CHAPTER 19

Dyes synthesised in the fibre

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).

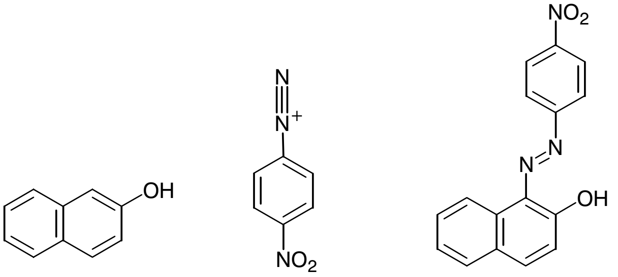
The developed azoic dyes used in cotton dyeing are the most important ingrain dyes but have gradually lost their market share. Reactive dyes have superseded them, apart from a few deep red and bordeaux combinations that give shades unobtainable with any other class of dye. The oxidation bases and ingrain 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.



1 **2** **3**

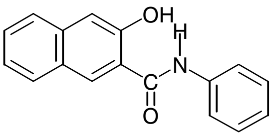
Figure 19.1

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 dyeing 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.

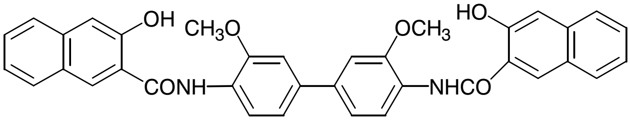
19.2.2 Coupling components

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-oxynaphthoic 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.

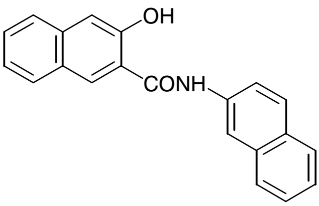
The anilides of BON acid are soluble in dilute NaOH solution and form the corresponding naphtholate ion. These relatively small molecules are of only low to moderate substantivity for cotton, but they diffuse rapidly into the fibres. In general, the higher the substantivity the better the rubbing fastness 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 dyeing so that the bath composition does not vary because of preferential absorption (Section 10.5.2). For



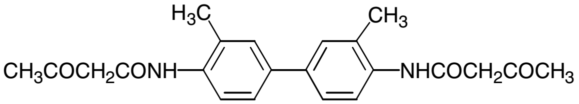
CI Azoic Coupling Component 2



CI Azoic Coupling Component 3



CI Azoic Coupling Component 7



CI Azoic Coupling Component 5

Figure 19.2 Molecular structures of some typical Naphtols

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 Naphtols 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.

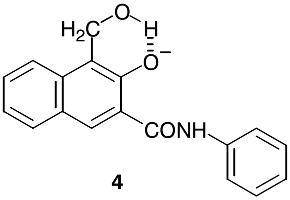


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Figure 19.3

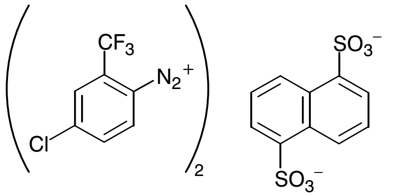
Azoic dyeing usually involves a single coupling component and a single diazonium ion. To obtain a specific shade, a mixture of two Naphtols of similar substantivity may sometimes be necessary, but usually with only a small amount of the second component. Mixtures of diazonium components are not used. 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 Naphtols. 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 (diazotised aniline). The formation of both diazoamino and diazotate derivatives (Scheme 19.1) is reversible and acidification of their solutions regenerates the diazonium ion. One



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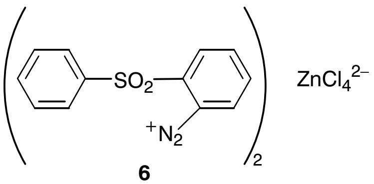

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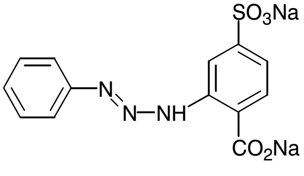

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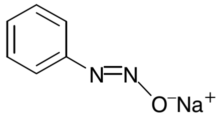

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Figure 19.4 CI Azoic Diazo Component 17 (**5**); CI Azoic Diazo Component 18 (**6**); stabilised forms of the phenyldiazonium ion (**7** and **8**) advantage of diazoamino or diazotate derivatives is that frequently both the stabilised diazonium component 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.

$$\mathrm{D{-}N{\equiv}N^{+} + H_2N{-}R{-}CO_2H \rightleftharpoons D{-}N{=}N{-}NH{-}R{-}CO_2H + H^{+}}$$

$$\mathrm{D{-}N{\equiv}N^{+} + NaOH \rightleftharpoons D{-}N{=}N{-}O^{-} + Na^{+} + H^{+}}$$

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 naphtholate 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 naphtholate 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 naphtholate 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

			Typical fastness grade		
CI Diazo component	CI Coupling component	Hue	Soda boiling	Light	Chlorine
37	2	Yellowish red	1–2	5	3
37	7	Red	3–4	5–6	4–5
37	23	Black	2–3	7	3–4
42	13	Bordeaux	4–5	6–7	4

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.

$$2\text{Dye—S—SO}_3^- + \text{S}^{2-} \longrightarrow \text{Dye—S—S—S—Dye} + 2\text{SO}_3^{2-}$$

$$\text{Dye—S—S—S—Dye} + \text{SO}_3^{2-} \longrightarrow \text{Dye—S—S—Dye} + \text{S}_2\text{O}_3^{2-}$$

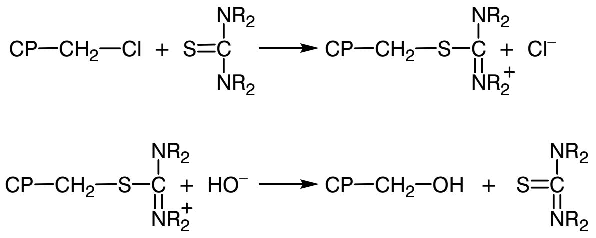
or

$$\text{Dye——SO}_3^- + \text{S}^{2-} \longrightarrow \text{Dye—S}^- + \text{S}_2\text{O}_3^{2-}$$

$$2\text{Dye—S}^- + \text{O}_2 + 2\text{H}^+ \longrightarrow \text{Dye—S—S—Dye} + \text{H}_2\text{O}_2$$

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).



$$\text{CP—CH}_2\text{—Cl} + \text{S}{=}\overset{\text{NR}_2}{\underset{\text{NR}_2}{\text{C}}} \longrightarrow \text{CP—CH}_2\text{—S—}\overset{\text{NR}_2}{\underset{\text{NR}_2^+}{\text{C}}} + \text{Cl}^-$$

$$\text{CP—CH}_2\text{—S—}\overset{\text{NR}_2}{\underset{\text{NR}_2^+}{\text{C}}} + \text{HO}^- \longrightarrow \text{CP—CH}_2\text{—OH} + \text{S}{=}\overset{\text{NR}_2}{\underset{\text{NR}_2}{\text{C}}}$$

CP = copper phthalocyanine

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-isoindoline 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.

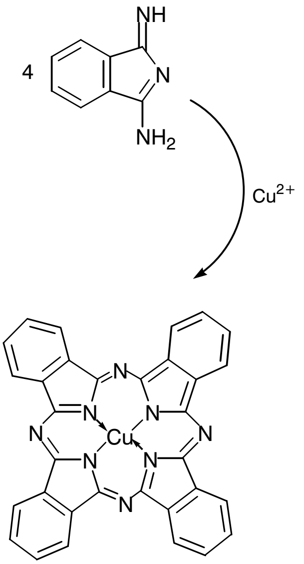


Figure 19.5 Formation of copper phthalocyanine from appropriate precursors

REFERENCE

1. J Shore, in *Cellulosics Dyeing*, J Shore, Ed (Bradford: SDC, 1995).

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 different nylons. 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

Dye type combinations	Fibre blends that can be dyed
Acid dyes	Nylon/wool, nylon/cationic nylon, nylon/urethane
Acid dye/basic dye	Nylon/anionic nylon, nylon/acrylic
Acid dye/cotton dye	Nylon/cellulose, wool/cellulose
Acid dye/disperse dye	Nylon/polyester, wool/polyester
Basic dye/cotton dye	Acrylic/cellulose
Basic dye/disperse dye	Acrylic/polyester, anionic polyester/polyester
Cotton dye/disperse dye	Cellulose/polyester, cellulose/acetate

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 hydros 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 dyebath 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

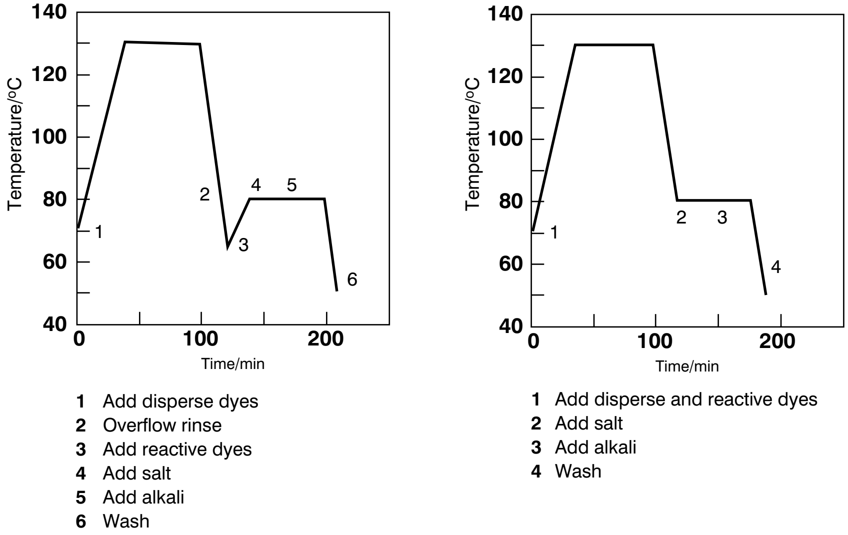


Figure 20.1 Rapid stepwise and all-in-one dyeing processes for cotton/polyester (time of rinsing and scouring not included)

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 dyeing 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.

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-sulphoxylate 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.

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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 D_{65} 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

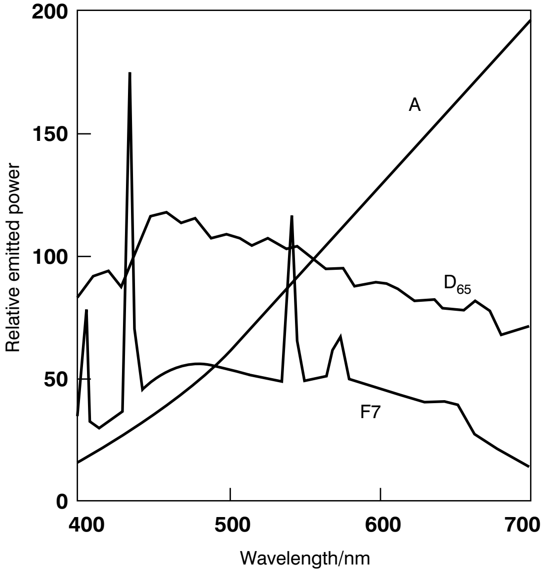

Figure 21.1 Relative spectral power distributions (SPDs) of some typical illuminants

$$\text{Hg} + \text{energy} \longrightarrow \text{Hg}^*, \text{Hg}^{**} \quad \text{(excited mercury atoms)}$$

$$\text{Hg}^*, \text{Hg}^{**} \longrightarrow \text{Hg} + \text{visible light} + \text{UV light}$$

$$\text{Phosphor} + \text{UV light} \longrightarrow \text{Phosphor}^* \quad \text{(excited)}$$

$$\text{Phosphor}^* \longrightarrow \text{Phosphor} + \text{visible light}$$

Scheme 21.1

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 D_{65} (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 D_{65}. 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 $BaSO_4$. 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).

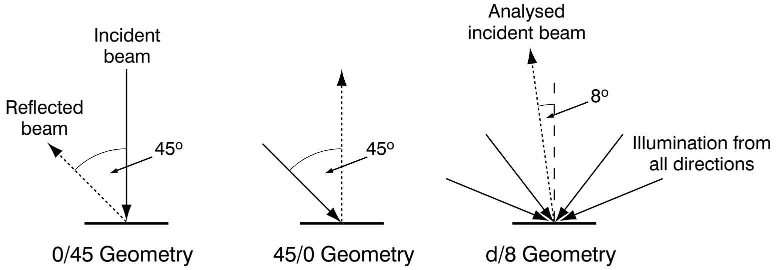

Figure 21.2 Some common spectrophotometer geometries

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.

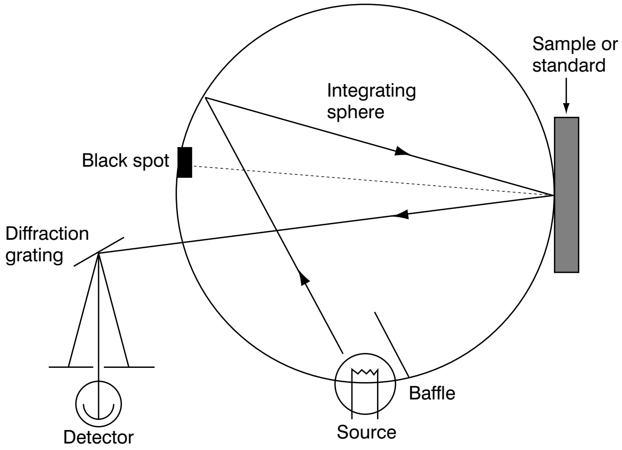

Figure 21.3 Schematic of a reflection spectrophotometer with an integrating sphere

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 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

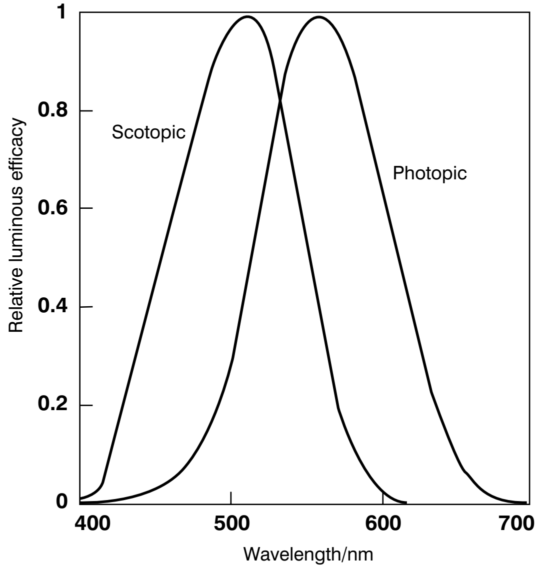

Figure 21.4 Relative photopic and scotopic luminous efficacies

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

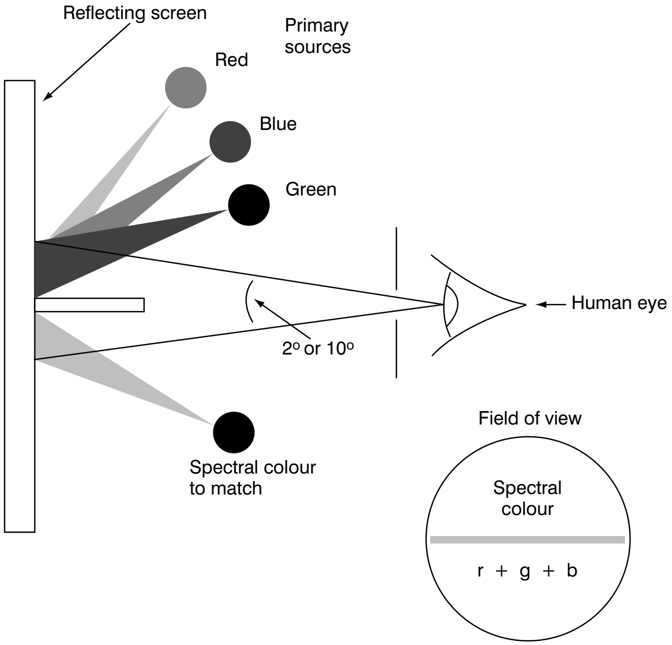

Figure 21.5 Schematic of the colour matching experiment with lights

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 $\bar{r}(\lambda)$, $\bar{g}(\lambda)$ and $\bar{b}(\lambda)$. The symbol (λ) 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:

$$C(\lambda) \equiv \bar{r}(\lambda)\,[R] + \bar{g}(\lambda)\,[G] + \bar{b}(\lambda)\,[B] \qquad (1)$$

This simply states that the spectral light of colour C and wavelength λ, at the given constant power, can be matched by additive mixing of amounts $\bar{r}(\lambda)$, $\bar{g}(\lambda)$ and $\bar{b}(\lambda)$ 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:

$$C(\lambda) + \bar{r}(\lambda)\,[R] \equiv \bar{g}(\lambda)\,[G] + \bar{b}(\lambda)\,[B] \qquad (2)$$

Alternatively, this may be written as:

$$C(\lambda) \equiv \bar{g}(\lambda)\,[G] + \bar{b}(\lambda)\,[B] - \bar{r}(\lambda)\,[R] \qquad (3)$$

giving a negative $\bar{r}(\lambda)$ 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.

$$r = \frac{\bar{r}}{\bar{r}+\bar{g}+\bar{b}} \quad g = \frac{\bar{g}}{\bar{r}+\bar{g}+\bar{b}} \quad b = \frac{\bar{b}}{\bar{r}+\bar{g}+\bar{b}} \quad r+g+b=1 \tag{4}$$

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 $\bar{r}(\lambda)$, $\bar{g}(\lambda)$ and $\bar{b}(\lambda)$ 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 $\bar{r}(\lambda)$, $\bar{g}(\lambda)$ and $\bar{b}$ (λ) 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 $\bar{r}(\lambda)$, $\bar{g}(\lambda)$ and $\bar{b}(\lambda)$ (2° visual field) into a set $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ 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

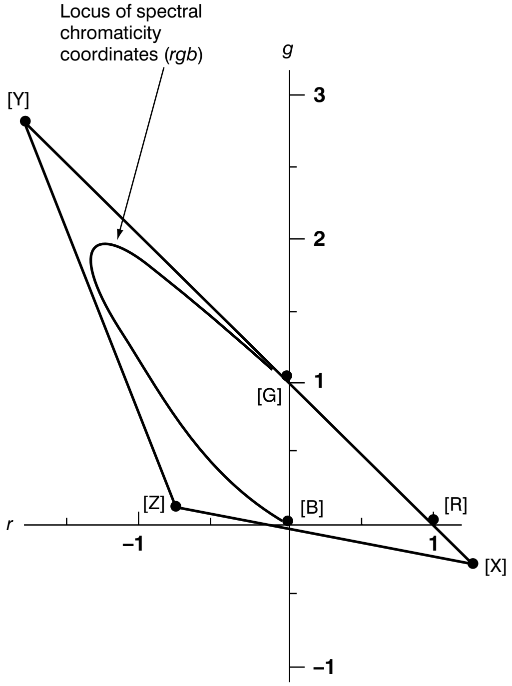

Figure 21.6 The CIE *rgb* chromaticity figure showing the coordinates of the primaries and the locus of the spectral colours (2° visual field)

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:

$$\begin{aligned}\bar{x}(\lambda) &= 2.77\bar{r}(\lambda) + 1.75\bar{g}(\lambda) + 1.13\bar{b}(\lambda)\\ \bar{y}(\lambda) &= 1.00\bar{r}(\lambda) + 4.59\bar{g}(\lambda) + 0.0601\bar{b}(\lambda)\\ \bar{z}(\lambda) &= 0.0565\bar{g}(\lambda) + 5.59\bar{b}(\lambda)\end{aligned} \qquad (5)$$

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, $\bar{r}_{10}(\lambda)$, $\bar{g}_{10}(\lambda)$ and $\bar{b}_{10}(\lambda)$ were similarly transformed into a new set $\bar{x}_{10}(\lambda)$, $\bar{y}_{10}(\lambda)$ and $\bar{z}_{10}(\lambda)$ 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.

$$x = \frac{\bar{x}}{\bar{x}+\bar{y}+\bar{z}} \quad y = \frac{\bar{y}}{\bar{x}+\bar{y}+\bar{z}} \quad z = \frac{\bar{z}}{\bar{x}+\bar{y}+\bar{z}} \quad x+y+z=1 \qquad (6)$$

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 apexes. 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.

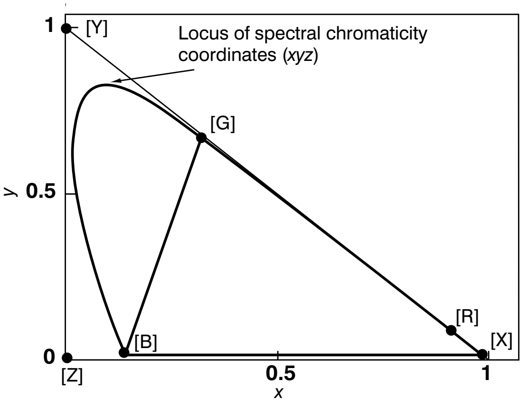

Figure 21.7 The CIE *xy* chromaticity figure for the 1931 standard observer (2° visual field)

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 $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ or $\bar{x}_{10}(\lambda)$, $\bar{y}_{10}(\lambda)$ and $\bar{z}_{10}(\lambda)$ 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:

$$C(\lambda) \equiv \bar{r}(\lambda)[R] + \bar{g}(\lambda)[G] + \bar{b}(\lambda)[B] \equiv \bar{x}(\lambda)[X] + \bar{y}(\lambda)[Y] + \bar{z}(\lambda)[Z] \qquad (7)$$

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 21.1 Data for CIE Illuminant D_{65} $S(\lambda)$ and the CIE 1964 supplementary standard observer (10°) and the calculation of the illuminant tristimulus values

λ (nm)	$S(\lambda)$	$\bar{x}_{10}$	$\bar{y}_{10}$	$\bar{z}_{10}$	$S.\bar{x}_{10}$	$S.\bar{y}_{10}$	$S.\bar{z}_{10}$
400	82.8	0.019	0.002	0.086	1.58	0.17	7.12
420	93.4	0.241	0.021	0.973	22.46	2.00	90.83
440	104.9	0.384	0.062	1.967	40.25	6.51	206.37
460	117.8	0.302	0.128	1.745	35.61	15.10	205.61
480	115.9	0.081	0.254	0.772	9.33	29.39	89.49
500	109.4	0.004	0.461	0.219	0.42	50.41	23.90
520	104.8	0.118	0.762	0.061	12.33	79.84	6.36
540	104.4	0.377	0.962	0.014	39.34	100.43	1.43
560	100.0	0.705	0.997	0	70.52	99.73	0
580	95.8	1.014	0.869	0	97.16	83.24	0
600	90.0	1.124	0.658	0	101.16	59.25	0
620	87.7	0.856	0.398	0	75.10	34.91	0
640	83.7	0.432	0.180	0	36.12	15.05	0
660	80.2	0.153	0.060	0	12.24	4.84	0
680	78.3	0.041	0.016	0	3.20	1.24	0
700	71.6	0.010	0.004	0	0.69	0.26	0
Sums		5.86	5.83	5.84	554.1	582.4	631.1

$$Y = 100 = k\sum(S\bar{y}_{10})k = \frac{100}{\sum(S\bar{y}_{10})} = \frac{100}{582.4} = 0.172$$

$$X = k\sum(S\bar{x}_{10}) = 0.172 \times 554.1 = 95.2$$

$$Z = k\sum(S\bar{z}_{10}) = 0.172 \times 631.1 = 108.4$$

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.

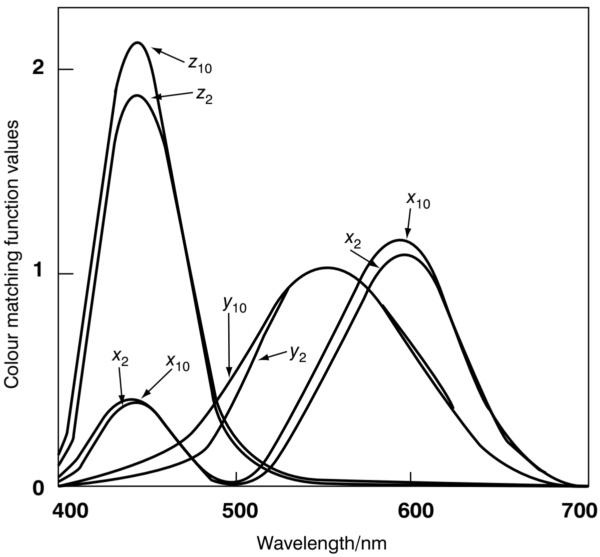

Figure 21.8 Colour matching functions for the 1931 (2°) and 1964 (10°) standard observers

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 $\bar{x}_{10}(\lambda)$, $\bar{y}_{10}(\lambda)$ and $\bar{z}_{10}(\lambda)$ 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:

$$C(\lambda) \equiv \bar{x}_{10}(\lambda)[X_{10}] + \bar{y}_{10}(\lambda)[Y_{10}] + \bar{z}_{10}(\lambda)[Z_{10}] \qquad (8)$$

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 $\bar{x}$ tristimulus values for all the wavelengths, and by the corresponding sums of $\bar{y}$ and $\bar{z}$ for the [Y] and [Z] primaries, as shown by the equation:

$$\text{White} \equiv \sum C(\lambda) \equiv \sum (\bar{x})\,[X] + \sum (\bar{y})\,[Y] + \sum (\bar{z})\,[Z] \qquad (9)$$

where the symbol Σ 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 $\Sigma(\bar{x})$ parts of the primary [X], $\Sigma(\bar{y})$ parts of the primary [Y] and $\Sigma(\bar{z})$ 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:

$$C(\lambda)\{\text{unit power}\} \equiv \bar{x}[X] + \bar{y}[Y] + \bar{z}[Z] \qquad (10)$$

states that a match of a spectral light of wavelength λ at unit power is possible by mixing the three primary lights [X], [Y] and [Z] in the proportions $\bar{x}$, $\bar{y}$ and $\bar{z}$, respectively. If we had to match the same spectral light, but at a total power of $S(\lambda)$, the matching condition would be described by the above equation multiplied by S, giving:

$$C(\lambda)\{\text{power } S(\lambda)\} \equiv S\bar{x}[X] + S\bar{y}[Y] + S\bar{z}[Z] \qquad (11)$$

where the tristimulus values are now $S\bar{x}$, $S\bar{y}$ and $S\bar{z}$.

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:

$$\begin{aligned}\text{Colour of light} &\equiv \sum [\mathrm{C}(\lambda)\{\text{power } S(\lambda)\}] \\ &\equiv \sum (S\bar{x})\,[\mathrm{X}] + \sum (S\bar{y})\,[\mathrm{Y}] + \sum (S\bar{z})\,[\mathrm{Z}]\end{aligned} \tag{12}$$

In this equation for the summations over all the wavelengths, the values of S, $\bar{x}$, $\bar{y}$ and $\bar{z}$, 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:

$$\mathrm{X} = \sum (S\bar{x}) \quad \mathrm{Y} = \sum (S\bar{y}) \quad \mathrm{Z} = \sum (S\bar{z}) \tag{13}$$

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:

$$\mathrm{X_n} = k\sum (S\bar{x}) \quad \mathrm{Y_n} = 100 = k\sum (S\bar{y}) \quad \mathrm{Z_n} = k\sum (S\bar{z}) \tag{14}$$

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:

$$k = \frac{100}{\sum (S\bar{y})} \tag{15}$$

Table 21.1 illustrates this type of calculation. It shows that Illuminant D_{65} 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 D_{65}. 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 minimises 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 [1,2]. These are defined by:

$$W_X(\lambda) = kS(\lambda)\bar{x}(\lambda) \qquad W_Y(\lambda) = kS(\lambda)\bar{y}(\lambda) \qquad W_Z(\lambda) = kS(\lambda)\bar{z}(\lambda) \qquad (16)$$

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 D_{65} and the 10° standard observer, for a wavelength interval of 20 nm (note that the summation gives the correct tristimulus values for Illuminant D_{65}). 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

Table 21.2 Weighting factors $W_{10,x}$, $W_{10,y}$ and $W_{10,z}$ for the combination of CIE Illuminant D_{65} and the 1964 standard (10°) observer for a wavelength interval of 20 nm and calculation of an object's tristimulus values

λ (nm)	$W_{10,x}$	$W_{10,y}$	$W_{10,z}$	R sample	$R.W_{10,x}$	$R.W_{10,y}$	$R.W_{10,z}$
400	0.058	0.012	0.222	0.027	0.002	0.000	0.006
420	2.951	0.280	13.768	0.031	0.091	0.009	0.427
440	7.227	1.042	36.808	0.038	0.275	0.040	1.399
460	6.578	2.534	37.827	0.043	0.283	0.109	1.627
480	1.278	4.872	14.226	0.056	0.072	0.273	0.797
500	−0.259	8.38	3.254	0.027	−0.007	0.228	0.088
520	1.951	14.030	1.025	0.071	0.139	0.996	0.073
540	6.751	17.715	0.184	0.084	0.567	1.488	0.015
560	12.223	17.407	−0.013	0.093	1.137	1.619	−0.001
580	16.779	14.210	0.004	0.099	1.661	1.407	0.000
600	17.793	10.121	−0.001	0.111	1.975	1.123	0.000
620	13.135	5.971	0.000	0.253	3.323	1.511	0.000
640	5.859	2.399	0.000	0.460	2.695	1.104	0.000
660	1.901	0.741	0.000	0.662	1.258	0.491	0.000
680	0.469	0.184	0.000	0.816	0.383	0.150	0.000
700	0.117	0.044	0.000	0.873	0.102	0.038	0.000
Sums	94.811	100.000	107.304		13.960	10.580	4.430
	X_n	Y_n	Z_n		X	Y	Z

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

for matching the colour of a spectral component of wavelength λ, with a power of $S(\lambda) \times R(\lambda)$, is:

$$\mathrm{C}(\lambda)\{\text{power } S \times R\} \equiv (SR\bar{x})\,[\mathrm{X}] + (SR\bar{y})\,[\mathrm{Y}] + (SR\bar{z})\,[\mathrm{Z}] \tag{17}$$

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:

$$\begin{aligned}\text{Object colour} &\equiv \sum[\mathrm{C}(\lambda)\{\text{power } S \times R\}] \\ &\equiv \sum(SR\bar{x})\,[\mathrm{X}] + \sum(SR\bar{y})\,[\mathrm{Y}] + \sum(SR\bar{z})\,[\mathrm{Z}]\end{aligned} \tag{18}$$

The tristimulus values of the colour of the object are given by the summations of the $SR\bar{x}$, $SR\bar{y}$ and $SR\bar{z}$ values over all the wavelengths, each multiplied by the normalisation constant k, calculated for the illuminant:

$$X = k\sum(SR\bar{x}) = \sum(RW_X) \quad Y = k\sum(SR\bar{y}) = \sum(RW_Y)$$
$$Z = k\sum(SR\bar{z}) = \sum(RW_Z) \tag{19}$$

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 $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ 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:

$$\text{Colour} \equiv X[X] + Y[Y] + Z[Z] \tag{20}$$

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

Table 21.3 Tristimulus values and corresponding chromaticity co-ordinates for typical dyed textile fabrics

	Tristimulus values (D_{65})			Chromaticity coordinates	
Fabric colour	X_{10}	Y_{10}	Z_{10}	x_{10}	y_{10}
Red	20.80	12.28	5.21	0.543	0.321
Bluish-red	19.49	12.40	13.55	0.429	0.273
Orange	41.35	27.60	10.34	0.522	0.348
Deep reddish-brown	12.45	8.20	3.28	0.520	0.343
Pale yellow	68.66	74.83	36.42	0.382	0.416
Deep yellow	53.26	47.96	7.34	0.491	0.442
Green	21.69	33.45	36.36	0.237	0.366
Dark green	11.18	17.07	18.24	0.240	0.367
Blue	14.78	15.69	36.34	0.221	0.235
Dark blue	6.07	6.73	13.37	0.232	0.257
Pale violet	52.03	51.58	72.46	0.296	0.293

tristimulus values. Table 21.3 lists tristimulus values and chromaticity coordinates for a range of coloured textile fabrics and illustrates these general trends.

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 ($X_1 = X_2$, $Y_1 = Y_2$ 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 $\bar{y}$ 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:

(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 D_{65}), 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 $S(\lambda) \times R(\lambda)$. 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 D_{65}, they give identical sets of tristimulus values for the two samples:

$$X_1 = X_2 \quad Y_1 = Y_2 \quad Z_1 = Z_2 \tag{21}$$

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)

	Illuminant D_{65}			Illuminant A		
	X	Y	Z	X	Y	Z
Non-metameric						
Sample 1	10.22	9.82	6.39	13.97	10.89	2.26
Sample 2	10.20	9.91	6.38	13.96	10.79	2.24
		Match			**Match**	
Metameric						
Sample 1	10.22	9.82	6.39	13.97	10.79	2.24
Sample 3	10.19	9.90	6.41	14.45	11.01	2.05
		Match			**Mis-match**	

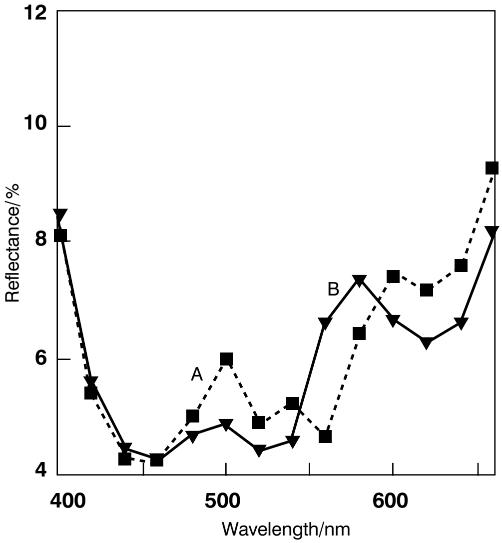

Figure 21.9 Reflection spectra of metameric textile samples

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:

$$X = \frac{X}{X+Y+Z} \quad Y = \frac{Y}{X+Y+Z} \quad Z = \frac{Z}{X+Y+Z} \tag{22}$$

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 ($\lambda = 750$ nm) with a violet spectral light ($\lambda = 380$ 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

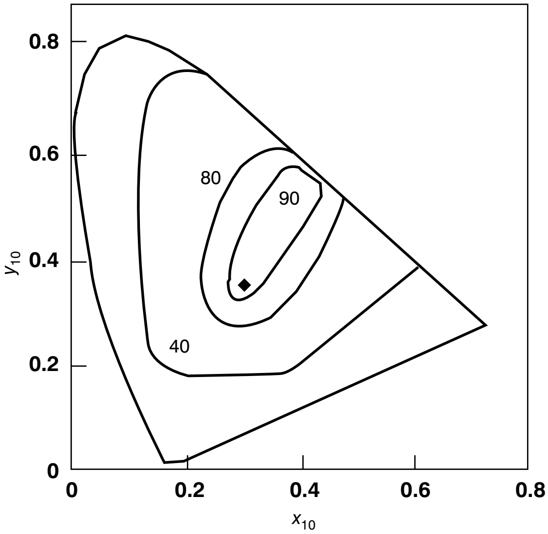

Figure 21.10 Contour diagram showing the range of chromaticity coordinates (CIE 1931) for values of Y equal to 40, 80 and 90. The point at the centre of the figure gives the chromaticity coordinates for Illuminant D_{65}

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:

$$W = Y + 800(x_n - x) + 1700(y_n - y) \qquad (23)$$

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 D_{65}. 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:

$$T_W = K(x_n - x) - 650(y_n - y) \qquad (24)$$

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.

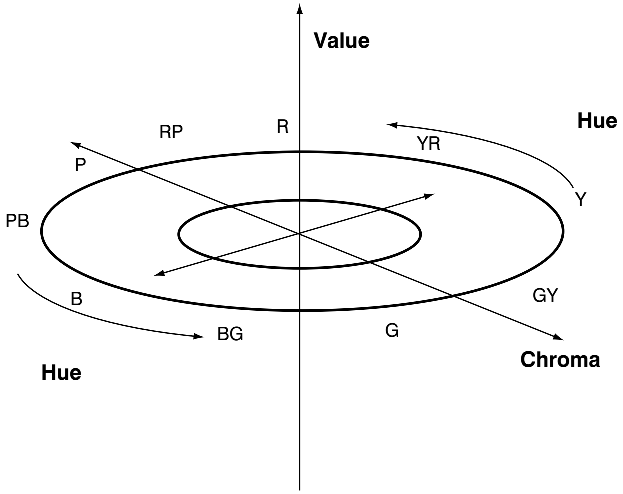

Figure 21.11 Illustration of the mutually perpendicular hue, value and chroma axes in the Munsell system

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 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).

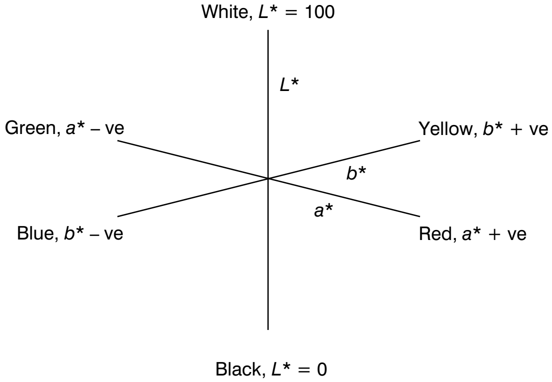

Figure 21.12 The mutually perpendicular L^*, a^* and b^* axes of the CIELAB colour space

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:

$$L^* = 116\left(\frac{Y}{Y_n}\right)^{1/3} - 16 \qquad (25)$$

a^* and b^* are given by:

$$a^* = 500\left(\left(\frac{X}{X_n}\right)^{1/3} - \left(\frac{Y}{Y_n}\right)^{1/3}\right) \tag{26}$$

$$b^* = 200\left(\left(\frac{Y}{Y_n}\right)^{1/3} - \left(\frac{Z}{Z_n}\right)^{1/3}\right) \tag{27}$$

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:

$$\begin{aligned} C^*_{ab} &= \sqrt{(a^{*2} + b^{*2})} \\ \tan(h_{ab}) &= \frac{b^*}{a^*} \end{aligned} \tag{28}$$

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° (a^*

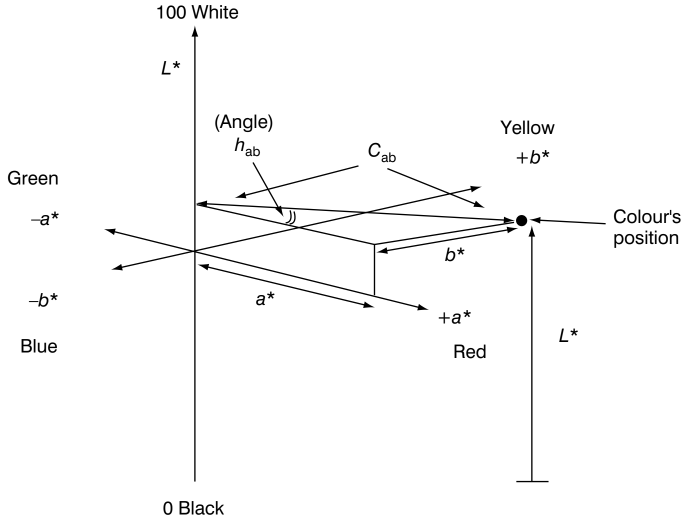

Figure 21.13 The CIELAB colour space showing the chroma and hue angle of a colour

Table 21.5 CIELAB data for the dyed fabrics samples in Table 21.3

	CIELAB co-ordinates Illuminant, D_{65}, 10° standard observer				
Fabric colour	L^*	a^*	b^*	C_{ab^*}	h_{ab}
Red	41.66	62.50	8.10	63.02	7.40
Bluish-red	41.84	45.76	–7.52	46.37	350.70
Orange	59.53	53.64	44.86	69.93	39.90
Deep reddish-brown	29.91	33.93	25.43	42.40	36.90
Pale yellow	89.31	–4.93	70.36	70.53	94.00
Deep yellow	58.00	–5.95	64.11	64.39	95.30
Green	64.52	–41.29	15.18	43.99	159.80
Dark green	45.18	–42.77	7.86	43.48	169.60
Blue	46.57	–13.31	–42.21	44.26	252.50
Dark blue	31.18	–3.36	–38.98	39.12	265.10
Pale violet	73.25	49.38	–21.59	53.89	336.40

axis, red) through 90° (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.

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).

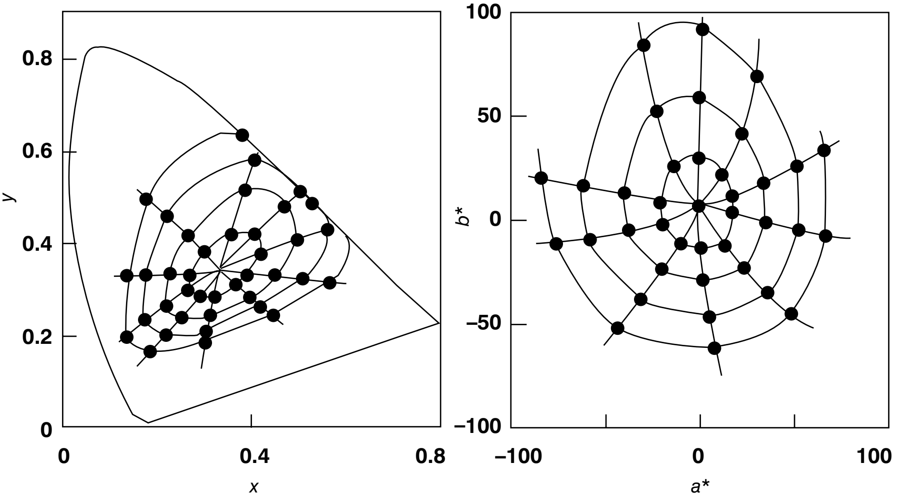

Figure 21.14 Graphs of *y* versus *x*, and of *b** versus *a** at constant *L**, for a series of Munsell paint chips

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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 ΔE^*_{ab} is:

$$\Delta E^*_{\mathrm{ab}} = \sqrt{\Delta L^{*2} + PQ^2} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (1)$$

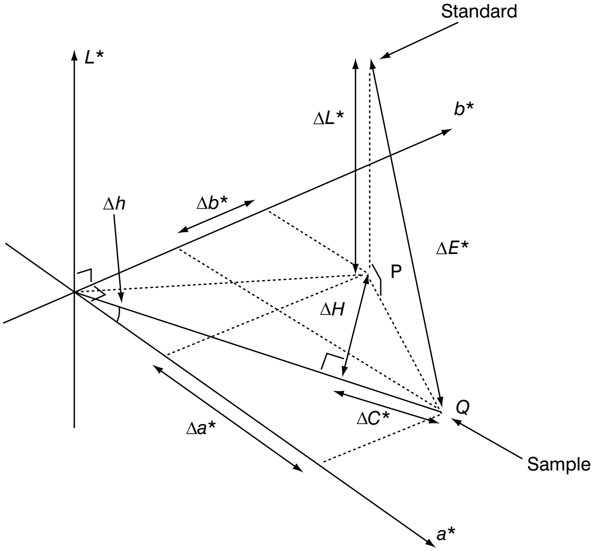


Figure 22.1 Differences in lightness, chroma, hue and colour in the CIELAB colour space

where:

$$\Delta L^* = L^*_{\text{sam}} - L^*_{\text{std}} \qquad \Delta a^* = a^*_{\text{sam}} - a^*_{\text{std}} \qquad \Delta b^* = b^*_{\text{sam}} - b^*_{\text{std}} \tag{2}$$

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 ΔE^*_{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 ΔE^*_{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.

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 ΔE^*_{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^*_{ab}), as well as in the lightness direction. The values of ΔE^*_{ab} for just visible differences in hue are therefore much smaller than those for just visible differences in lightness or saturation (Figure 22.2).

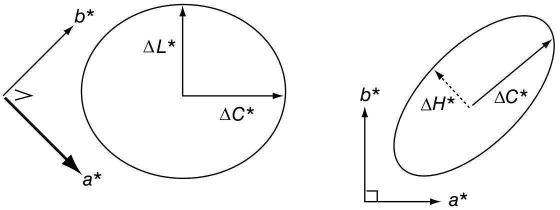


Figure 22.2 Values of L^* and C^*_{ab} for colours of constant hue, and of a^* and b^* for colours of constant L^*, that are just perceptibly different from a colour standard

For similar colours, whose coordinates are close together in the colour space, it is possible to define a difference in chroma ΔC^*_{ab} and a difference in hue ΔH^*_{ab}. The value of C^*_{ab} is given by:

$$C^*_{ab} = \sqrt{a^{*2} + b^{*2}} \qquad (3)$$

and:

$$\Delta C^*_{ab} = C^*_{sam} - C^*_{std} \qquad (4)$$

Figure 22.1 shows how the law of Pythagoras gives:

$$\Delta E^{*\,2}_{\mathrm{ab}} = \Delta L^{*2} + PQ^2 = \Delta L^{*2} + \Delta H^{*\,2}_{\mathrm{ab}} + \Delta C^{*\,2}_{\mathrm{ab}} \tag{5}$$

Since ΔL^*, ΔE^*_{ab} and ΔC^*_{ab} are known, the value of ΔH^*_{ab} is calculated by difference:

$$\Delta H^*_{\mathrm{ab}} = \sqrt{\Delta E^{*\,2}_{\mathrm{ab}} - \Delta L^{*2} - \Delta C^{*\,2}_{\mathrm{ab}}} \tag{6}$$

The values of ΔL^*, ΔC^*_{ab} and ΔH^*_{ab} give a more useful indication of the colour difference between a sample and a standard than a simple measure of ΔE^*_{ab} because they define the colour difference in terms of characteristics used by a human observer. In colour matching, the value of ΔH^*_{ab} will have stricter tolerances than those for ΔL^* and ΔC^*_{ab}.

The objective of CIELAB was a more uniform colour space in which instrumental colour differences such as ΔE^*_{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 ΔE^*_{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, ΔE^*_{ab} is double the value for the blue pair, and that, in each case, ΔH^*_{ab} is less than both ΔL^* and ΔC^*_{ab}.

Table 22.1 Comparison of colour differences found for acceptable matching of yellow and blue dyeings

	Difference			
Colour	ΔL^*	ΔC^*_{ab}	ΔH^*_{ab}	ΔE^*_{ab}
Brilliant Yellow	0.99	1.20	0.76	1.73
Deep Blue	0.60	0.52	0.30	0.85

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.

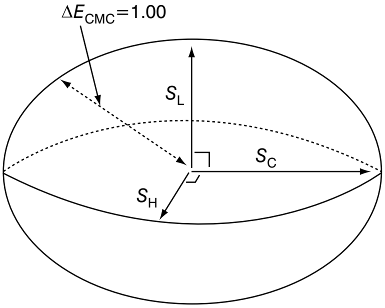


Figure 22.3 Illustration of a CMC acceptability ellipsoid showing the three semi-axes

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:

$$S_L = \frac{0.040975L^*}{1 + 0.01765L^*} \text{ for } L^* > 16, \quad S_L = 0.511 \text{ for } L^* < 16 \tag{7}$$

$$S_C = \frac{0.0638C^*_{ab}}{1 + 0.0131C^*_{ab}} + 0.638 \tag{8}$$

$$S_H = S_C\left\{(T.f) + 1 - f\right\} \tag{9}$$

In the equation for S_H, the values of the parameters f and T are given by:

$$f = \sqrt{\frac{{C^*_{ab}}^4}{1900 + {C^*_{ab}}^4}} \tag{10}$$

$$T = 0.36 + \left| 0.4 \cos(h_{ab} + 35) \right| \text{ for } h_{ab} < 164° \text{ but } > 345° \tag{11}$$

$$T = 0.56 + \left| 0.2 \cos(h_{ab} + 168) \right| \text{ for } h_{ab} > 164° \text{ but } < 345° \tag{12}$$

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 thus reflect the visual non-uniformity of the CIELAB colour space.

The CMC colour difference is defined by:

$$(\Delta E_{CMC})^2 = \left(\frac{\Delta L^*}{l \times S_L}\right)^2 + \left(\frac{\Delta C^*_{ab}}{c \times S_C}\right)^2 + \left(\frac{\Delta H^*_{ab}}{S_H}\right)^2 \tag{13}$$

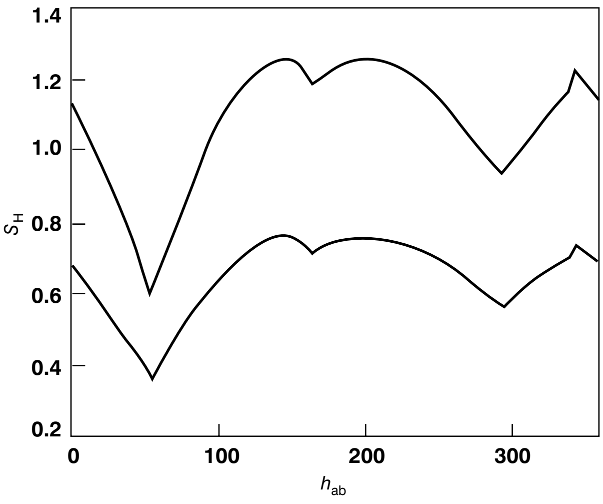


Figure 22.4 Variation of S_H with hue angle at two chroma values

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 $\Delta E_{CMC} = 1.0$. 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 ΔE_{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 $\Delta E_{CMC} = 1.0$ 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.

22.1.4 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:

$$S_L = 1 \quad S_C = 1 + 0.045C^*_{ab} \quad S_H = 1 + 0.015C^*_{ab} \tag{14}$$

The BFD colour difference equation is similar to that of the CMC system, but has an additional term depending on ΔC^*_{ab} and ΔH^*_{ab}. In addition, the lightness difference (ΔL_{BFD}) 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 ΔL^*, ΔC^*_{ab} and ΔH^*_{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 ΔL^*, ΔC^*_{ab} and ΔH^*_{ab} directions, respectively. Thus, a sample whose coordinates place it the 627 box is lighter than the standard with a positive value of ΔL^* 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

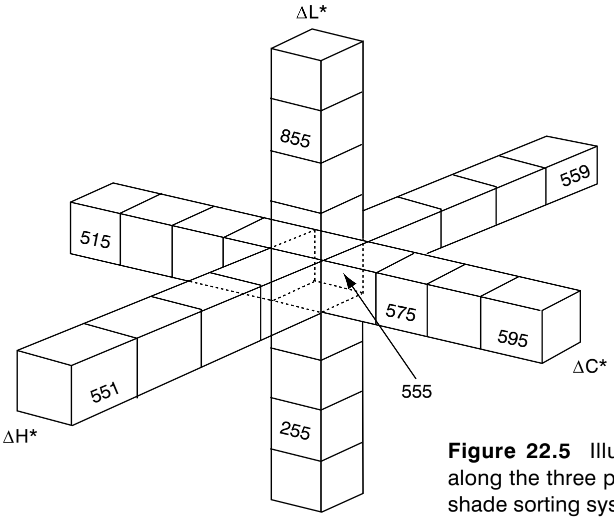
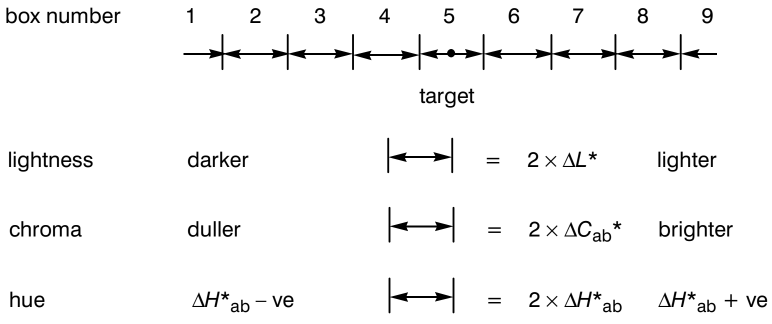


Figure 22.5 Illustration of the boxes lying along the three perpendicular axes in the 555 shade sorting system

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 $\Delta L^* = 0.5$, $\Delta C^*_{ab} = 0.3$ and $\Delta H^*_{ab} = 0.2$

ΔL^* darker		ΔC^*_{ab} duller		ΔH^*_{ab} greener	
1	−4.50	**1**	−2.70	**1**	−1.80
	−3.51		−2.11		−1.41
2	−3.50	**2**	−2.10	**2**	−1.40
	−2.51		−1.51		−1.01
3	−2.50	**3**	−1.50	**3**	−1.00
	−1.51		−0.91		−0.61
4	−1.50	**4**	−0.90	**4**	−0.60
	−0.51		−0.31		−0.21
	−0.50		−0.30		−0.20
5	standard	**5**	standard	**5**	standard
	+0.50		+0.30		+0.20
6	+0.51	**6**	+0.31	**6**	+0.21
	+1.50		+0.90		+0.60
7	+1.51	**7**	+0.91	**7**	+0.61
	+2.50		+1.50		+1.00
8	+2.51	**8**	+1.51	**8**	+1.01
	+3.50		+2.10		+1.40
9	+3.51	**9**	+2.11	**9**	+1.41
	+4.50		+2.70		+1.80
ΔL^* lighter		ΔC^*_{ab} brighter		ΔH^*_{ab} redder	



Scheme 22.1

dimension of a box in that direction is twice the tolerance. It also illustrates the relation between the tolerances for ΔL^*, ΔC^*_{ab} and ΔH^*_{ab} and the box number specification. The sample corresponding to box 627 is less saturated than the standard. Its ΔC^*_{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 ΔH^*_{ab} that is positive and at 3 to 5 times the hue tolerance. Since ΔH^*_{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:

$$\Delta h_{ab} = h_{ab}(\text{sam}) - h_{ab}(\text{std}) \qquad \Delta H^*_{ab} \text{ is +ve if } \Delta h_{ab} \text{ is +ve} \tag{15}$$

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 metameric 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 i of colorants in a sample, the global Kubelka–Munk *K/S* value at a given wavelength is:

$$\frac{K}{S} = \frac{K_t + \sum(K_i C_i)}{S_t + \sum(S_i C_i)} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{16}$$

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_∞ 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 i 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:

$$\frac{K}{S} = \frac{K_t + \sum(K_i C_i)}{S_t} = \left(\frac{K}{S}\right)_t + \sum\left(C_i \frac{K_i}{S_t}\right) = \left(\frac{K}{S}\right)_t + \sum(C_i a_i) \tag{17}$$

The value of *K/S* for the undyed material is the value $(K/S)_t$, 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

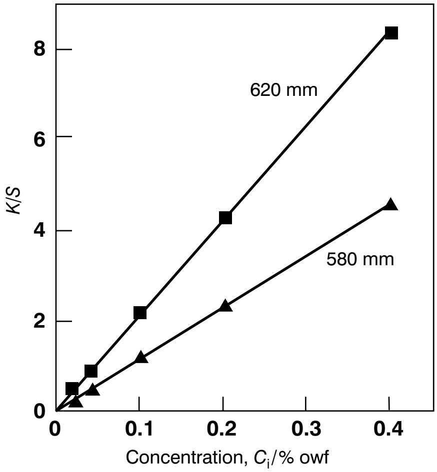


Figure 22.6 Graphs of *K*/*S* versus dye in the fibre at various wavelengths for dyeings of a disperse dye (Blue 5GL) on polyester

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:

$$\frac{K}{S} = \left(\frac{K}{S}\right)_t + C_i a_i = \frac{(1-R_\infty)^2}{2R_\infty} \tag{18}$$

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:

$$\left(\frac{K}{S}\right)_{std} = \left(\frac{K}{S}\right)_t + C_1 a_1 + C_2 a_2 + C_3 a_3 = \left(\frac{K}{S}\right)_m \tag{19}$$

Since the values of $(K/S)_{std}$ for the standard, $(K/S)_t$ 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

	Values of reflectance, *R* (%) (with *K/S* in parentheses)			Values of a_i		
	440 nm	520 nm	620 nm	440 nm	520 nm	620 nm
Yellow 5GL	8.56 (4.88)	69.51 (0.07)	83.27 (0.02)	24.28	0.24	0.01
Blue 5GL	38.53 (0.49)	28.70 (0.89)	9.63 (4.24)	2.31	4.34	21.13
Red FFN	26.93 (0.99)	9.83 (4.14)	76.65 (0.04)	4.81	20.59	0.11
Red BF	36.76 (0.54)	12.06 (3.21)	81.98 (0.02)	2.58	15.94	0.03
Undyed fabric	78.67 (0.03)	82.70 (0.02)	84.43 (0.01)			
Target shade	4.44 (10.28)	4.41 (10.36)	6.23 (7.06)			

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:

$$R = 0.0856, \quad \frac{K}{S} = \frac{(1-0.0856)^2}{2\times 0.0856} = 4.88 \tag{20}$$

For the undyed polyester, the reflectance at 440 nm is 78.67% and:

$$R = 0.7867, \quad \left(\frac{K}{S}\right)_t = \frac{(1-0.7867)^2}{2\times 0.7867} = 0.029 \tag{21}$$

For the dyeing with 0.20% Yellow 5GL at 440 nm:

$$\frac{K}{S} = \left(\frac{K}{S}\right)_t + C_i a_i, \quad 4.88 = 0.029 + 0.20\times a_i, \quad a_i = 24.28 \tag{22}$$

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:

$$\begin{aligned}\text{At 440 nm, } 10.28 &= 0.03+24.28C_1+2.31C_2+4.81C_3\\ \text{At 520 nm, } 10.36 &= 0.02+0.24C_1+4.34C_2+20.59C_3\\ \text{At 620 nm, } 7.06 &= 0.01+0.01C_1+21.13C_2+0.11C_3\end{aligned} \tag{23}$$

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.

$$\left(\frac{K}{S}\right)_m = F_m = \left(\frac{K}{S}\right)_t + C_1a_1 + C_2a_2 + C_3a_3 \tag{24}$$

$$F_m = \frac{(1-R_m)^2}{2R_m} \text{ or } R_m = (1+F_m) - \sqrt{F_m^2 + 2F_m} \tag{25}$$

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 D_{65} and the 1964 supplementary standard observer, the CIELAB colour difference (ΔE^*_{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.

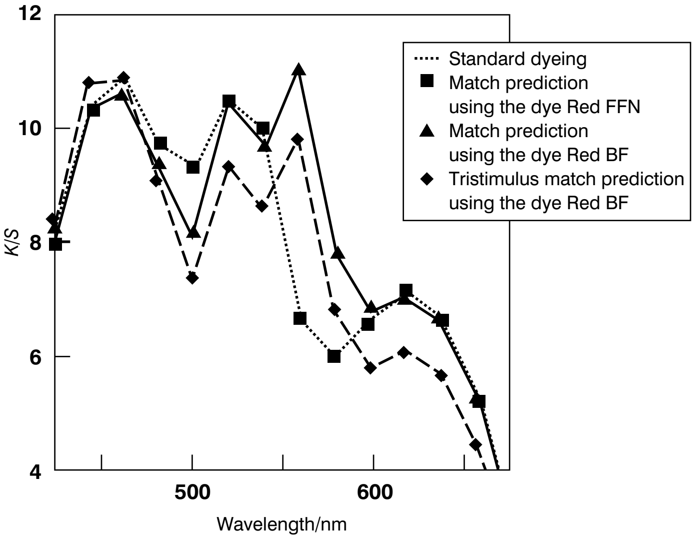


Figure 22.7 Predicted spectra (*K*/*S* versus wavelength) for matching the standard shade in Table 22.3

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 Eqns 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 $(K/S)_t$ placed on the left hand side.

$$\begin{aligned} 10.28 - 0.03 &= 24.28C_1 + 2.31C_2 + 2.58C_3 \\ 10.36 - 0.02 &= 0.24C_1 + 4.34C_2 + 15.94C_3 \\ 7.06 - 0.01 &= 0.01C_1 + 21.13C_2 + 0.03C_3 \end{aligned} \tag{26}$$

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

Matrix A				Matrix C		Matrix B
24.28	2.31	2.58		C_1		10.28 – 0.03 = 10.25
0.24	4.34	15.94	×	C_2	=	10.36 – 0.02 = 10.34
0.01	21.13	0.03		C_3		7.06 – 0.01 = 7.05

$$A \times C = B \tag{27}$$

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 × C_1) plus (2.31 × C_2) plus (2.58 × C_3). 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.

For calculating a dyeing formula, Matrix C is the unknown. It is obtained by dividing Matrix B by Matrix A, or, in other words, Matrix B is multiplied by the inverse of Matrix A .

$$C = \frac{B}{A} \quad \text{or} \quad C = B \times A^{-1} \tag{28}$$

The inverse of Matrix A (Matrix A^{-1}) is a 3 × 3 matrix of numbers that when multiplied by Matrix A gives the Identity Matrix. The latter is a square matrix

Table 22.5 Illustration of matrix multiplication to give the Identity matrix

Matrix A				Matrix A^{-1}				Identity matrix, ($A \times A^{-1}$)		
24.28	2.31	2.58		0.0413	–0.0067	–0.0031		1	0	0
0.24	4.34	15.94	×	0.0000	–0.0001	0.0473	=	0	1	0
0.01	21.13	0.03		–0.0006	0.0629	–0.0128		0	0	1

Table 22.6 Dyebath formulation by matrix multiplication

Matrix A^{-1}				Matrix B		Matrix C
0.0413	–0.0067	–0.0031		10.25		0.332
0.0000	–0.0001	0.0473	×	10.34	=	0.332
–0.0006	0.0629	–0.0128		7.05		0.553

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 × 3 rows). In the usual algebraic notation:

$$\frac{A}{A} = A \times A^{-1} = 1.0 \tag{29}$$

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 × 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 ($A \times A^{-1}$):

$$(24.28 \times 0.0413) + (2.31 \times 0) + (2.58 \times -0.0006) = 1.00 \tag{30}$$

The second value down the left column of the identity matrix (A × A^{-1} is given by:

$$(0.24 \times 0.0413) + (4.34 \times 0) + (15.94 \times -0.0006) = 0 \qquad (31)$$

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 metameric 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:

$$\left(\frac{K}{S}\right)_m = F_m = \left(\frac{K}{S}\right)_t + C_1a_1 + C_2a_2 + C_3a_3 + \ldots \qquad (32)$$

$$R_{\mathrm{m}} = (1 + F_{\mathrm{m}}) - \sqrt{F_{\mathrm{m}}^2 + 2F_{\mathrm{m}}} \tag{33}$$

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 (δX/δC). It is called a partial derivative and written δX/δC 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:

$$\mathrm{dX} = \mathrm{slope}\left(\frac{\delta \mathrm{X}}{\delta \mathrm{C}}\right) \times \mathrm{dC} \tag{34}$$

Similarly:

$$\mathrm{dY} = \left(\frac{\delta \mathrm{Y}}{\delta \mathrm{C}}\right)\mathrm{dC} \quad \mathrm{dZ} = \left(\frac{\delta \mathrm{Z}}{\delta \mathrm{C}}\right)\mathrm{dC} \tag{35}$$

The total change of each tristimulus value can be written with a term for the effect of each dye concentration:

$$\begin{aligned}
\mathrm{dX} &= \left(\frac{\delta \mathrm{X}}{\delta \mathrm{C}_1}\right)\mathrm{dC}_1 + \left(\frac{\delta \mathrm{X}}{\delta \mathrm{C}_2}\right)\mathrm{dC}_2 + \left(\frac{\delta \mathrm{X}}{\delta \mathrm{C}_3}\right)\mathrm{dC}_3 \\
\mathrm{dY} &= \left(\frac{\delta \mathrm{Y}}{\delta \mathrm{C}_1}\right)\mathrm{dC}_1 + \left(\frac{\delta \mathrm{Y}}{\delta \mathrm{C}_2}\right)\mathrm{dC}_2 + \left(\frac{\delta \mathrm{Y}}{\delta \mathrm{C}_3}\right)\mathrm{dC}_3 \\
\mathrm{dZ} &= \left(\frac{\delta \mathrm{Z}}{\delta \mathrm{C}_1}\right)\mathrm{dC}_1 + \left(\frac{\delta \mathrm{Z}}{\delta \mathrm{C}_2}\right)\mathrm{dC}_2 + \left(\frac{\delta \mathrm{Z}}{\delta \mathrm{C}_3}\right)\mathrm{dC}_3
\end{aligned} \tag{36}$$

This is expressed as the usual matrix multiplication:

$$\begin{matrix} \frac{\delta X}{\delta C_1} & \frac{\delta X}{\delta C_2} & \frac{\delta X}{\delta C_3} \\ \frac{\delta Y}{\delta C_1} & \frac{\delta Y}{\delta C_2} & \frac{\delta Y}{\delta C_3} \\ \frac{\delta Z}{\delta C_1} & \frac{\delta Z}{\delta C_2} & \frac{\delta Z}{\delta C_3} \end{matrix} \times \begin{matrix} \delta C_1 \\ \delta C2 \\ \delta C3 \end{matrix} = \begin{matrix} dX \\ dY \\ dZ \end{matrix} \tag{37}$$

$$\text{Influence Matrix I} \times \text{Matrix C} = \text{Matrix T}$$

or:

$$I \times C = T \tag{38}$$

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:

$$X = \sum W_X R \tag{39}$$

calculated over 16 equally spaced wavelengths, where W_X 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:

$$\frac{dX}{dC_1} = \sum W_X \left(\frac{dR}{dC_1} \right) = \sum W_X \left(\frac{dR}{dF} \right) \left(\frac{dF}{dC_1} \right) \tag{40}$$

Since F in this equation is K/S, dF/dC_1 is the value of a_1. Differentiation of:

$$F = \frac{(1-R)^2}{2R} \tag{41}$$

gives:

$$\frac{dF}{dR} = \frac{(R^2-1)}{2R^2} \text{ or } \frac{dR}{dF} = \frac{2R^2}{(R^2-1)} \tag{42}$$

The values of *R* used in the calculation are usually those of the target sample. Thus, the equation for $\partial X/\partial C_1$ becomes:

$$\frac{dX}{dC_1} = \sum W_X \left(\frac{dR}{dF}\right)\left(\frac{dF}{dC_1}\right) = \sum\left(W_X \times \frac{2R^2}{(R^2-1)} \times a_1\right) \qquad (43)$$

for which all the values are known at each wavelength. The other eight values in the Influence Matrix I are calculated similarly.

It is now possible to calculate the values of the Concentration Matrix C. To do this, the Tristimulus Matrix T is multiplied by the inverse of the Influence Matrix. The latter (I^{-1}) is called the Correction Matrix:

$$I \times C = T \text{ so } C = T \times I^{-1} \qquad (44)$$

Once the required concentration changes have been calculated, the new more appropriate values are given by:

$$\begin{aligned} \text{New } C_1 &= \text{Old } C_1 + dC_1 \\ \text{New } C_2 &= \text{Old } C_2 + dC_2 \\ \text{New } C_3 &= \text{Old } C_3 + dC_3 \end{aligned} \qquad (45)$$

where the 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 dX, dY and dZ.

This calculation sequence is repeated until values of dX, dY and dZ are within acceptable limits, such as less than 0.02, or until ΔE^*_{ab} or ΔE_{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 C_1 = 0.361% (Yellow 5GL), C_2 = 0.285% (Blue 5GL) and 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 ΔE^*_{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 22.7 Tristimulus matching of the formula with Red BF; target tristimulus values X = 5.88, Y = 5.72, Z = 4.99

	1	2	3	4
Iteration	initial			final
C_1 Yellow 5GL	0.332	0.357	0.361	0.361
C_2 Blue 5GL	0.332	0.289	0.285	0.285
C_3 Red BF	0.553	0.509	0.498	0.497
X	5.31	5.80	5.87	5.88
Y	5.15	5.63	5.72	5.72
Z	5.07	4.99	4.99	4.99
dX	0.57	0.08	0.01	0.00
dY	0.57	0.09	0.00	0.00
dZ	–0.08	0.00	0.00	0.00
ΔE^*_{ab}	3.40	0.55	0.05	0.00
dC_1	0.025	0.004	0.0006	4.9×10^{-5}
dC_2	–0.043	–0.004	–0.0004	-6.0×10^{-6}
dC_3	–0.044	–0.110	–0.0007	-7.0×10^{-5}

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:

$$N = \frac{m!}{3! \times (m-3)!} \qquad (46)$$

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 D_{65} 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.

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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.

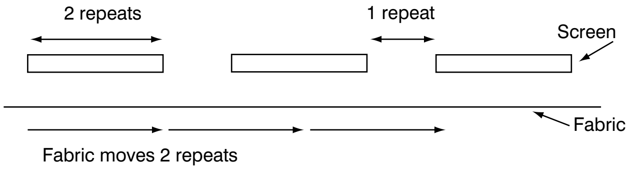


Figure 23.1 Screen placement and fabric movement as a function of repeat size in automated flat screen printing

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.

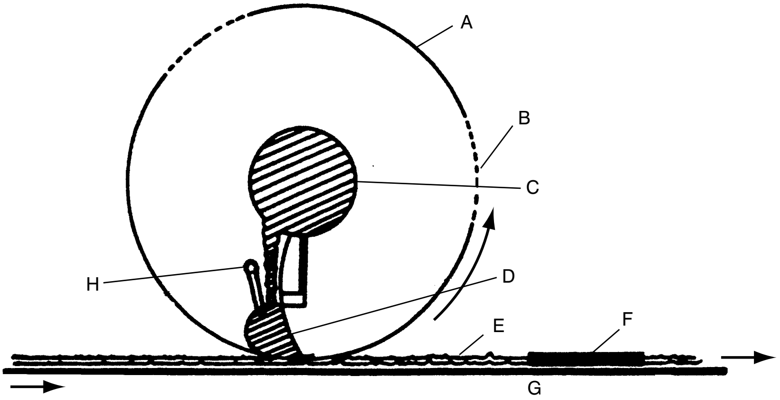
The screen mesh varies from about 60 up to 150 holes per linear inch depending upon the type of pattern and the fabric. There is always a tendency for the edges of printed areas to have a serrated appearance. This comes from the arrangement of the spaces between the threads along the edge of an open 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.



A	Screen
B	Open (design) area
C	Print paste feed
D	Squeegee blade
E	Fabric
F	Printed area
G	Blanket
H	Level control (from end of screen)

Figure 23.2 Interior of a rotary printing screen (from *Colour for Textiles, A User's Handbook*, Wilfred Ingamells, SDC, 1993 – Chapter 6, Figure 14, p. 129)

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 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.

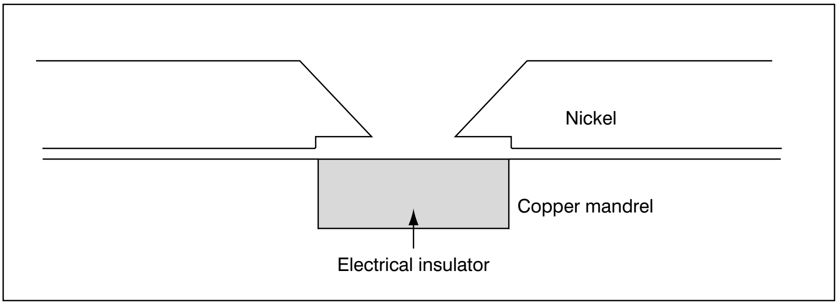


Figure 23.3 Electroplating of a nickel screen (from *Textile Printing*, 2nd Edn, L W C Miles (Ed), SDC, 1994 – Chapter 2, Figure 18, p. 47)

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

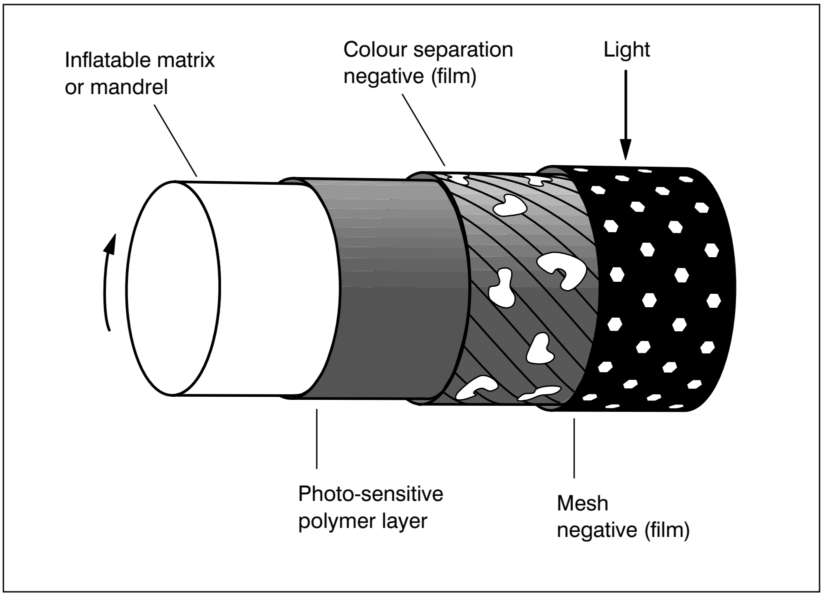


Figure 23.4 Arrangement of films for producing a galvano nickel screen (from *Textile Printing*, 2nd Edn, L W C Miles (Ed), SDC, 1994 – Chapter 2, Figure 21, p. 50)

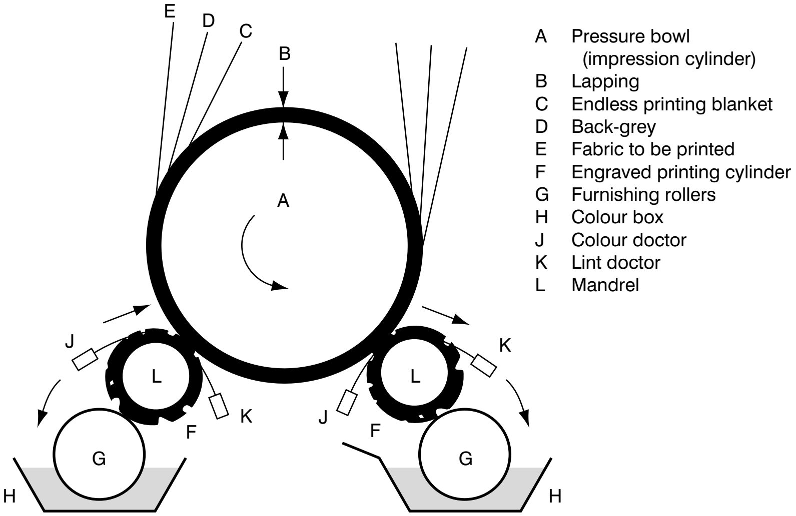


Figure 23.5 Illustration of colour boxes on the printing bowl (from *Textile Printing*, 2nd Edn, L W C Miles (Ed), SDC, 1994 – Chapter 1, Figure 4, p. 12)

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

$$\mathrm{Cu + 4HNO_3 \rightleftharpoons Cu(NO_3)_2 + 2NO_2 + 2H_2O}$$

$$\mathrm{Cu + 2Fe^{3+} \rightleftharpoons Cu^{2+} + 2Fe^{2+}}$$

Scheme 23.1

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 dyed 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 ($HOCH_2SO_2^-$). On heating, these decompose liberating formaldehyde and the sulphoxylate ion (HSO_2^-), a powerful reducing agent (Scheme 23.2). The decomposition of thiourea dioxide also generates sulphoxylate. On heating, thiourea dioxide first rearranges to formamidine sulphinic 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.

$$\mathrm{HOCH_2SO_2^-} \rightleftharpoons \mathrm{CH_2O} + \mathrm{HSO_2^-}$$

Scheme 23.2

$$\mathrm{(NH_2)_2C{=}SO_2} \rightleftharpoons \mathrm{NH_2C({=}NH){-}SO_2H}$$

$$\mathrm{NH_2C({=}NH)SO_2H} + \mathrm{H_2O} \longrightarrow \mathrm{(NH_2)_2C{=}O} + \mathrm{H_2SO_2}$$

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).

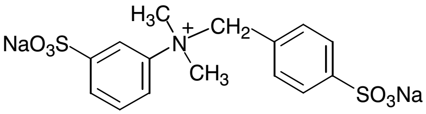


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Figure 23.6 *p*-Sulphobenzyl-dimethylanilinium-*m*-sulphonate

$$R_3N^+{-}CH_2C_6H_4SO_3^- + Ar{-}NH_2 \longrightarrow R_3NH^+ + Ar{-}NH{-}CH_2C_6H_4SO_3^-$$

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 steamed. 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.

$$\text{Dye}{-}SO_2CH{=}CH_2 + HSO_3^- \longrightarrow \text{Dye}{-}SO_2{-}CH_2CH_2{-}SO_3^-$$

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 coagulate on the fabric surface and coalesce into a coherent film. By regulating 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

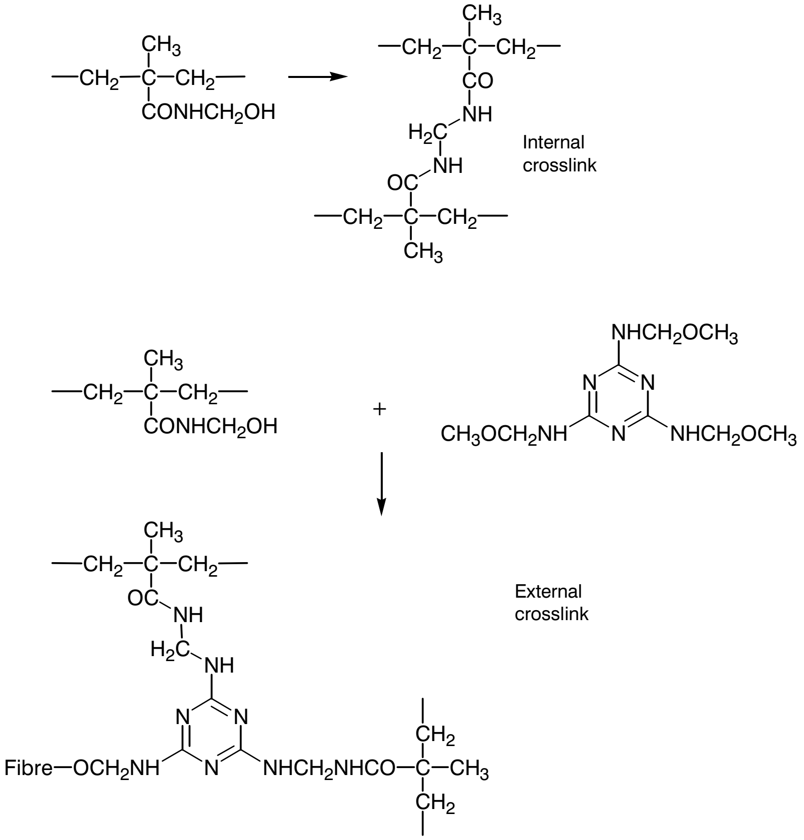

Figure 23.7 Internal and external crosslinking of a binder during curing

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

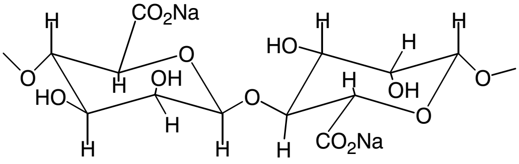

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Figure 23.8 Sodium alginate

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*-nitrobenzene sulphonate 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 ($HOCH_2SO_2Na$) 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 diazoamino 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 (aminoimino-isoindolene), 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 (NH_2CSNH_2) and thiodiethyleneglycol ($HOCH_2CH_2SCH_2CH_2OH$) 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 vaporised 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 vaporised 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 dyeing, the partition coefficients are much higher than for aqueous systems and the dye rapidly adsorbs 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 vaporised 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

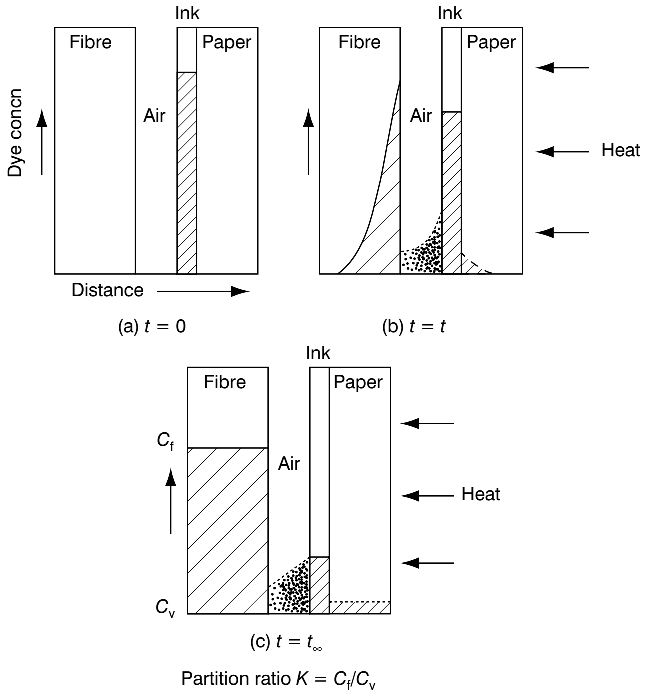

Figure 23.9 Dye transfer during vapour phase printing (from *Textile Printing*, 2nd Edn, L W C Miles (Ed), SDC, 1994 – Chapter 3, Figure 1, p. 74)

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.

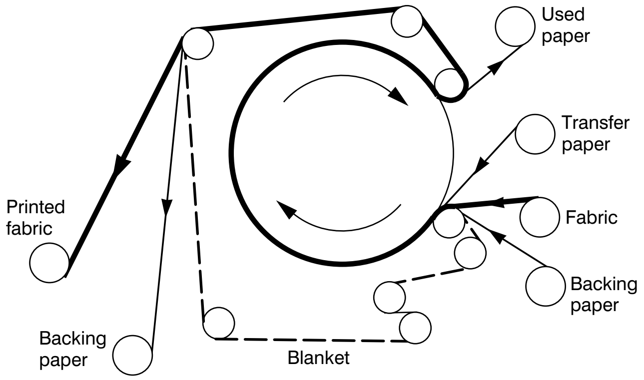

Figure 23.10 Continuous transfer printing unit (from *Textile Printing*, 2nd Edn, L W C Miles (Ed), SDC, 1994 – Chapter 3, Figure 5, p. 80)

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;

Table 23.1 Typical non-emulsion pigment printing paste

Chemical	Amount (%)	Role
Pigments	15	Colorants
Trimethylolmelamine	14	Pigment binder
$NH_4(H_2PO_4)$ 10% aq	1	Catalyst for binder crosslinking
Water	35	
Gum tragacanth dispersion 6%	35	Thickener

Table 23.2 Approximate composition of a pigment-illuminated discharge print paste for a fabric already dyed with reactive dyes

Chemical	Amount (%)	Role
Pigments		Colorants
Zinc formaldehyde-sulphoxylate	5	Discharge reducing agent
Reactive acrylic copolymer	10	Pigment binder
Tartaric acid	1	Catalyst for binder crosslinking
White spirit	60	Emulsion thickener
Carboxymethylcellulose	7	Natural thickener
Water	11	
Urea	5	Humectant
Emulsifiant	1	

(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;

(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 Poisseuille equation gives the flow rate of liquid through cylindrical holes:

$$Q = \frac{Pa^4}{8l\eta} \tag{1}$$

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 η 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 Poisseuille 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, d*v*/d*x*. The viscosity is therefore:

$$v = \frac{f/A}{\mathrm{d}v/\mathrm{d}x} \tag{2}$$

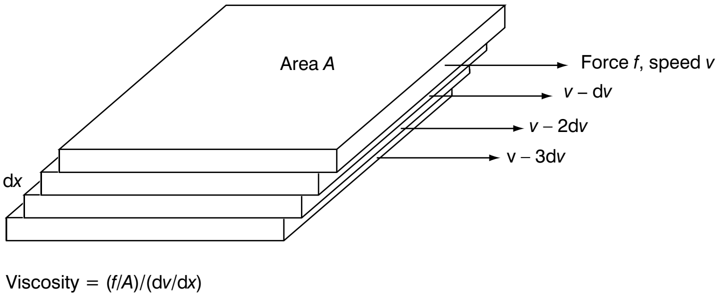

Figure 23.11 Flow of liquid layers beneath a rigid plate illustrating the definition of viscosity

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.

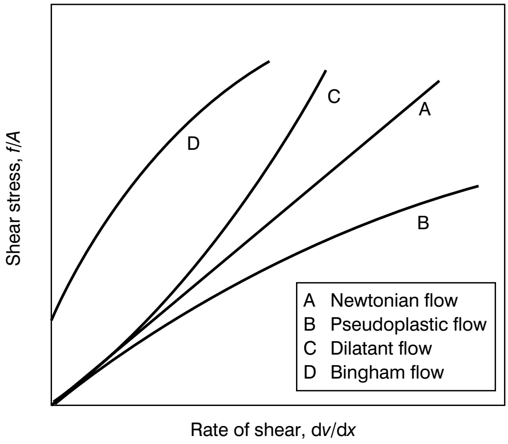

Figure 23.12 Shear stress versus rate of shear for different types of liquids

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.

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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:

$$A(\lambda) = \log\left(\frac{I_0}{I_t}\right) = \varepsilon(\lambda)Cl = \log\left(\frac{100}{T(\lambda)}\right) \qquad (1)$$

where A is the absorbance or optical density at wavelength λ, I_0 is the intensity of the incident light of fixed wavelength λ, 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, ε is the absorptivity or extinction coefficient at wavelength λ, and T is the percentage transmission of the monochromatic light through the solution. The symbol λ in brackets after A, T and ε, 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 ε 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 ε 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 ε has units of l mg^{-1} cm^{-1}.

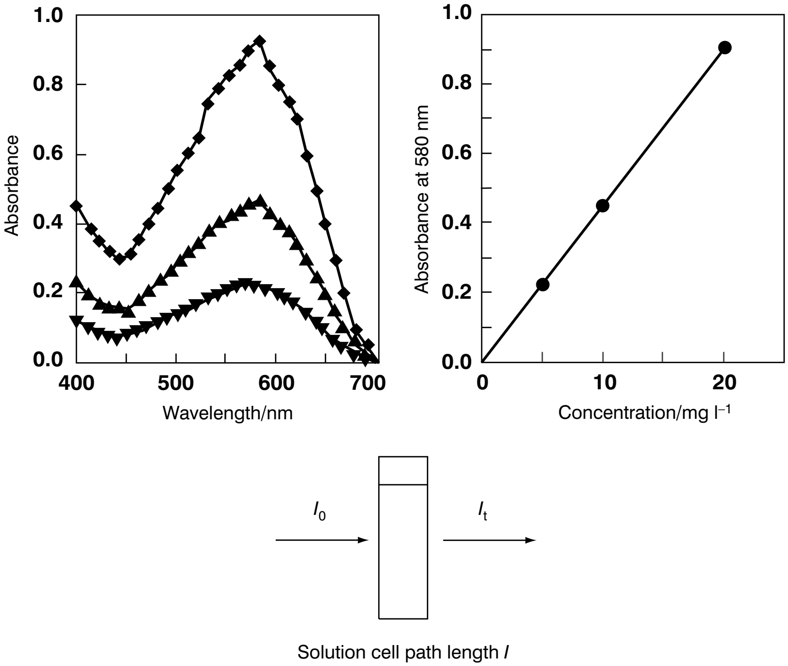


Figure 24.1 A spectrophotometric cell holding a dye solution, its absorption spectra for three different dye concentrations, and the graph of absorbance as a function of concentration

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).

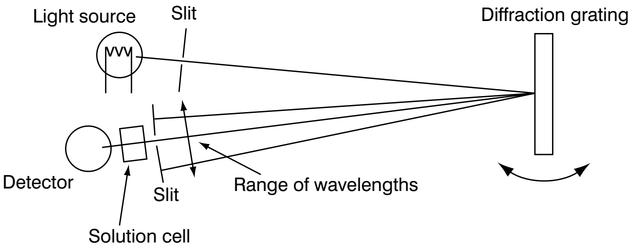


Figure 24.2 Schematic of a simple solution absorption spectrophotometer

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]:

$$\text{Colour strength} = \sum_{\lambda=380}^{\lambda=780} [(K/S)\times(x_{10}+y_{10}+z_{10})] \qquad (2)$$

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 (ΔE^*_{ab}, 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 shows 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

Table 24.1 Relation between CIELAB colour differences for fading and staining and the Grey Scale fastness grade

CIELAB colour difference for fading	Colour fastness grade	CIELAB colour difference for staining
<0.40	5	<1.10
0.40–1.25	4–5	1.10–3.25
1.25–(1.7)–2.10	4	3.25–(4.3)–5.15
2.10–2.95	3–4	5.15–7.25
2.95–(3.4)–4.10	3	7.25–(8.5)–10.25
4.10–5.80	2–3	10.25–14.45
5.80–(6.8)–8.20	2	14.45–(16.9)–20.45
8.20–11.60	1–2	20.45–29.05
>11.60	1	>29.05

intermediate grades for sample colour contrasts between those of two adjacent Grey Scale pairs. These are expressed as 3–4, 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 ΔE^*_{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–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 (4–5, 3–4, 2–3 and 1–2).

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 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

Fastness grade	Shade change of tested sample	Fastness	Staining of adjacent white sample
Grade 5	No change	Excellent	No staining
Grade 4	Slight loss in depth	Good	Very slight staining
Grade 3	Appreciable loss	Fair	Moderate staining
Grade 2	Significant loss	Poor	Significant staining
Grade 1	Great loss in depth	Very poor	Deep staining

Table 24.3 Description of the light fastness grades

Fastness grade	Degree of fading	Light fastness
Grade 8	None	Outstanding
Grade 7	Very, very slight	Excellent
Grade 6	Slight	Very good
Grade 5	Moderate	Good
Grade 4	Appreciable	Moderate
Grade 3	Significant	Fair
Grade 2	Extensive	Poor
Grade 1	Very extensive	Very poor

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 ΔE^*_{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 (ΔE^*_{ab}) and the lightness difference (ΔL^*). 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].

Table 24.4 Conditions of the ISO washing fastness tests

Test	Temperature (°C)	Time (min)	Steel balls	Chemicals
ISO 1	40	30	0	Soap
ISO 2	50	45	0	Soap
ISO 3	60	30	0	Soap + Na_2CO_3
ISO 4	95	30	10	Soap + Na_2CO_3
ISO 5	95	240	10	Soap + Na_2CO_3

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 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.

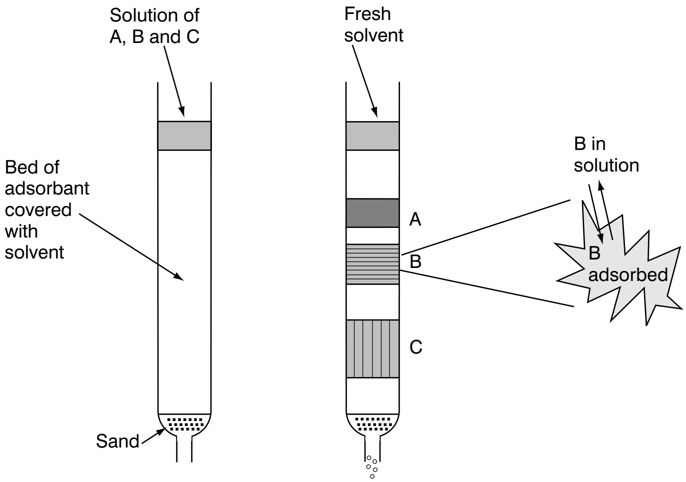


Figure 24.3 Illustration of the initial and final chromatography column, of the type used by Tswett, with an enlargement showing the adsorption equilibrium

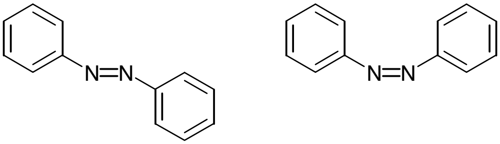
The stationary phase may consist of particles packed into a column or forming a plane, thin sheet such as the fibres in a sheet of paper or a layer of adsorbent coated onto a glass plate. In column chromatography, the flow of the mobile phase is either vertically downward under the influence of gravity, 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 (Al_2O_3) or silica gel (SiO_2). 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.



1 **2**

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

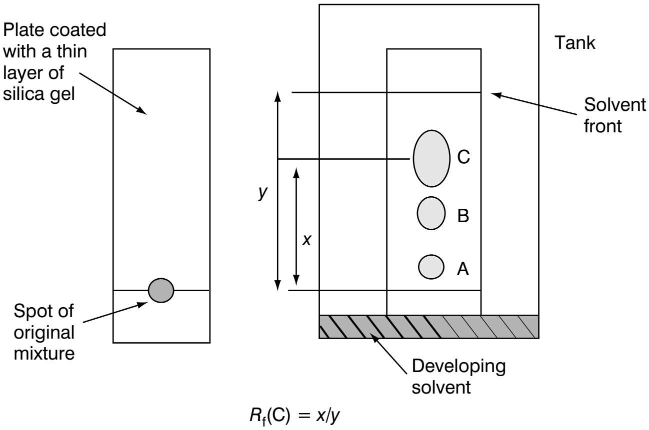


Figure 24.5 Thin layer chromatography

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.

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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 smoothes its surface and loosens

Table 25.1 Mechanical finishing processes and their objectives

Process	Objective
Calendering	Pressing and smoothing the surface of the fabric
Napping or raising	Breaking fibres in the yarn surface and raising a pile
Brushing	Laying the pile in the same direction
Shearing	Cutting the pile fibres all to the same length
Compressive shrinking	Compressing the fabric to the dimensions it would have after shrinkage caused by washing

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 strains introduced during manufacture or use will invariably result 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 unfixed 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 polymerisation 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

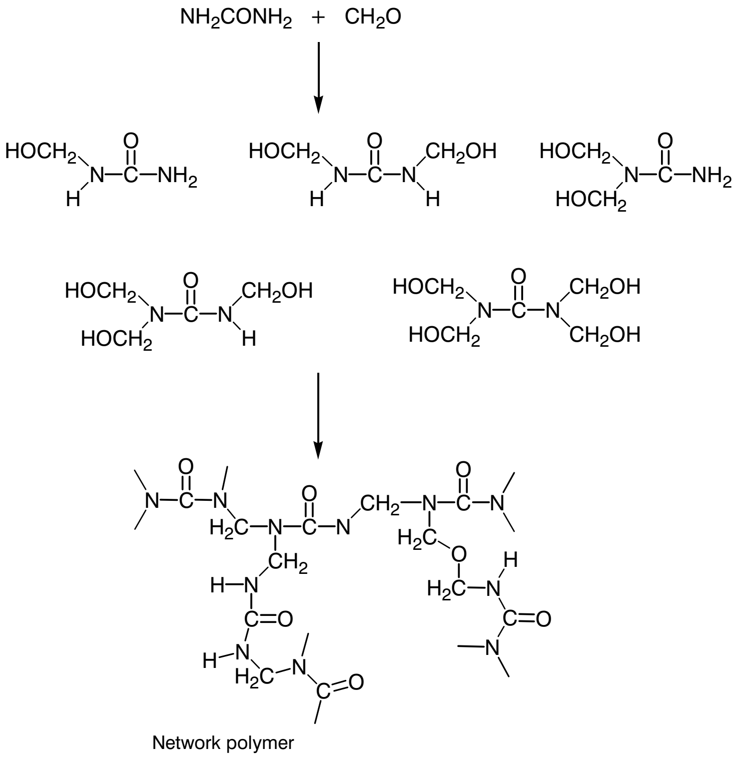


Figure 25.1 Condensation polymerisation of urea and formaldehyde

$$\mathrm{R{-}NHCH_2OH + R{-}NH_2 \rightleftharpoons R{-}NHCH_2NH{-}R + H_2O}$$

$$\mathrm{2R{-}NHCH_2OH \rightleftharpoons R{-}NHCH_2OCH_2NH{-}R + H_2O}$$

Scheme 25.1

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

	Untreated	5% Urea – CH_2O 1:2/ $Zn(NO_3)_2$	5% DMDHEU* $MgCl_2$
Crease recovery angle (dry) **	150	260	265
% Loss of abrasion resistance		42	25
% Loss of weft tear strength		38	22
% Loss of weft tear strength after chlorine bleaching and ironing		59	25

* See Figure 25.2

** Average for creasing across the warp and weft directions

$$\text{Resin—NH}_2 + Cl_2 \rightleftharpoons \text{Resin—NHCl} + HCl$$

$$\text{Resin—NHCl} + H_2O \rightleftharpoons \text{Resin—NH}_2 + HOCl$$

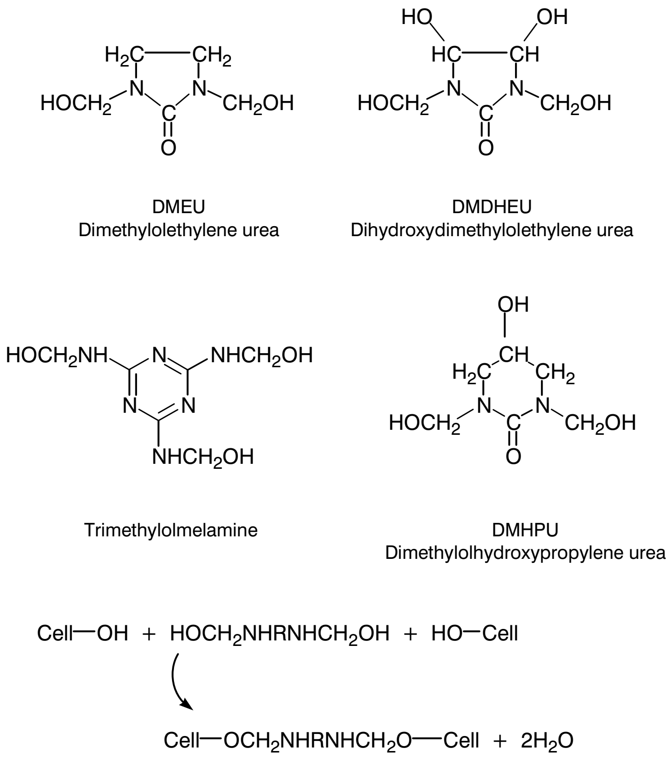
$$2HOCl + R\text{—}CHO \longrightarrow Cl_2 + R\text{—}CO_2H + H_2O$$

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

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.



DMEU
Dimethylolethylene urea

DMDHEU
Dihydroxydimethylolethylene urea

Trimethylolmelamine

DMHPU
Dimethylolhydroxypropylene urea

$$\text{Cell—OH} + \text{HOCH}_2\text{NHRNHCH}_2\text{OH} + \text{HO—Cell} \rightarrow \text{Cell—OCH}_2\text{NHRNHCH}_2\text{O—Cell} + 2\text{H}_2\text{O}$$

Figure 25.2 Typical crosslinking agents for crease-resist fabrics of cellulosic fibres

Table 25.3 Typical composition of a crease-resist finishing bath

Chemical	Amount in the bath solution %	Function
DMDHEU	6.0	Crosslinking agent
$MgCl_2.6H_2O$	2.0	Acid catalyst for DMDHEU
Ethyl silicate ester	0.5	Increases resistance to abrasion and tearing
Polyethylene glycol	0.5	Softening agent
Non-ionic surfactant	0.1	Wetting agent

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).

$$R\text{—}NHCH_2NH\text{—}R + H_2O \rightleftharpoons 2\,R\text{—}NH_2 + CH_2O$$

$$R\text{—}NHCH_2OH \rightleftharpoons R\text{—}NH_2 + CH_2O$$

Scheme 25.3

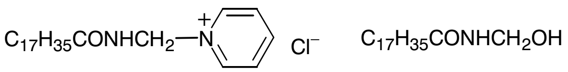
For durable-press finishing, the fabric is impregnated with the same types of polymer or crosslinking precursors and dried without curing. Once the finished article has been assembled, it is hot pressed in the required shape, when crosslinking and polymerisation occur stabilising the form of the article. 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^{3+} 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.



1 **2**

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

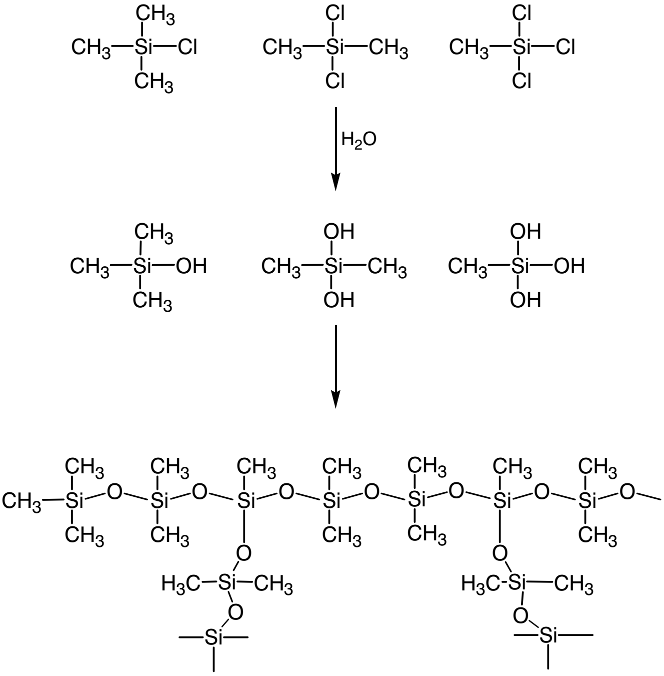


Figure 25.4 Polymerisation of methylsilanols

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 25.5). 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.

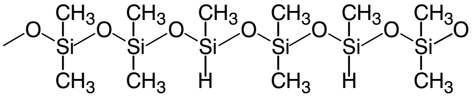


Figure 25.5 Reactive polysiloxanes

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.

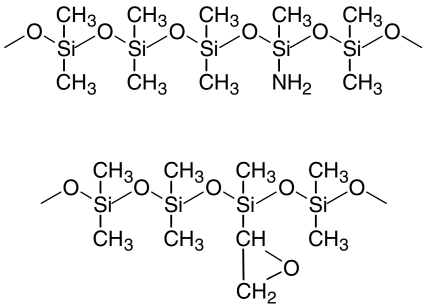


Figure 25.6 Functionalised polysiloxanes

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.

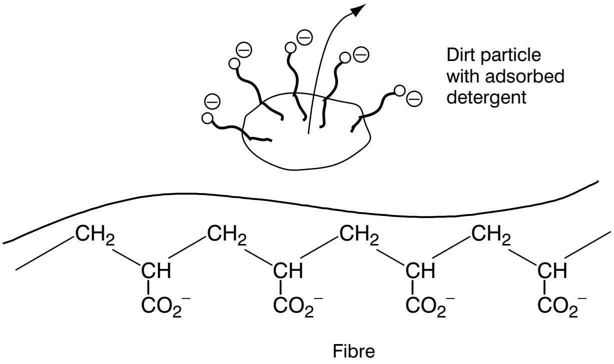


Figure 25.7 Function of a polyacrylate soil-release finish

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:

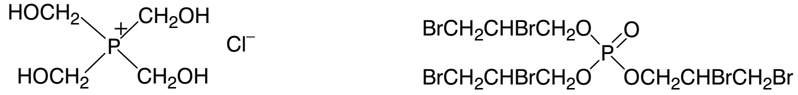
(1) decomposition of the chemical on heating to give a non-combustible gas that envelops the fibres and excludes oxygen. Ammonium salts that release ammonia on heating are typical examples, but they are water-soluble and not resistant to washing;
(2) decomposition on heating to produce a deposit on the 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.

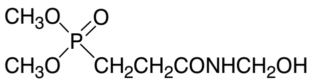
The release of these gases prevents oxygen from reaching the fibres. Borax coats the fibres with boron oxide and reduces the evolution of combustible gases. To increase washing fastness, various insoluble salts such as metal oxides can be precipitated in the fibres.

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)



THPC,
tetrahydroxymethylphosphonium chloride

BAP,
tri-dibromoallyl phosphate



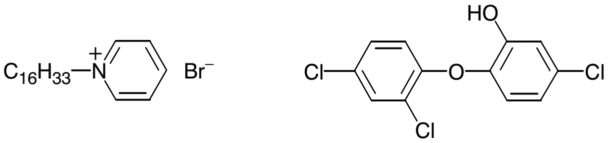
Pyrovatex (Ciba)

Figure 25.8 Typical flame-retardant chemicals

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 quaternary 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).



3 **4**

Figure 25.9

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

1. M Lewin, Ed, *Handbook of Fiber Science and Technology, Vol. II, Functional Finishes*, Parts A and B (New York: Marcel Dekker, 1983, 1984).