried out at relatively low temperatures for short times and the dye–fibre system does not come to equilibrium. The desorption of the dye from the fibre is therefore influenced mainly by kinetic factors.

There is a variety of testing procedures. To some extent, these have arisen because:
(1) washing conditions vary from one country to another;
(2) the method depends upon the use of the material being washed;
(3) to evaluate repeated washing, accelerated test methods are used.

The situation becomes even more complicated when one considers that the degree of fading of a dyeing on washing depends upon the following factors, all of which must be standardised:
(1) the temperature. This may range from 20 to as high as 95 °C;
(2) the type and amount of detergent that is added to the washing bath. This may or may not include alkalis, phosphates, silicates, optical brightener, chlorine or peroxide bleach. In many testing procedures, a standard detergent formulation is required;
(3) the extent of mechanical action. This can be varied by changing the agitation speed in a washing machine or by adding steel ball bearings to the revolving test bath;
(4) the washing liquor-to-goods ratio and the hardness of the washing water;
(5) the rinsing, drying or pressing methods used to restore the sample after the test.

Most testing standards include several tests of increasing severity. These tests have successively higher washing temperatures, increasing wash times, possibly decreasing liquor ratios and the more severe tests may have higher levels of mechanical agitation as well as small amounts of chlorine bleach in the wash.

Some tests are carried out in typical domestic washing machines, others use a wash wheel. The latter consists of capped 2.0 l steel beakers, containing the solution and sample, fastened onto the periphery of a wheel that can be rotated around its horizontal axle through a temperature controlled water bath with periodic reversal of the direction of rotation. A standard size sample of the fabric to be tested is usually stitched between two samples of white fabric, one of the same and the other of a different type of fibre. To assess staining, it is now common practice for one of the white fabric pieces to be composed of several bands of different fibres. After the test, the degrees of colour change and staining of the white fabrics are assessed with the appropriate Grey Scales or by colorimetric measurements. The conditions for the ISO test for colour fastness to domestic washing and commercial laundering are given in Table 24.4. These tests are carried out using a wash wheel with a 5 g l⁻¹ standard soap solution at a liquor ratio of 50:1.

As for other types of fastness testing, procedures for washing fastness assessment are in constant evolution. Some of the current concerns include the effect of residual chlorine in tap water on the fading of cotton fabrics dyed with some sensitive reactive dyes and the effect on the fabric colour of repeated washing with solutions of domestic detergents involving activated hydrogen peroxide [7].
24.3.6 Other fastness properties

There are a large number of procedures for testing the fastness of dyeings to other conditions besides exposure to light and washing. Some of these tests are rather specialised and require specific equipment. Some are of general application (fastness to rubbing), others are used for testing fabrics for specific uses (fastness to chlorine water) or that must undergo further processing (fastness to mercerisation).

The fastness test to crocking or rubbing, for example, is widely used on a variety of fabrics to evaluate the transfer of surface dye from the test fabric to a piece of white cotton against which it is rubbed. In the dyehouse, the extent of removal of surface colour after soaping the dyeing is often rapidly assessed by rubbing a sample of the wet fabric against a piece of dry cotton. For a more quantitative and reproducible assessment, however, a crockmeter is used. This is a device in which the area of contact, the time of abrasion and the applied force on the fabric can be controlled. The test can be carried out under dry or wet conditions. The fastness to perspiration is a specific test in which a fabric sample stitched between two layers of white fabric is treated with solutions containing the amino acid histidine, which simulate natural perspiration, firstly at room temperature and then at body temperature for 4 h.

There is a multitude of different tests. The book *Methods of Test for Colour Fastness of Textiles and Leather* published by the SDC [6] is essential for anyone working in this field.

24.4 IDENTIFICATION OF DYES ON THE FIBRE [8]

The identification of the actual colorants present in a dyed textile material is a complex task and infrequently realised. The analysis is usually complicated by the

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**Table 24.4 Conditions of the ISO washing fastness tests**

<table>
<thead>
<tr>
<th>Test</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Steel balls</th>
<th>Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 1</td>
<td>40</td>
<td>30</td>
<td>0</td>
<td>Soap</td>
</tr>
<tr>
<td>ISO 2</td>
<td>50</td>
<td>45</td>
<td>0</td>
<td>Soap</td>
</tr>
<tr>
<td>ISO 3</td>
<td>60</td>
<td>30</td>
<td>0</td>
<td>Soap + Na₂CO₃</td>
</tr>
<tr>
<td>ISO 4</td>
<td>95</td>
<td>30</td>
<td>10</td>
<td>Soap + Na₂CO₃</td>
</tr>
<tr>
<td>ISO 5</td>
<td>95</td>
<td>240</td>
<td>10</td>
<td>Soap + Na₂CO₃</td>
</tr>
</tbody>
</table>

*Note: The conditions for ISO 5 are for use in the dyehouse.*
presence of several dyes, often of different chemical types. It is thus usually impossible to identify the individual dyes in a dyeing, but the dyeing class they belong to can often be ascertained.

A number of procedures have been published [9], the most common being that of Clayton once published by the SDC [10]. Other are listed in the references. These schemes are quite lengthy but by a process of careful observation, and elimination of possibilities, the dyeing classes of dyes present in a textile material can usually be successfully determined. The usual procedure is first to identify the types of fibres present in the sample. For example, if cotton is absent this considerably reduces the number of dye types that might be present. Alternatively, the presence of polyester would be a good indication that it may be dyed with disperse dyes. The dyed sample may then be heated with various chemical solutions or solvents and any reversible or irreversible colour change noted. Tests for reversible reduction and re-oxidation, and the accompanying colour changes may provide evidence for the presence or specific chemical classes of dyes such as anthraquinone or Indigoid types. Sulphur dyes are easily recognised by the emission of hydrogen sulphide when heated with acidic reducing agents. Stripping of the colour is attempted by heating with various solutions. If this is successful, the coloured solution may be tested by means of a dyeing trial using different fibres. The presence of certain types of dyes can also be detected by the metals they contain such as chromium, copper or nickel. A sample may be ashed (decomposed by heating in air and burning off the carbon formed) and the residue of oxides tested for such metals.

24.5 SEPARATION OF DYES BY CHROMATOGRAPHIC TECHNIQUES [11]

24.5.1 Introduction

Chromatography is a technique used for the separation of the components of a mixture of substances. In many cases, the qualitative separation is followed by quantitative analysis. A Russian botanist, Michael Tswett, first used this technique. He was able to separate the coloured pigments extracted from plants. A solution of the plant pigments was placed on top of a glass column containing a packing of calcium carbonate particles in a solvent. The solvent was then gradually drained from the column bottom while being replaced with fresh solvent at the top. The coloured pigments passed down the column and separated into a
series of coloured bands. It was this separation of coloured compounds that led to
the use of the name chromatography after the Greek word for colour. Today, the
technique is applicable to all kinds of ionic and organic compounds, coloured or
otherwise. In the case of non-coloured compounds, various methods are used to
detect the position of each substance during the separation or as it is eluted
(washed) from the column.

All chromatographic methods use a stationary and a mobile phase, the two
being immiscible. The function of the stationary phase is to interact with the
substances to be separated so that their transport through the medium by the
mobile phase is retarded. This interaction may involve:

(1) reversible adsorption on the surface of a solid. Under appropriate conditions a
substance will tend to be adsorbed when its concentration in the mobile
phase is relatively high but will desorb back into the mobile phase when its
concentration in this phase is low. Thus, desorption occurs once the more
concentrated solution of the substance has flowed further along the column
and been replaced by a more dilute solution;

(2) partition between the mobile solvent phase and another immiscible liquid
supported on the stationary solid phase. Such partition is a consequence of
differing solubilities in the mobile and stationary liquids. In this case, the
separation can be considered to consist of multiple liquid–liquid extractions
of the various substances. Separation is possible when the substances have
different values of their partition coefficients;

(3) reversible ion exchange between the mobile and stationary phases. In this
case, the solid stationary phase has either cationic or anionic sites capable of
binding ions of the opposite charge originally present in the mobile phase.

In many respects, the molecular interactions involved are similar to those that
apply during dyeing processes. The components of a mixture are separated because
of their different retentions by the stationary phase. In Tswett’s separation of plant
pigments, the different components were adsorbed on the surface of the calcium
carbonate particles to different degrees. Those that were only weakly adsorbed
travelled along the column quite rapidly and were eventually eluted from it. The
more strongly adsorbed components were retained to different degrees by the
adsorption process and their separation resulted in a series of coloured bands at
different positions along the column. The longer a component remained adsorbed
on the adsorbent surface, the shorter distance it travelled along the column in the
mobile phase.
The stationary phase may consist of particles packed into a column or forming a plane, thin sheet such as the fibres in a sheet of paper or a layer of adsorbent coated onto a glass plate. In column chromatography, the flow of the mobile phase is either vertically downward under the influence of gravity, as in Tswett’s separation of plant pigments (Figure 24.3), or it results from the initial pressurisation of the mobile phase entering the column. In planar chromatography on a sheet, the liquid mobile phase is transported through the stationary phase by capillary action, sometimes downward assisted by gravity, and often upward against the gravitational attraction.

The application of chromatography to the separation of dyes is relatively simple because the colours of the components are readily visible at all times during the separation. We will briefly examine the five major chromatographic methods used for dye separations. These are classical column, thin layer, ion exchange, high-pressure liquid and paper chromatography. These techniques are valuable for testing the homogeneity of dye samples, separating mixtures of dyes, examining their chemical reactions, and in some cases for dye identification.

24.5.2 Adsorption chromatography

The conditions for adsorption chromatography are those described above for the
separation of plant pigments. Separation is achieved by the selective adsorption of the substances by the solid stationary phase. The most common adsorbents are finely powdered alumina (Al₂O₃) or silica gel (SiO₂). These are available with different adsorptive capacities depending upon their degree of hydration. The initial mobile phase is usually a non-polar or slightly polar solvent. The adsorbed substances will spend more time on the adsorbent surface, the higher their polarity and the lower the polarity of the mobile phase. The separation is thus aided by gradually increasing the polarity of the developing solvent, or eluent, and depends upon the different components of the mixture having different interactions with the adsorbent phase as the composition of the mobile phase changes.

One of the classic separations in dye chemistry was the separation of the geometrical isomers of azobenzene. When a solution of azobenzene in benzene is exposed to light, the more stable trans isomer (1, in Figure 24.4) is partially converted into cis-azobenzene (2). The two isomers can be separated on an alumina column using benzene as the eluent. The polar cis-azobenzene is more strongly adsorbed by the alumina and the non-polar trans-azobenzene passes through the column.

Figure 24.4 Trans-azobenzene (1) and cis-azobenzene (2)

This type of column chromatography is useful for separations on both the analytical and preparative scales. Dyes can be analysed using 2 mm glass tubes containing a small amount of adsorbent and mere milligrams of dyestuff. Purification of dyes for research purposes is possible using large diameter tubes packed with adsorbent. Adsorption chromatography is more valuable for non-ionic dyes such as disperse dyes. Polar ionic dyes are very strongly adsorbed by activated alumina and silica gel. It is possible, however, to separate these types of dyes using less powerful adsorbents such as cellulose powder, calcium carbonate or hydrated alumina and eluents containing water.
24.5.3 Thin layer chromatography [12]

Thin layer chromatography (TLC) allows separations based on selective adsorption but, in this case, the adsorbent is in the form of a thin layer spread on a flat surface such as a glass or plastic plate. The adsorbent is usually a hydrated silica gel or alumina mixed with a binder to provide good cohesion of the layer and adhesion to the supporting glass or plastic sheet. The substances to be separated are placed onto the adsorbent layer by spotting their concentrated solution in a volatile solvent onto a small zone about 2 cm from the bottom of the plate. Once the application solvent has evaporated, the bottom end of the plate where the spot is located is placed in a shallow layer of the developing solvent in a closed container saturated with the solvent vapour. The solvent rises up through the thin layer of adsorbent by capillary action and passes through the small zone where the substances to be separated are located. Polar compounds that are strongly adsorbed only travel a short distance as they spend little time in the rising mobile phase. The less strongly adsorbed compounds tend to move along with the rising solvent and thus travel further (Figure 24.5).

When satisfactory development has been achieved, the plate is allowed to dry and the position of each compound noted. The positions of coloured dyestuffs are obvious. In the case of colourless compounds, their location is usually detected by examination of the plate under an ultraviolet lamp. The silica gel for TLC usually

\[ R_f(C) = \frac{x}{y} \]

Figure 24.5 Thin layer chromatography
contains a fluorescent chemical and under a UV lamp the adsorbed compounds show as dark spots against the fluorescent background. Alternatively, the plate is sprayed with a fine mist of chemical solution (indicators, oxidants, and so on), which converts the colourless compounds into coloured ones. Each substance is assigned a value of $R_f$, the ratio of the distance it travelled and the distance the solvent front has moved (Figure 24.5).

The secret for successful TLC is to apply the minimum quantity of the mixture to be separated. This usually leads to minimum dispersion of the spot of compound, and easy evaluation of the $R_f$ value. It also avoids the problem of 'tailing', where each compound moves along the plate but leaves a tail behind it that obscures the spots of other compounds. In order to identify dyes by comparison of their $R_f$ values, it is usual to run the unknown dye along with a known sample. This is necessary because the $R_f$ value for a particular dye is quite sensitive to changes in the separation conditions, particularly the adsorptivity of the alumina or silica gel that varies with the degree of hydration. Two spots of the same hue with the same $R_f$ value provide an indication, not a proof, that they may be identical dyes. Additional proof can be obtained by scratching the coloured spots from the TLC plate, extracting the dyes and comparing other properties of their solutions such as their spectra.

In two-dimensional thin layer chromatography, a separation is carried out with a first developing solvent along one edge of the plate. After development and drying, the edge of the plate closest to where the first separation occurred is placed in the developing tank but containing a different developing solvent and a second separation is achieved at right angles to the first. This provides a high-resolution separation. It is applicable, for example, to the separation of amino acids, but has not been much used in dye chemistry.

TLC is valuable for the separation of mixtures of dyes and for establishing their homogeneity. It is quite easy for example to demonstrate that two dyes with the same Colour Index number contain different shading dyes. For the separation of disperse dyes, a solution of the dyes in acetone or dichloromethane is spotted onto a silica gel coated plate and development is carried out using for example a 9:1 v/v benzene/acetone or 19:1 v/v chloroform/methanol mixture. Disperse dyes can be extracted from dyed polyester and nylon using dimethylsulphoxide or dimethylformamide, followed by evaporation under vacuum and TLC analysis. The method is also useful for analysis of various types of reactive dyes. For example, TLC of typical vinyl sulphone reactive dyes with a 2:2:1 v/v butyl
acetate/acetic acid/water mixture on a silica gel coated plate shows the presence of
the sulphatoethyl, hydroxyethyl and vinyl sulphones in order of increasing $R_f$.

24.5.4 Ion exchange chromatography
Ion exchange chromatography (IEC) is similar to adsorption chromatography except that the substances that are retained are ionic and have the opposite charge to the ionic sites present in the solid stationary phase. The separation is achieved using a column packed with an ion exchange resin similar to the types used for water treatment (Section 8.3.2). This technique is particularly useful for the purification of small amounts of ionic dyes and for the separation of various sulphonated intermediate compounds used in dye synthesis.

24.5.5 Paper chromatography [13]
In paper chromatography (PC), the stationary phase is a paper sheet, the mobile phase flowing either downward under the force of gravity, or upwards by capillarity. The surfaces of the cellulose fibres are hydrated with water molecules and separation is achieved by differences in the partition of the compounds between this surface and the more hydrophobic developing solvent. The solvent always contains a small amount of water to maintain hydration of the cellulose surface. The fibres in chromatography paper have often been quite severely modified during paper manufacture. The DP is much lower than that of cotton and a number of functional groups are present from hydrolysis and oxidation reactions that occur during paper manufacture. These groups certainly influence the separation behaviour of ionic dyes. Treated papers are available that are cationic, anionic or hydrophobic in character, even though partition between the hydrated cellulose surface and the mobile phase is still the major separation mechanism. Again, after development, each substance is characterised by its $R_f$ value.

Vat dyes can be separated using hydros and tetraethylenepentamine as the mobile phase in an inert gas atmosphere at room temperature or using an aqueous hydros, NaOH and pyridine solution at higher temperature. PC has also been used to examine the formation of vinyl sulphone reactive dyes from their sulphatoethyl precursors in alkaline solution as well as their subsequent hydrolysis. In this case, a mixture of water, 85% formic acid, ethanol and butanol in a 15/15/25/50 volume
ratio is used as the developing solvent. For this developing medium, the more ionic sulphatoethyl form prefers the hydrated cellulose surface and thus has a low \( R_f \) value and the less ionic vinyl sulphone prefers the more hydrophobic mobile phase and has a higher \( R_f \) value. The \( R_f \) of the hydroxyethyl form is somewhat lower than that of the vinyl sulphone because of its ability to hydrogen bond to the hydrated cellulose and separation of the two is quite easy. The acidic medium minimises reaction of the vinyl sulphone with water and with the cellulose. The \( R_f \) values of hydrolysed reactive dyes can be correlated with their substantivity for cellulose and thus their ease of washing-off after dyeing cellulosic fibres.

TLC and PC are particularly useful techniques for dye analysis because they can be carried out rapidly on a small scale.

24.5.6 High pressure liquid chromatography [14]

In high pressure liquid chromatography, the substances present in the mobile liquid phase interact with an immiscible liquid adsorbed or bonded onto the surface of solid particles or coated onto the walls of a capillary tube. The immobile liquid phase is often a liquid polymer that is insoluble in the eluting solvent. The various compounds have different solubilities in the stationary and mobile liquid phases and are partitioned between them to different extents. In this way, a compound that is very soluble in the stationary liquid phase will be retained in the column whereas one that is more soluble in the moving solvent will be transported along the column and reach the end sooner.

The liquid mobile phase that passes through the packed column or capillary tube is generally under considerable pressure in order to achieve a practical flow rate. As each dye is eluted from the column after separation, the solution passes through a spectrophotometer cell where its absorption of visible light of the appropriate wavelength allows its detection. For the separation of complex mixtures, the composition of the eluent can be gradually changed to modify its polarity. Alternatively, separation can be achieved using a pressurised mobile liquid phase and a solid adsorbent. This is a situation analogous to column or thin layer chromatography but is more versatile because of the ease of programming a wide gradient of solvent polarity. A wide variety of liquid chromatographic techniques are available and this has become an invaluable research tool in dye chemistry.
REFERENCES

6. Methods of Test for Colour Fastness of Textiles and Leather (BS1006:1990), available from the SDC.
CHAPTER 25

Textile finishing

25.1 INTRODUCTION

The operations carried out in a textile finishing mill include:
(1) preparation, in which the goods are scoured and bleached in readiness for finishing;
(2) dyeing or printing;
(3) mechanical finishing procedures, usually performed on dry material;
(4) thermal processes including drying and heat setting;
(5) wet finishing processes in which the goods are treated with solutions of appropriate chemicals and subsequently dried.

Textile finishing involves treating a textile material in such a way that the product has the desired aesthetic and functional properties required for its intended use and therefore has greater market value. The desired properties may include the fabric’s dimensions and their stability, its weight, drape, appearance, softness and handle, as well as any required functional properties such as resistance to creasing, flames, water, oil, dirt or bacteria. Textile finishing is therefore an extremely diverse field involving an extensive range of chemicals. This chapter will only provide a brief survey.

Much of this diversity arises from the many different properties that are possible using various finishing techniques, even for the same fabric. The degree of permanency of a particular finish for a fabric depends on its intended use. For example, a crease-resist finish for a cotton/polyester shirting fabric must obviously have a much higher resistance to repeated washing than a flameproof finish used for theatre curtains. Some temporary finishes are, however, useful for facilitating the assembly of a material into a final article. The chemicals used may weight the fabric to make it easy to slide and handle, or allow smooth penetration of a sewing needle to minimise needle breakages.

The majority of chemical finishing methods are used for fabrics containing cellulosic fibres. Before 1950, washing cotton fabrics invariably resulted in severe creasing and shrinkage. Hot pressing or ironing of the washed article, under damp...
conditions with stretching, produced a smoother appearance and the desired shape. Materials made from synthetic fibres, on the other hand, can be washed and spun or drip dried with virtually no creasing or change in dimensions. At worst, a light ironing might be needed for a completely smooth appearance. The development of new chemical finishes for crease-resist cotton began in the 1950s, once the new synthetic fibres began their rapid ascent in the marketplace. Cotton has remained the major textile fibre because of these chemical finishing techniques, its success aided by blending it with polyester staple to produce fabrics with even better performance.

Anyone involved in textile coloration must be aware of the influence of preparation processes on the dyeing behaviour of the fibres. Poorly prepared goods will be difficult to wet and to colour evenly. Equally important, the colourist must also know how the finishing methods will influence the final colour of the goods and their colour fastness properties. Without this information, the colourist will not be able to satisfy a client's colour and fastness specifications.

### 25.2 MECHANICAL FINISHING METHODS

Most mechanical finishing processes modify the appearance and handle of a fabric. Table 25.1 lists some typical mechanical finishing operations and their objectives. These processes are used on a variety of fabrics containing different types of fibres. Their major effect is to modify the fabric surface, usually either to make it smoother, or to raise a pile. Both effects can cause a change in the perceived colour of the material because they modify the reflection of light from the fabric surface.

Napping, or raising, and calendering are the most common mechanical finishing methods for fabrics. In napping or raising, the fabric passes over rapidly rotating rollers covered with thousands of fine steel wires projecting from their surface. The points or small hooks on the wire tips break fibres in the yarn surface and pull out their ends, thus producing the characteristic soft fluffy surface or nap. This gives a thicker, warmer material since the trapped air is a good thermal insulator. The penetration of the pins into the surface yarns must be limited to avoid excessive abrasion and weakening of the yarns. The presence of a lubricant helps to minimise fibre damage. Other related mechanical processes used on fabrics with a nap or pile include brushing and shearing (Table 25.1).

In calendering, the fabric passes between heavily loaded rollers. At the nip, the high pressure exerted on the fabric flattens and smooths its surface and loosens
TEXTILE FINISHING

any yarns stuck together with finishing chemicals. The fabric becomes softer and more flexible. By wrapping the fabric through a series of calender rollers, the face in contact with a roller alternates from one roller to the next. The rollers may have identical or different surfaces, such as all steel, or alternating steel and cotton-covered rollers. In some cases, the metal rollers may be heated. To increase the lustre of a fabric, the linear speed of the polished steel rollers may be much higher than that of the fabric generating a polished surface by friction. To enhance this glazing effect, the fabric may be friction-calendered after applying a solution of starch or gum and drying. These chemicals simply fill in the natural undulations of the fabric surface, increasing the smoothness and lustre. Often, relatively inexpensive natural polymers are used simply to increase the weight and decrease the flexibility of a fabric to facilitate sewing up into garments. Heated engraved rollers are used in processes similar to calendering for embossing the fabric surface. These types of finishes are often not resistant to washing unless carried out in combination with a reactive polymer such as those used for crease-resist finishing (Section 25.4.1).

One desirable characteristic of a textile material is dimensional stability. This means that the material will not easily stretch or shrink during normal use. Sections 7.3.5 and 7.4.2 discuss the shrinkage and felting of woollen articles, and the remedies for this. The elasticity and easy deformation of many knitted materials often lead to poor dimensional stability. Knitted fabrics require careful manipulation during processing to avoid their over-extension.

When cotton fibres absorb water, they swell and the fibre diameter may increase by as much as 18%, much more than the relative increase in fibre length. Viscose fibres swell even more. Water absorbed by these cellulosic fibres acts as a plasticiser. Any strain introduced during manufacture or use will invariably result

<table>
<thead>
<tr>
<th>Process</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calendering</td>
<td>Pressing and smoothing the surface of the fabric</td>
</tr>
<tr>
<td>Napping or raising</td>
<td>Breaking fibres in the yarn surface and raising a pile</td>
</tr>
<tr>
<td>Brushing</td>
<td>Laying the pile in the same direction</td>
</tr>
<tr>
<td>Shearing</td>
<td>Cutting the pile fibres all to the same length</td>
</tr>
<tr>
<td>Compressive shrinking</td>
<td>Compressing the fabric to the dimensions it would have after shrinkage caused by washing</td>
</tr>
</tbody>
</table>
in shrinkage on wetting because the absorbed water allows the cellulose chains to move to relatively strain-free positions. To avoid this, some cotton fabrics undergo a treatment called compressive shrinkage (e.g. Sanforising). The material is compressed to the dimensions it would have after relaxation by washing. In one method, the humid fabric is firmly held against the outer surface of a thick rubber belt which has been stretched by passing it around a small diameter roller. As the rubber belt leaves the roller, the stretched surface relaxes and compresses the fabric held against it in the warp direction. The degree of compressive shrinkage is greater, the smaller the diameter of the roller stretching the belt surface.

25.3 THERMAL FINISHING PROCESSES

Drying is by far the major thermal process for all textile goods. During manufacture of a fabric, there may be as many as three drying operations. These contribute significantly to the total cost of production.

For fabrics, drying in a tenter frame is common. The fabric selvages are either held by clips, or set onto small vertically oriented pins, mounted on horizontal continuous chains running alongside the selvages. The chains run continuously down each side of a hot air drying oven and back to the start. By increasing the distance between the chains, the two edges of the fabric can be gradually pulled apart so that the fabric dries at the required final width. When using pins, it is possible to overfeed the fabric onto the pins at a speed slightly above that of the chains. In this way, some lengthways shrinkage is possible without producing undue tension in the fabric.

The hot air for drying is usually generated by heat transfer from steam-heated pipes, or from the combustion of gas. To improve the efficiency of heat transfer to the wet web, the circulating hot air often impinges on the fabric surface at relatively high speeds from appropriately placed slots or jets. A tenter frame usually has a series of independently operated sections so that the temperature in each section can be controlled.

Fabrics are also dried by passage over a series of smooth, steam-heated metal cylinders. The fabric face in contact with the heated surface alternates from one cylinder to the next. The initial cylinders often have a lower temperature than the later ones to provide more gradual heating and drying of the goods. This avoids undue migration of unixed chemicals and their deposition on the heated metal surface. Drying on hot cans smoothes the fabric surface giving a just-pressed appearance. In the hot flue dryer, the fabric passes in vertical loops through a hot
air chamber guided by a series of rollers. Again, to increase drying efficiency, hot air from jets impinges on the fabric surface at high speed. The festoon dryer is useful when fabric must not be under tension. The fabric passes through the hot air chamber in long loops that hang from a series of moving bars.

The drying of yarn packages in hot air is particularly inefficient unless the air passes through the packages. Despite their expense, microwave and radio frequency dryers are becoming more popular. The electromagnetic radiation is able to penetrate into the wet package interior to effect uniform drying and the rate of heating drops sharply once all the water has evaporated so that over-drying is avoided (Section 12.3.2).

Thermal drying of a dyed material may cause a slight change in colour related to changes in the fabric surface and possibly to some thermal instability of the dyes present. The perceived colour is often a function of the final humidity and temperature of the goods. Hot air for drying is frequently generated by burning gas and circulating the combustion gases into the drying chamber. A gas flame is sufficiently hot that a low concentration of nitrogen oxides can develop from reaction of oxygen and nitrogen in the air. Oxides of nitrogen are effective oxidising and diazotising agents that rapidly fade the colours of sensitive dyes and modify finishing chemicals.

Heat setting is the other major thermal process in finishing. It gives fabrics of improved dimensional stability during subsequent washing or heating. Heat setting of synthetic fibre materials is usually carried out using a tenter frame. It may be possible to dry the fabric in the first sections of the frame, and then to heat set it in the latter sections operating at higher temperature. Section 13.9.3 discusses the effects of the heat setting of nylon fabric on its dyeing behaviour. Section 7.3.4 discusses the principles and conditions for setting of wool and Sections 3.4 and 4.2.3 look at the heat setting of fabrics made from thermoplastic synthetic fibres.

25.4 CHEMICAL FINISHING OF FABRICS FROM CELLULOSIC FIBRES

Most chemical finishing methods are for fabrics containing cellulosic fibres. They give fabrics containing cotton and viscose the easy-care properties usually associated with fabrics made from synthetic fibres such as nylon and polyester. In particular, the use of crease-resist and durable-press finishes for fabrics containing cellulosic fibres is widespread. The fabrics produced have good crease resistance and dimensional stability.
Some chemical finishing methods are quite simple, such as drying a material after rinsing it in a dilute solution of a softening agent. Others are much more complex, such as the continuous pad-cure finishing of a cotton fabric to give it wash-fast flame resistance. Almost all chemical finishes give the material characteristics that it would not otherwise have. Good fastness to washing of a finish usually involves combining the functional chemicals with polymer precursors. These undergo further polymerisation in the fibre, or react with the cellulose, and by so doing anchor the functional chemicals in place.

Many such finishes are produced by the same series of operations. Firstly, continuous padding of the dry fabric impregnates the fibres with a solution or dispersion of the required chemicals (Section 10.5.2). The padding solution invariably contains a wetting agent and often a softening agent. Newer processes involve the add-on of the minimum amount of solution to minimise migration of chemicals during drying and the cost of drying. Low add-on techniques include the superficial application of the chemicals as a thin layer of foam or liquid. Alternatively, after padding of a woven fabric, vacuum slot extraction decreases the amount of solution in the material, the extract being recycled. This technique has had a considerable impact in the crease-resist finishing of cotton/polyester fabrics. Vacuum extraction leaves sufficient chemical solution in the wetted cotton fibres to promote the desired crease-resist effects but removes it from the polyester fibre surfaces where it has no beneficial influence.

After padding, the fabric is dried under conditions that minimise migration of unfixed chemicals to the yarn surfaces where water is evaporating (Section 10.5.3). Accumulation of chemicals at the yarn surfaces produces a stiffer fabric of harsh handle and inferior performance. Finally, curing of the dried fabric promotes the reaction of the chemicals together or with the cellulose.

Stringent performance requirements often make the finishing operation the key step in the production of a material with a particular functionality, such as water repellence. Many chemical finishing methods cause visible changes in the colour of a dyed fabric, or modify some of the colour fastness properties. Such effects must be known in advance to avoid off-shade and sub-standard products unacceptable to the customer.

25.4.1 Crease-resist finishes

In crease-resist finishing of cotton, the first step is padding the material with a solution containing a condensation polymer precursor and a suitable polymer-
isation catalyst. Drying and curing in a tenter frame follow this. On heating, the polymer precursor either reacts with hydroxyl groups in the cellulose to form crosslinks between adjacent polymer chains, or it polymerises in the amorphous regions of the fibres. Crosslinks between the polymer chains considerably limit the movement of the cellulose molecules so that creasing is more difficult. Such reinforcement of the fibre network improves the dimensional stability of the cotton during washing.

Crease formation in a fabric is complex. It depends on the strength of intermolecular bonds between the polymer chains of the fibre. If these are strong, as in wool, the chains will extend on bending or stretching the fibres but the strong intermolecular bonds do not break. They will pull the polymer chains back to approximately their original positions once the fibres relax. The helical molecular structure of keratin imparts a natural elasticity to wool fibres that is also significant (Section 7.3.2). Cotton fibres are much more rigid fibres. The hydrogen bonds between cellulose chains are relatively weak, particularly in the amorphous regions. On folding a cotton fabric, the hydrogen bonds break easily as the cellulose chains are stressed by bending of the fibres. New hydrogen bonds then form with the chains in their new positions and the new crease is stabilised. This is particularly easy if the cotton is wet. The crosslinks between the polymer chains, introduced during finishing, reinforce the cotton fibres and prevent the permanent displacement of the polymer chains when the fibres are stressed. It is therefore much more difficult for creases to form, or for the fabric to shrink on washing.

The types of chemicals used for crease-resist finishing of cotton are condensation products of the urea-formaldehyde type capable of forming network polymers (Figure 25.1). Urea and formaldehyde react together to form a series of hydroxymethylureas with up to four hydroxymethyl or methylol groups per urea molecule. When these types of functional compound are heated in the presence of an acid catalyst, they undergo condensation to a network polymer. The two main condensation reactions involved in polymer formation are shown in Scheme 25.1. Urea-formaldehyde and the similar melamine-formaldehyde products do not give extensive crosslinking of the cellulose. They are still used today in the finishing of viscose materials and for some cotton goods.

The thermal curing of these chemicals with an acidic catalyst considerably weakens the cellulose and makes the fabric more rigid. The decreased tear strength and the lower resistance to abrasion of treated fabrics are quite significant (Table 25.2) and depend on the quantity of chemicals used and the severity of the curing operation. The incorporation of polyester staple fibres into the yarns, along
with the cotton, compensates somewhat for this loss of mechanical resistance. If the crosslinking of the cotton is carried out under moist or even wet conditions, by a pad–batch procedure followed by washing and drying, the tear and abrasion resistance and the wet crease recovery are higher than when using thermal curing, but the dry crease recovery is somewhat less.

When crease-resist fabrics are bleached with hypochlorites, chlorine reacts with any residual amino groups in the condensation polymer. The chloroamino groups
Table 25.2 Influence of crease-resist finishing on fabric properties

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>5% Urea – CH2O 1:2/ Zn(NO3)2</th>
<th>5% DMDHEU* MgCl2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crease recovery angle (dry) **</td>
<td>150</td>
<td>260</td>
<td>265</td>
</tr>
<tr>
<td>% Loss of abrasion resistance</td>
<td>42</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>% Loss of weft tear strength</td>
<td>38</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>% Loss of weft tear strength after chlorine bleaching and ironing</td>
<td>59</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

* See Figure 25.2
** Average for creasing across the warp and weft directions

Scheme 25.2

Produced will decompose on heating under humid conditions, for example on ironing, liberating hypochlorous acid, a strong oxidising agent. Aldehyde groups in the cellulose reduce this to give hydrochloric acid. The result is severe depolymerisation of the cellulose, yellowing and weakening of the fabric (Scheme 25.2).

The newer types of methylolamino crease-resist chemicals for cotton are mixtures of cyclic methylolurea derivatives. They are mainly bifunctional compounds that give increased crosslinking of the cellulose and less polymer formation in the voids of the fibres. They have much lower chlorine retention, their tertiary amino groups being less nucleophilic. Considerable care, however, is still required to avoid excessive weakening of the cellulose fibres. Figure 25.2 shows the structures of some modern crease-resist reactants. Table 25.3 gives the recipe of a typical crease-resist finishing formula for padding a 50/50 cotton/polyester fabric indicating the role of each particular chemical.
Table 25.3 Typical composition of a crease-resist finishing bath

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Amount in the bath solution %</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMDHEU</td>
<td>6.0</td>
<td>Crosslinking agent</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>2.0</td>
<td>Acid catalyst for DMDHEU</td>
</tr>
<tr>
<td>Ethyl silicate ester</td>
<td>0.5</td>
<td>Increases resistance to abrasion and tearing</td>
</tr>
<tr>
<td>Polyethylene glycol</td>
<td>0.5</td>
<td>Softening agent</td>
</tr>
<tr>
<td>Non-ionic surfactant</td>
<td>0.1</td>
<td>Wetting agent</td>
</tr>
</tbody>
</table>

Many of these finishing treatments give fabrics that are noticeably more rigid. The solutions used therefore often contain softening agents and lubricants, as well as additives to minimise the decrease in tear strength and abrasion resistance.
Another preoccupation has been the tendency of treated cotton to liberate formaldehyde during use. This arises from the hydrolysis of the polymer crosslinks and the decomposition of residual methylolamino groups (Scheme 25.3).

\[
\begin{align*}
R-\text{NHCH}_2\text{NH}-R + \text{H}_2\text{O} & \rightarrow 2 \text{R-NH}_2 + \text{CH}_2\text{O} \\
R-\text{NHCH}_2\text{OH} & \rightarrow \text{R-NH}_2 + \text{CH}_2\text{O}
\end{align*}
\]

Scheme 25.3

For durable-press finishing, the fabric is impregnated with the same types of polymer or crosslinking precursors and dried without curing. Once the finished article has been assembled, it is hot pressed in the required shape, when crosslinking and polymerisation occur stabilising the form of the article. Formaldehyde generation is sometimes a problem if articles are stored between drying and curing. The crease-resist finishing of cotton and cotton/polyester fabrics is therefore often a compromise involving maximising the desirable properties of crease resistance and recovery and dimensional stability, while maintaining adequate mechanical and tactile properties of the fabric along with minimum chlorine retention and formaldehyde release. Some effects of crease-resist finishing on fabric properties are given in Table 25.2.

Soil-release, flame-retardant and water-repellent chemicals for fabrics containing cellulosic fibres are invariably combined with the crosslinking agents used for crease resistance. The padding bath compositions are then quite complex. The greater the number of chemicals in the bath, the higher the risk of their incompatibility.

25.4.2 Water-repellent finishes

A film of wax such as paraffin, or of a hydrophobic insoluble soap such as aluminium stearate, on the surface of a fabric containing hydrophilic fibres such as cotton will make it water-repellent. This can be achieved by treating the fabric with an emulsion of paraffin. If the wax particles in the emulsion have an anionic emulsifying agent adsorbed onto their surface, addition of a polyvalent cation such as Al\(^{3+}\) or Zr\(^{4+}\) helps to reduce the cotton's negative surface charge so that the paraffin particles are not repelled by it. The resistance of the water-repellent finish to repeated washing is improved by combination of the paraffin with a crease-resist
resin. Insoluble soaps are usually applied by firstly impregnating the fabric with a soluble sodium soap. Treatment in a second bath containing a solution of an appropriate polyvalent metal salt such as Al\(^{3+}\) precipitates the hydrophobic soap on the fibre surfaces.

A number of relatively permanent hydrophobic finishes involve reaction of the cellulose hydroxyl groups with acid chlorides, isocyanates, pyridinium salt derivatives (1, in Figure 25.3) or N-methylolamides of fatty acids (2). Some of these reactive chemicals need an organic solvent; others can be used in aqueous dispersion. These reactive chemicals give finishes that are resistant to washing and dry cleaning. Again, for cotton, they are often combined with crease-resist chemicals.

\[
\text{C}_17\text{H}_{35}\text{CONHCH}_2\text{N}^+\text{Cl}^- \quad \text{C}_17\text{H}_{35}\text{CONHCH}_2\text{OH}
\]

Figure 25.3

A film of hydrophobic chemical on the fibre surfaces provides water repellence, but the fabric still retains a reasonable degree of air permeability as the yarn interstices are still not completely filled. Total water impermeability requires a coating of rubber or polyvinyl chloride on one face of the fabric. This drastically reduces the air permeability. Because of this, water impermeable coatings are used mainly for industrial applications rather than for clothing.

The types of fabrics used for water-repellent finishes must have a smooth, compact construction with little space between the yarns. The fabric must be also be free of hydrophilic surface active agents that decrease the adhesion of the hydrophobic finish to the fibre surfaces. Water repellence increases with an increase in the proportion of hydrophobic fibres in the fabric but the use of cotton is not excluded. In fact, cotton/nylon and cotton/polyester blends are popular for rainwear fabrics. The swelling of the cotton fibres that occurs on water absorption helps to close up the yarn assemblies and prevents water penetration.

25.4.3 Silicone finishes

Modern water-repellent chemicals are often emulsions of polydimethylsiloxanes. These chemicals spread rapidly all over the fibre surface during impregnation and, on curing, form a layer of resistant hydrophobic liquid polymer on the fibre
surfaces. These chemicals not only promote water repellence but also give the fabric a soft, smooth handle.

Hydrolysis of chloromethylsilanes and polymerisation of the silanols produced gives polysiloxanes (Figure 25.4). Dichlorodimethylsilane hydrolyses to a diol that gives a linear condensation polymer, whereas trichloromethylsilane gives a triol and thus leads to a network polymer. Trimethylsilanol from chlorotrimethylsilane will not polymerise but will block a growing polysiloxane chain. By varying the relative proportions of these three chemicals, the molecular weight and properties of the silicone polymer produced can be varied. The amount of methylsilanetriol controls the degree of polymer crosslinking while that of the trimethylsilanol controls the chain length. Polysiloxanes, commonly called silicones, are available as liquids, rubbers and solids. They have many industrial uses as lubricants and elastomers.

The silicones used in textile finishing are partially polymerised methylsilanols in an organic solvent or aqueous dispersion. They contain an organometallic catalyst to promote additional polymerisation on the fibre surface during curing. The water...
repellence of the treated fabric depends on the orientation of the polysiloxane molecule on the fibre surface. The polar oxygen atoms along the silicone chain are oriented towards the polar fibre and the methyl groups away from it. This is assisted by the incorporation of zirconium or titanium compounds. In this way, the surface of the fibres presents an array of hydrophobic methyl groups that provide the water repellence and smooth handle. The adhesion of the silicone depends on the fibre surface being free of surface-active wetting agents so that good rinsing of the fabric after the previous treatment is essential.

Since the liquid polysiloxane film does not have strong adhesion to the surface, the finish is not very resistant to laundering and dry cleaning. Reactive silicone finishes that undergo more extensive polycondensation to a crosslinked polymer are more durable. One type of reactive polysiloxane has methylhydrogensiloxane units (Figure 25.3). The reactive silicon–hydrogen bond reacts with water to produce hydrogen and a silanol group that then undergoes further polycondensation resulting in chain crosslinking. Because hydrogen is generated, good ventilation is necessary during use and for storage of drums containing the silicone emulsion. A mixture of the silicone dispersion and organometallic catalyst is padded onto the fabric. This is then cured to cause the desired reactions. The resulting network polymer film on the fibre surface is resistant to laundering and dry cleaning while imparting water repellence and a soft handle to the fabric.

![Figure 25.5 Reactive polysiloxanes](image)

Another type of reactive silicone finish depends on crosslinking a polysiloxane by means of reaction with methylsilanetriol generated by hydrolysis of its methyl ether. This type of crosslink is longer than those formed by condensation of hydroxyl groups in a polysiloxane. Polysiloxanes with short crosslinks are used mainly for water-repellent finishes. The more elastic types, with longer methylsilanetriol generated crosslinks, are softeners. In addition, a range of polysiloxanes with other functional groups is now available (Figure 25.6). These include polysiloxanes with amino or epoxy groups, the numbers of such groups depending upon the particular effect required. They are excellent durable
softening agents. Polysiloxanes with a grafted polyoxyethylene side chain are relatively hydrophilic. If the polyoxyethylene chain is long enough, the polymer can even be water-soluble. When used with a methylolamino crease-resist chemical, the polyoxyethylene chain can bond to the fabric and imparts a soft hydrophilic surface.

The stability of the polysiloxane emulsions is critical. Separation of the polymer may cause uneven water-repellent deposits on the fabric surface and equipment. This also applies to other types of polymer emulsions. Polysiloxane emulsion technology has developed to the point that some microemulsions of these products can even be applied in a jet dyeing machine where the shear forces generated would rapidly crack most polymer emulsions.

The application of any type of hydrophobic finish on the fibre surface that requires thermal curing may result in decreased rubbing fastness of fabric containing polyester fibres dyed with disperse dyes. On curing, the disperse dyes migrate from the polyester fibres into the layer of hydrophobic chemical on the fibre surface, in which they are very soluble. The concentration of dye in this surface layer can become high enough that it is easily transferred to white or pale coloured adjacent fabric by abrasion.

25.4.4 Anti-soil and soil-release finishes

Soil-release finishes allow the easy removal of dirt and oil picked up by a fabric during use. Most types of dirt are hydrophobic and adhere well to hydrophobic synthetic fibres such as polyester and nylon. The ready accumulation of static electric charge by synthetic fibres also leads to more soiling than for more
hydrophilic fibres. Static charge is more readily dissipated by cotton because it absorbs more water from the atmosphere than a typical synthetic fibre.

Section 13.12.2 deals with the use of stain blocking chemicals on nylon carpets. Stain or soil repellent finishes invariably contain a fluoropolymer, possibly in combination with a silicone polymer. The 'Scotchguard' finish is a typical example. The chemicals are applied as an emulsion followed by drying and curing. They leave a thin film of polymer on the fibre surfaces of very low adhesive capability so that dirt does not stick to the film. This is a key characteristic of fluoropolymers. Polytetrafluoroethylene exposes an array of fluorine atoms along the polymer chain. The fluorine atom is the most electronegative atom known and other atoms do not form even weak bonds with it.

Soil-release and soil anti-redeposition chemicals facilitate the release of dirt already on the fibre surface during washing. They are usually hydrophilic anionic polymers often based on polyacrylic acid derivatives. A film of such a hydrophilic polymer on the fibre surface does not strongly attract hydrophobic dirt so that it is more readily emulsified by the detergent solution during washing. The negative charges of the carboxylate groups in the polyacrylic acid film repel the dirt particles and prevent any redeposition (Figure 25.7). This occurs because the dirt particles also have a negative charge from the detergent molecules adsorbed on their surface.

\[
\begin{align*}
&\text{Fibre} \\
&\text{Dirt particle with adsorbed detergent}
\end{align*}
\]

Figure 25.7 Function of a polyacrylate soil-release finish

25.4.5 Flame-retardant finishes
The majority of organic polymers are sensitive to heat. At high temperatures, in the range 100 to 300 °C, they will either melt or decompose. Decomposition will usually lead to the formation of flammable gases. Below the decomposition
temperature, the majority of synthetic fibres will first melt on exposure to heat. Drops of molten polymer can cause serious burns. For some uses, such as theatre curtains, protective clothing and children’s nightwear, a fabric must be non-flammable. Cellulose chars and burns quite readily. Cotton or regenerated cellulose materials pose a serious fire hazard because the flammable gases generated on combustion permit rapid propagation of flames. Because of more stringent government regulations, the use of flame-retardant finishes is now common for cotton fabrics for children’s nightwear. The processes used to decrease the flammability of cellulose are very similar to those used for crease-resist finishes but include other chemicals based on phosphorous or halogenated derivatives that impart the required flame resistance along with crease resistance. Careful selection of chemicals and curing conditions is required to avoid excessive losses in fabric strength and a harsh handle.

Minimising flammability involves three major principles:

1. Decomposition of the chemical on heating to give a non-combustible gas that envelops the fibres and excludes oxygen. Ammonium salts that release ammonia on heating are typical examples, but they are water-soluble and not resistant to washing;

2. Decomposition on heating to produce a deposit on the fibre surface that blocks the release of combustible gases. They may also catalyse the dehydration of cellulose and minimise gas release. Many of the phosphorous- or boron-based finishes probably work on this principle;

3. Decomposition to generate free radicals that combine with the free radicals needed for flame propagation. Organobromine compounds decompose to give free bromine atoms that are effective in this way.

For decreasing the flammability of cellulosic fibres, it is usual to apply a chemical finish to the material. Some artificially-made fibres contain additives that reduce their flammability. These are either reactive chemicals incorporated into the polymer chains during polymerisation, or chemicals added to the polymer liquid or solution before filament spinning. There are, of course, a number of artificially-made fibres with outstanding heat and flame resistance such as polyaramids (Kevlar, Nomex) and polybenzimidazoles.

When flame-resistant material will not be washed during use, adequate protection is possible by impregnating with a soluble salt solution and drying. Common chemicals include ammonium carbonate and borax. Ammonium carbonate decomposes on heating to form ammonia, water and carbon dioxide.
The release of these gases prevents oxygen from reaching the fibres. Borax coats the fibres with boron oxide and reduces the evolution of combustible gases. To increase washing fastness, various insoluble salts such as metal oxides can be precipitated in the fibres.

Modern finishes for flame-resistant cotton and viscose use reactive chemicals that are combined with crease-resist resins. A solution or dispersion of the mixture of chemicals is padded onto the material. This is then dried, cured and possibly washed. This type of chemical finishing of cellulosic goods is extremely severe and invariably has an influence on the dyes present in the fibres. Both the colour and the colour fastness properties may be affected. These types of finishes often give products with a harsh handle and the use of softening agents is common. Alternatively, to avoid stiffening of the fabric, the chemicals can be applied using a cold pad–batch method. They give a flame resistant finish with good washing fastness. Many are known by their commercial names (Figure 25.8).

![Figure 25.8 Typical flame-retardant chemicals](image)

### 25.5 OTHER TYPES OF FINISHING CHEMICALS

Bacteria or fungi (mildew) will grow on the surface of many fibres particularly under warm damp conditions. This can cause coloured spots that are extremely difficult to remove and has an unpleasant, mouldy odour. The bacteria may even feed on natural polymers causing considerable damage to the fibres. When the fabric will be stored for more than a few days, it will normally be rinsed with a dilute solution of an anti-bacterial agent before drying. These agents are usually organic quarternary ammonium salts, such as hexadecylpyridinium bromide (3, in
Figure 25.9, also commonly called cetyl pyridinium bromide), or toxic organohalogen compounds such as chlorophenols (4). Permanent moth-proofing of wool involves finishing by a dyeing process with colourless anionic organohalogen compounds that behave like acid dyes (Section 7.4.4).

Softening agents are widely used in textile finishing. The goods are usually rinsed in a solution of the chemical and then dried. If not polysiloxanes, they are often cheaper surface active chemicals, or closely related derivatives, whose molecules have long hydrocarbon segments. They may be anionic, cationic or non-ionic. They lubricate the fibre surface and reduce friction. In addition, many such ionic chemicals minimise build-up of static electricity.

During the finishing of many fabrics, solutions or dispersions of chemicals may be dried into the material simply to increase its weight, improving the draping characteristics. The classic example of this is weighted silk. Their presence often increases the fabric stiffness. The objectives of applying such chemicals can be quite varied and the finish is often not permanent.

REFERENCE