

- 21 Simpson W S, 'Efficient flameproofing agents for wool', *Proc. 4th Int. Wool Text. Conf.*, Berkeley, Calif., *App. Polymer Symp.*, 1971, **18**, 1177–82.
- 22 Basch A, Zvilichovsky B, Hirshmann B and Lewin M, 'The chemistry of THPC-urea polymers and relationship to flame-retardance on wool and wool-polyester blends', *J. Polymer Sci. (Chem.)*, 1979, **17(1)**, 39–47.
- 23 Benisek L, 'Improvement of the natural flame-resistance of wool, Part I: Metal-complex applications Part II: Multi-purpose finishes', *J. Text. Inst.*, 1974, **65**, 102–8, 140–5.
- 24 Benisek L, 'Part III Vanadium, molybdenum and tungsten complexes', *ibid*, 1976, **67**, 226–7.
- 25 Beck P J, Gordon P G and Ingham P E, 'Thermogravimetric analysis of flame retardant treated wools', *Text. Res. J.*, 1976, **46**, 478–83.
- 26 Ingham P E, 'The pyrolysis of wool and the action of flame retardants', *J. Appl. Polymer Sci.*, 1971, **15**, 3025–41.
- 27 Ingham P E and Benisek L, 'The hydrolysis of fluorozirconate on wool', *J. Text. Inst.*, 1977, **68**, 176–83.
- 28 Leaver I, 'Photo-protective mechanisms in wool. A study of the photo-protective effect of a thiourea/formaldehyde treatment', *Text. Res. J.*, 1978, **48**, 610–8.
- 29 Dodds M M, 'Stable colours for wool carpets', *WRONZ Technical Bulletin*, November 1996.
- 30 Cegarra J, Ribe J and Miro P, 'Use of 2,4 Dihydroxybenzophenone-2-ammonium sulphonate to prevent the yellowing of wool by ultra-violet radiation', *J. Soc. Dyers and Col.*, **88**, 293–6.
- 31 Waters P J and Evans N A, 'The effect of phenylbenzotriazole derivatives on the photoyellowing of wool', *Text. Res. J.*, 1978, **48**, 251–5.
- 31a Anon., 'Launch of new UV-absorber for wool', *Australasian Text.*, 1991, **11**, No. 2, 33.
- 32 Simpson W S, 'Photoprotection of wool fabrics by dyestuffs', *WRONZ Communication*, **77**, 1982.
- 33 Simpson W S and Page C T, 'Inhibition of light tendering of wool', *6th Int. Wool Text. Res. Conf.*, Pretoria, 1980, **V**, 183–93.
- 34 Namath Y K, 'Mechanisms of stainblocking', *Notes on research No. 481*, Text. Res. Inst., Princeton, USA, 1994.
- 35 Anon., 'Stainblockers for nylon fabrics', *Report No. 31*, Technical Information Centre, Text. Res. Inst., Princeton, USA, 1989.
- 36 Anon., 'Stain Resistance: Pile Floor Coverings', *AATCC Tech. Manual*, Vol. 75, 2000, Amer. Assoc. of Text. Chem. and Col., USA, 319–21.
- 37 Benisek L and Craven P C, 'Machine-washable, water- and oil-repellant, flame-retardant wool', *Text. Res. J.*, 1980, **50**, 705–10.
- 38 *Ibid.* 'Machine washable, flame-retardant water, oil, petrol and acid repellent wool'. 1984, **54**, 350–2.
- 39 *Ibid.* 'Flame-retardant multi-purpose finishes for wool', 1979, **49**, 395–7.
- 40 Guise G B and Freeland G N, 'Treatment of wool fabrics with mixtures of fluorochemicals and shrink-resist polymers', *Text. Res. J.*, 1982, **52**, 182–5.
- 41 Barr T and Speakman J B, 'The action of ethylene sulphide on wool', 1944, *J. Soc. Dyers and Col.*, **60**, 238–45.
- 42 McKinnon A J, 'The formation of co-polymers of butadiene with acrylonitrile and methacrylate by iron-salt-hydrogen peroxide initiation', *J. Appl. Polymer Sci.*, 1970, **14**, 3033–47.

- 43 Burke M, Kenny P and Nicholls C H, 'Free radicals in irradiated wool: Estimation and role in polymerisation of acrylonitrile', *J. Text. Inst.*, 1962, **53**, T370–8.
- 44 Stannett V, Araki K, Gervasi J A and McLesky S W, 'Radiation grafting of vinyl monomers to wool', *J. Polymer Sci.*, 1965, **A3**, 3768–74.
- 45 Simpson W S and van Pelt W B, 'New catalysts for graft copolymer formation in wool fibres', *J. Text. Inst.*, 1966, **57**, T493–504.
- 46 Ibid. 'Graft copolymerisation of acrylonitrile in wool', 1967, **58**, T316–25.
- 47 Early D B and Simpson W S, 'Wool copolymer ion-exchange materials', *Proc. 5th Int. Wool Text. Res. Conf.*, Aachen, 1975, **II**, 52–62.
- 48 Simpson W S, 'Polymer deposition in wool', *IWS Product Development Report* No. 143, Parts I and II, 1971 (copies available from WRONZ).
- 49 Simpson W S, Bratt R L and Noonan K K, 'The wear performance of carpets made from wool', *J. Text. Inst.*, 1973, **64**, 449–53.
- 50 Simpson W S, 'Production and properties of wool with incorporated polymers', *Proc. 4th Int. Wool Text. Conf.*, Berkeley, Calif, *Appl. Polymer Symp.*, No. 18. J Wiley and Sons, NY, 585–92, 1971.
- 51 Crewther W G and Pressley T A, 'Carbonising investigations, Part VI: A comparison of different types of surface active agents in laboratory carbonising', *Text. Res. J.*, 1959, **29**, 482–6.
- 52 Hille E and Zahn H, 'Peptidyl shift during wool carbonising', *J. Text. Inst.*, 1960, **51**, Part II, T1162–7.
- 53 Crewther W G, 'Thiol-disulphide interchange reactions in the setting of single wool fibres', *J. Soc. Dyers Col.*, 1966, **82**, 54–8.

8.1 Introduction

The physical and chemical properties of wool vary greatly between breeds of sheep, the climates in which the wools are grown and the diet and health of the sheep. The physical properties vary in terms of fibre diameter, length and crimp whereas the chemical properties exhibit variety in terms of amino acid content. Additionally, wools also vary in base colour and have root tip differences that affect both dyestuff diffusion rates and mechanical properties. It is also common to blend wools having different base colours, diameters and fibre lengths. Such blends often exhibit markedly different dyeing properties and careful selection of dyestuff and dyeing auxiliary are required to ensure that the appearance of the coloured fibre is acceptable.

Dyeing can take place at a number of points in the production process. Wool can be dyed in either loose, slubbing, yarn, fashioned garment or piece form, and the fibre may be treated to impart shrink resistance either before or after dyeing.

Wool is often blended with other natural and synthetic fibres to combine the properties of handle, comfort and drape of the wool fibre with the additional properties of the other fibre. For example, wool is often blended with nylon to improve the resistance to wear in carpets and footwear. Blending polyester with wool is also common in apparel, as it allows the production of permanent-press tailored garments. Polyurethane elastomeric fibres are increasingly used in many apparel fabrics and when blended with wool provide additional comfort by allowing a degree of recoverable stretch. The use of both natural and synthetic fibres in blends with wool provides an additional challenge to the wool dyer.

Wool dyeing, like all forms of dyeing, is becoming more regulated. Shades need to be matched under a variety of illuminants, often to a spectral rather than a physical standard. The use of spectrophotometers to measure and specify colour has become commonplace and several colour difference

equations have been developed to improve the quality control in colour matching. As a consequence, the dyer often has to use a wider choice of dyes in order to ensure a satisfactory match under the specified illuminants and colour difference equations. Environmental requirements are also becoming more regulated and the dyer must take care to apply safe working practices whilst ensuring that production meets the environmental legislation relating to effluent, consumer protection and disposal or recycleability.

The market is demanding a quicker development and production cycle and, for this reason, there is an increasing demand for delaying colouration to a later stage in the process sequence from loose fibre to garment or carpet.

This chapter examines the types of dyestuffs available to the wool dyer to ensure that the dyeing process meets the necessary shade, level dyeing and environmental requirements, and that the resultant fibre has sufficient colour fastness to withstand both processing and consumer fastness demands, without adversely affecting the fibre quality.

8.2 Dyestuff chemistry

8.2.1 Natural dyestuffs

Before the introduction of synthetic dyes, the most important dyestuffs used for colouring wool were the natural dyes, such as those extracted from insects and plants. In ancient times, the dyestuffs applied to wool were chosen not only on the availability of natural dyes but also the culture. For example, green was the colour of Mohammed's coat and as such is sacred, so a Muslim would not produce a carpet with green as the principal colour. In Persia, blue was popular as it depicts heaven, whilst further east in Mongolia it symbolises power and authority. Red generally stands for wealth and joy whilst in China yellow is the Emperor's colour. The availability of natural dyes varied from region to region. The main source of dye was from vegetable or animal origin and a range of hues was available as follows:

| | |
|---|---------------------------|
| Madder (<i>Rubia Tinctorum</i>) | Red, crimson, maroon |
| Fustic (<i>Morus Tinctoria</i>) | Yellow, olive with chrome |
| Logwood | Black with chrome |
| Oak apples | Black |
| Indigo (<i>Indigofera – I. Tinctoria</i>) | Blue |
| Cochineal | Scarlet |
| Resedon plant | Yellow |
| Saffron crocus | Yellow |

Browns and greys were produced by blending naturally coloured wools.

Cochineal is the only dye listed from animal origin. It is the extract of the female beetle that lives on the *Coccus Cacti* plant, and its main use is to produce scarlet uniform cloths.

Red was the principal colour used on oriental wool carpets, and the natural dye most widely available. It comes mainly from madder, which is a perennial plant that grows some 3–4 feet high, and the dye called Alizarin can be extracted from the root of the plant after it is 3 years old. The dye is extracted by boiling the rasped root in water, followed by filtering to give the impure dissolved dye.¹ This solution is evaporated to dryness and the residue is powdered and spread on a cellulose cloth. Heat is applied and the impurities are adsorbed by the cellulose whilst the colour – Alizarin – sublimates onto the surface in the form of red/orange crystals.

The ancient dyers had only a limited number of dyes to work with. Their quality and strength varied considerably from one manufacturer to another and impurities affected the shade, making shade matching and shade reproducibility difficult.

Most natural dyes require a mordant, which means that they combine with a metal to produce strong intense colours. Most mordant dyes are poly-genetic which means that they produce a different shade with different metal mordants. Alizarin, for example, produces a bright red shade with either a calcium or an aluminium mordant, whilst a chrome mordant gives a maroon shade and an iron mordant produces a dull violet. The metal mordant can also affect the colour fastness properties of the dyed wool. The aluminium complex is of low light fastness, iron and chrome complexes are light fast but the chrome complex is superior, being both wetfast and lightfast.

8.2.2 Synthetic dyes

In 1869, Alizarin was synthesised and its commercial production commenced in 1871. The synthetic version of this anthraquinone-based dyestuff soon replaced the natural product. Following this, the increased knowledge of dyestuff chemists led to the production of many synthetic dyestuffs that were suitable for application to either mordanted wool or as acid dyes to unmordanted wool. As well as anthraquinone, the azo chromophore became established, as well as triphenylmethane based chromophores, for special shades such as bright greens, turquoise and violet hues. Further developments of synthetic dyestuffs continued with the development of afterchrome, acid levelling, fast acid (half milling), acid milling and 1:1 metal complex dyestuff ranges.

Until the 1960s, wool was traditionally used for both clothing and furnishings. In apparel, wool is mainly used for outerwear, overcoats, hats, suiting, knitwear, socks and uniforms. In furnishings, wool is used for

bedding, carpets and upholstery. However, in recent years significant lifestyle changes have occurred. With the advent of the domestic washing machine the requirements for clothing for a large proportion of consumers have changed from one of formal attire to a wash-and-wear culture. Consumers require fabrics that have easycare properties in terms of washability, ease of tumble drying and minimum iron, whilst maintaining garment quality. Synthetic fibres such as nylon, polyester and blends of polyester with cotton and viscose were able to conform to this wash-and-wear culture, whereas wool had a marked disadvantage in that finished wool garments, whether they were woven or knitted, woollen or worsted, exhibited a marked tendency to shrink during even mild hand or machine washing. This problem has been overcome by the development of effective shrink-resist processes and by expanding the use of wool into fibre blends.

These shrink-resist processes modify the wool fibre to restrict the fibre's natural ability to undergo felting shrinkage. An additional application of a polymer resin renders wool knitwear fully machine-washable. This shrink resistant fibre is more receptive to dyestuff, but also exhibits a markedly lower colour fastness.

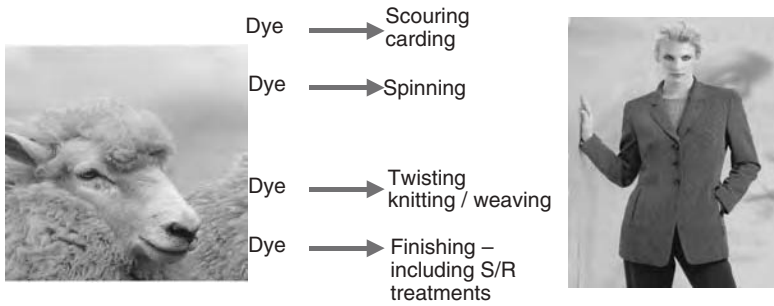
Blends of wool with synthetic fibres have also been developed. In this way the natural properties such as handle, comfort, and drape of wool have been complemented by the additional easycare properties of synthetic fibres that impart strength, washability and stability. Also, elastomeric fibres such as *Lycra* are becoming important.

These developments led to a need for faster dyestuffs that could withstand domestic washing, even in deep intense shades on either plain or multicoloured garments. To cope with these domestic changes, the industry had to quickly refocus on the types of dyes available. In response to these demands for higher colour fastness, new dyestuff ranges were developed and 1:2 metal complex and reactive dyes were introduced.

8.3 Dyeing of different substrate forms

Wool can be dyed at a number of stages in the production process (see Fig. 8.1). The properties of the wool dyestuffs employed must meet both the fastness requirements of subsequent processing and the consumer fastness standards.

Loose stock and slubbing undergo considerable processing after dyeing, such as scouring to remove spinning oils and, often, milling treatments. Therefore, the dyestuffs employed must meet the demands of these processes and, to do so, the higher fastness dyestuffs are applied. In wool fabric dyeing, levelness is essential and dyestuffs with adequate migration properties are preferred. However, this is not always feasible. For example, if



8.1 Different stages of the production process at which wool can be dyed.

wool fabric is to be dyed prior to milling, then it must be dyed with dyestuffs that are fast to milling. If the dyer cannot be sure of achieving a level fabric with such dyestuffs, then the only option is to alter the point in the processing route at which the wool is dyed. This can be achieved by electing to dye the wool in loose fibre form with faster, less level dyeing dyestuffs. Extensive fibre mixing during mechanical processing from loose stock to yarn achieves the essential visual evenness of colouration.

Hence, generally, the processing route will determine dye selection but in certain instances the lack of a suitable dye class will re-determine the point in the processing route that the fibre is dyed.

When dyeing wool to be used in a multicoloured fabric, the fibre must be dyed in either loose fibre, slubbing or yarn form, and dyestuffs must be carefully selected to ensure the integrity of each shade throughout subsequent processing. In the area of machine-washable wools, the effect of the shrink-resist process can have a marked effect on colour fastness. Machine-washable wool is normally dyed at one of three stages of the production process, namely:

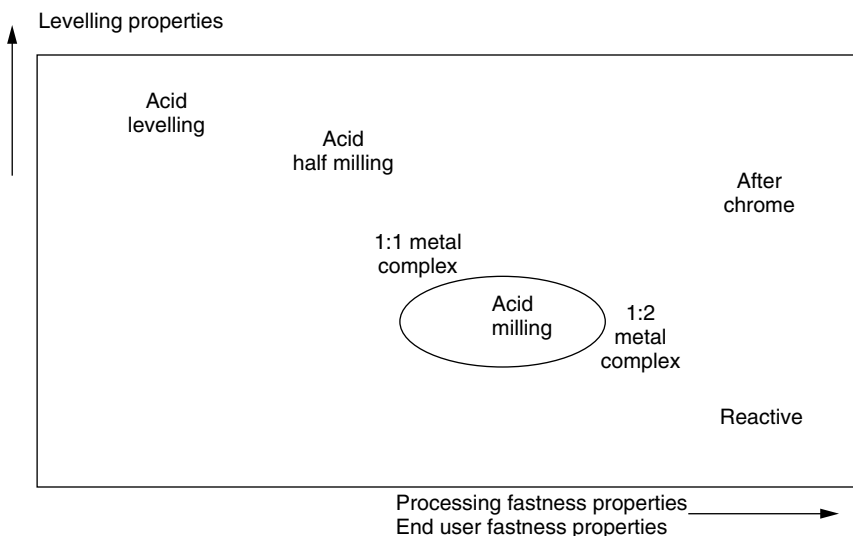
- As fully shrink-resist fibre, e.g. chlorine/resin-treated slubbing or yarn.
- As partially shrink-resist fibre, followed by a resin application after dyeing.
- As untreated wool that will undergo a subsequent oxidative shrink-resist treatment.

The first route is the most demanding in terms of level dyeing properties because the resin often contains a cationic charge that greatly increases the rate of dyestuff exhaustion. Conversely, in the third route the wool is normally dyed in either loose or slubbing form. The dyeing does not need to be perfectly level because subsequent blending will improve levelness, but colour fastness is vital because the subsequent oxidative shrink resist treatment will markedly lower the wet fastness properties of the wool substrate.

8.4 Classification of wool dyestuffs

The commercially available ranges of wool dyestuffs have differing dyeing properties. Wool dyestuffs vary in terms of molecular size and the polarity of the molecule. Most wool dyestuffs contain ionic solubilising groups that are based on the sodium salts of either sulphonic or carboxylic acid groups. The number of solubilising groups present within the dye molecule influences the solubility, dyeing properties, and wet fastness. Generally, dyestuffs with lower relative molecular mass and high polarity have the highest migration properties, whilst exhibiting the lowest wet-fastness properties. The classification of dyestuff ranges in terms of migration and wet-fastness properties is illustrated in Fig. 8.2.

With the exception of afterchrome dyes, the dyestuffs with the highest wet fastness have the lowest migration properties. Afterchrome dyestuffs do not follow this trend because this class of dye is initially applied as an acid levelling dye and then, during the separate chroming stage, the dye forms coordinate bonds with the fibre. These bonds bring about a substantially improved wet fastness. For example, C.I. Mordant Blue 79 is both an acid dye and an afterchrome mordant dye. When applied as an acid levelling dye it produces a bright red shade, but as an afterchrome dye it produces a deep blue shade. The red acid dye has poor wet fastness whilst the blue chromed dye has exceptionally high wet fastness. Both dyes are equally level dyeing as they are applied in the same way, prior to chroming.



8.2 Classification of wool dyestuffs.

8.4.1 Mordant dyestuffs

An increase in the availability of dyestuffs exhibiting a range of hues meant that their polygenetic potential, i.e. their ability to complex with a variety of metal ions resulting in different colours of mordant dyes was no longer necessary and chromium became established as the main mordant. Chromium produces dyes of high wet fastness and generally good light fastness. The first synthetic dyestuffs were applied to wool in three ways:

- as pre-mordant dyes
- as metachrome dyes
- as afterchrome dyes

In each case, an excess of chromium is added either before, during or after the application of dyestuff. The results of all three methods is thought to be production of metal complex dyestuffs tightly bound within the fibre in the form of an insoluble dyestuff lake. The metachrome dyes are the easier to apply as this involves a single application procedure, but some dyeings have a tendency to exhibit poor rubbing fastness due to the precipitation of complexed dyestuff in the dyebath, and subsequently some of it being deposited on wool fibre surfaces.

The afterchrome process was the most widely used because it gives the highest wet fastness properties and the best levelling properties. The afterchrome dyestuffs give good coverage of different wools but are difficult to strip or reprocess due to the stability of the fibre bonds.

8.4.2 Acid levelling dyestuffs

Acid levelling dyes have relative molecular mass (r.m.m.) values of around 300–600. The dye molecules rapidly diffuse into the wool fibre² and, although exhaustion can be so rapid as to be initially unlevel, the dyes readily migrate at the boil to give a level appearance. The levelling properties of this class of dyestuff are good because during dyeing at the boil an equilibrium level of exhaustion exists. The degree to which this equilibrium favours the fibre or the solution phase is determined by the pH, the temperature, the amount of anionic sulphate ions added in the form of Glaubers salt and the number of solubilising groups on the dye molecule. As the pH, the temperature, the number of sulphate ions and the number of anionic solubilising groups increase, the equilibrium shifts towards the solution phase and consequently the degree of dyebath exhaustion decreases. This class of dyestuff is ideally suited to application on fabrics and yarns where levelness is paramount. They exhibit moderate wet-contact fastness but are not fast to either hand or machine washing. They are widely

used for dyeing pale to medium depth shades on wool and wool/nylon carpet yarn in hank form. The dyes give acceptable penetration of both velvet and high twist yarns and adequate levelness, even under the adverse conditions encountered in hank dyeing caused by unpredictable flow due to poor packing and channelling. Dye molecules can be either mono or disulphonated. The two solubilising groups on the disulphonated molecule renders it more level dyeing than the monosulphonated dye as its equilibrium level of exhaustion at the boil favours the solution phase to a greater extent than that of monosulphonated dyes. However, the wool exhibits an increase in affinity for disulphonated levelling dyestuffs during cooling from the boil to about 70°C. This can lead to an increase in the uptake of dyestuff as the dyebath cools, which potentially affects the reproducibility of shade from batch to batch. Careful control of the dyeing process, including the rate of cooling, is recommended to ensure that the final yarn is level and on shade.

Acid levelling dyes are applied from an acidic bath at around pH 3.5 in the presence of 10% sodium sulphate. The sulphate anions compete with the dye anions for the protonated cationic sites on the wool. If sulphate anions are not present, then the level of migration in the boiling phase will reduce and the dyeing time required to achieve adequate levelness and penetration will increase. Dyed wool can be stripped or relevelled by re-boiling for 30–60 minutes in a bath containing sodium sulphate. In severe cases of unlevelness, for example that caused when a circulation pump fails, the wool can be relevelled by stripping the dye with a cationic levelling auxiliary, followed by redyeing.

8.4.3 Fast acid dyes

This group of dyes have a higher r.m.m. (typically 500–700) than acid levelling dyes and hence exhibit improved levels of wet contact fastness. They are typically applied to wool fabric and yarn in medium to deep shades and, although they are not fast to washing, achieve acceptable fastness to carpet water and shampoo contact tests and to perspiration tests. Their migration properties are lower than those of levelling dyes and dyeing is carried out from acetic acid at around pH 4–5. This slightly higher pH reduces the rate of dye exhaustion and improves the migration properties. An example of the modern range of fast acid dyes is the *Sandolan MF* range (Clariant). This type of dye has excellent migration properties relative to the molecular size because levelling properties are greatly enhanced by the addition of a mildly cationic dye substantive levelling agent.³ The dye-levelling agent complex acts to reduce the rate of dye uptake during the heating phase and promote migration during the boiling phase. This type of dye is widely used for producing both brilliant and trichromatic combination shades on wool

fabrics and on carpet yarns. The dyes are usually monosulphonated and give good partition of wool/nylon blends providing a reserving agent is employed to balance the shade depth on each fibre.

8.4.4 Acid milling dyes

These are larger dye molecules with typical r.m.m. values of 600–1000. Due to the higher r.m.m., two or more solubilising groups are common in order to impart adequate solubility. Some dyes in this group also have an additional hydrophobic alkyl chain that further increases the molecular weight and provides additional fibre attraction in the form of van der Waals forces. This class of dyestuff has limited levels of migration but extremely high wet fastness properties. The dyes are generally fast to wet contact tests and have good fastness to washing up to medium depths of shade and, as their name suggests, have a degree of fastness to milling processes. Adequate levelling cannot be achieved by allowing for migration at the boil and hence the rate of dyestuff exhaustion during the heating phase needs careful control. The choice of application method is important. Loose fibre dyeing is normally carried out at a fixed pH in the range of 4 to 6, with a weakly cationic levelling auxiliary. Wool yarn, piece goods and fully fashioned garments are often dyed with an acid donor and a weakly cationic levelling auxiliary. The weakly cationic leveller forms a complex with the anionic groups within the dyestuff and this complex will exhaust onto the fibre more slowly. The acid donor can be an ammonium compound that breaks down at or near the atmospheric boil to expel ammonia into the atmosphere and liberate an acid into the dyebath. The resultant lowering of the dyebath pH causes the dye to exhaust onto the fibre. Another commonly used type of acid donor is based on organic esters. These products decompose as a function of time and temperature and the dyebath pH is gradually lowered to around pH 5, which helps ensure the gradual level uptake of dyestuff. Acid milling dyestuffs are generally brilliant in shade but have a tendency towards poor combinability. They are normally applied as self shades or as binary combinations to achieve brilliant shades. The limited combinability of acid milling dyes has restricted their use in trichromatic combination shades. They also have a tendency to highlight the naturally occurring root tip differences within the fibre, so some attention must be given to wool blend selection.

8.4.5 1:1 Metal complex dyestuffs

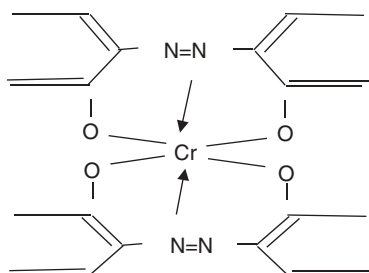
The first commercial metal complex dye ranges were introduced early in the twentieth century. The original type used a dye molecule capable of forming a complex with a chromium atom in the ratio 1:1. Typically, an

o,o'-dihydroxy azo dye was combined with a single chromium atom that carried a cationic charge, and was partially quenched by water. The dye usually contains an ionic sulphonic acid group, which imparts solubility and neutralises the cationic charge on the chromium atom. This class of dye has very good levelling properties when applied to wool at pH levels of around 1.8–2.0 and is ideal for the level dyeing of acid milled and pre-carbonised fabrics. Carbonising is an acid bake process to remove vegetable matter (see Sections 2.7.1 and 7.12), which tends to make wool fibre surfaces more anionic in character. The means by which such dyes are absorbed by the fibre is unclear but the most likely mechanism is that the dye attraction is initially ionic, via the sulphonic acid group. This would explain the high migration properties. It is also thought likely that the dye may form larger 1:2 metal complexes within the fibre. There is no evidence that this class of dye can form coordinate links with the fibre and, as such, their fastness properties are not as good as afterchrome dyes. Indeed, the use of 1:1 metal complex dyes on washable wools is restricted because their shade is unstable when the wool dyeings are washed with modern detergents containing perborate.

8.4.6 1:2 metal complex dyestuffs

Metal complex dyes are dull in shade by comparison with many acid dyes but, providing the right dyes are selected, they are combinable. 1:2 metal complex dyestuffs are formed by the complexing of a metallic atom such as chromium or cobalt with two dye molecules (Fig. 8.3). The resultant larger dye molecule can form strong links with the fibre and so they tend to have low migration properties. There are typically three distinct types of 1:2 metal complex dye, unsulphonated, monosulphonated and disulphonated. The disulphonated type are the most soluble and have a greater pH dependence. This means they have a low neutral affinity and require more acid to achieve exhaustion, but in practice they have the advantage of the highest fastness to domestic washing since any desorbed dye has only limited affinity for adjacent fibres at the pH conditions experienced with domestic detergents. Disulphonated dyes are, however, more fibre selective than the mono or unsulphonated dyes and care must be taken to avoid skittery dyeing.

Modern commercial ranges, such as *Lanaset* (Ciba) and *Lanasan CF* (Clariant), consist of optimised mixtures of the three different types of 1:2 metal complex dye, and are formulated to give good combinability, good coverage of fibre irregularities and good overall fastness properties. Acid milling and 1:2 metal complex dyes have similar application requirements and are often applied in combination to brighten the shades obtainable with metal complex recipes.



8.3 A typical structure of a 1:2 metal complex dyestuff. Molecular weight is usually 500–1000. Chromium is 2–5% by weight of the dye molecule for the commercially-traded product.

8.4.7 Reactive dyestuffs

Reactive dyes are medium molecular weight acid dyes with a reactive group capable of reacting with wool amino groups. This reaction involves the formation of a covalent bond, which means the dye becomes attached to the fibre and once fixed cannot normally be removed in subsequent processing. The degree of fixation of reactive dyes depends upon the type of reactive group employed and upon the application conditions. Clearing is necessary to remove unfixed dye, and the ease of clearing of individual dyes is an important factor in achieving high wet fastness. Reactive dyes usually have brilliant hues and have become ideally suited to dyeing bright shades for machine-washable wools.

The high colour fastness of 1:2 metal complex and reactive dyes is to some extent negated by the poor level dyeing properties and, as such, their use has traditionally been restricted to dyeing loose fibre and slubbing. However, the increasing importance of machine-washable wools in knitted articles has led to a requirement to apply reactive dyestuffs to other fibre forms such as yarn and garment. In wool garment dyeing, special application processes have been developed to ensure that adequate levelness can be achieved in garment dyeing. The dye is applied at the boil at neutral pH until the garment seams are penetrated and then the dyebath is gradually acidified to allow the dye to feed slowly onto the fibre.

8.5 Commercial forms of dyestuffs

Traditionally, wool dyestuffs have been supplied as powders with adequate solubility to ensure that they dissolve readily in hot water. The dye is manufactured as a wet presscake and then dried. Diluents are added to standardise the dyestuff to the required selling strength and the final solubility of the commercial product depends upon the molecular mass, the

number of solubilising groups present and the influence of the diluents. Commercial products are often supplied at more than one selling strength and the solubility of the different strengths can vary due to the influence of the diluent. Common salt and Glaubers salt can reduce the solubility of some dyestuffs when used as a diluent whereas naphthalene sulphonate can improve the solubility. Hence, when a particular dyestuff is sourced from two different suppliers, it is not uncommon to find that the solubility can vary greatly. Dyestuffs are now also supplied in both liquid and granular forms. The liquid form is ideally suited to dyes that are applied in large quantities, but the dyestuff must have sufficient solubility to prevent precipitation during storage, and stirring prior to use is advisable. Protection from frost is also important to prevent precipitation.

Granular forms are the product of modern spray-drying techniques. They have a lower surface area compared to the powder form and, as such, tend to be less hygroscopic. An advantage of this property is that the dyestuffs are easier to handle during weighing because they flow more readily than powder forms and can even be used in automatic dispensers. The lower moisture regain of the granular form can improve the accuracy and reproducibility of dyestuff weighing, particularly when dyestuffs are stored in moist storage areas.

8.6 Levelness

The importance of achieving satisfactory levelness of wool dyeings has been noted in previous descriptions of dye selection and application methods. This subject is of such fundamental importance for consumer acceptance that the practical problems and means of overcoming them are dealt with in more detail here.

It cannot be too often stressed that wool presents very special problems in achieving appropriately uniformly dyed products because of raw material variations between fibres, between fleeces and between large amalgamated wool lots. The four factors which need to be considered are:

- Substrate form and substrate preparation
- Dyeing machinery
- Dyestuff selection
- Application method

The substrate form and the appropriate machine required to dye it govern the dyestuff selection, which in turn governs the choice of application method.

8.6.1 Substrate

In terms of the substrate, the dyer often takes the blame for faults that were present in the substrate prior to dyeing but which only became apparent

during dyeing. Hence the old saying of 'well prepared is half dyed' is always true. Typical causes of these dyeability variations are insufficiently scoured fabric and pre-carbonised wools. In the case of pre-carbonised wool, residual acid within the fibre will facilitate a more rapid rate of dye uptake. Dyestuffs with limited migration properties such as fast acid and acid milling dyes can only be applied to such fabrics after complete neutralisation of residual acid. In practice, pre-carbonised fabrics are neutralised with either dilute sodium hydroxide or by treating in a solution of 5–10% sodium acetate.

Wool exhibits naturally occurring root tip differences. Fibre tips are damaged by exposure to weathering from wind, rain and light. The tips are more hydrophilic than the fibre root so they exhibit a higher affinity for dyestuff. Initially, the fibre tip appears deeper in shade and the overall appearance can be unsatisfactory. During prolonged boiling, the fibre degrades and this affinity difference is reduced. Hence, migrating dyestuffs will tend to cover root tip difference more readily than dyes that have limited migration properties. Acid levelling, 1:1 metal complex and fast acid dyes give good coverage of root tip affinity differences whereas acid milling, 1:2 metal complex and fibre reactive dyes highlight such differences. Some dyes can actually migrate from tip to root during boiling to such an extent that it is possible to achieve reverse tippiness where the fibre root finally dyes more deeply than the fibre tip. In practice, levelling auxiliaries reduce the effects of tippiness. This type of auxiliary is fibre substantive and increases the rate of dye uptake on both the fibre tip and root, and promotes coverage of such dyeability variations.

8.6.2 Machinery

In yarn, piece and garment dyeing, levelness is paramount and, as such, most of the machinery developments of recent years have focused on improving levelness. In yarn dyeing, hank dyeing is still popular because of the bulky handle it produces, but the winding and unwinding operations are inefficient and the restricted liquor circulation and liquor channelling can lead to unlevelness. Package dyeing provides a much more uniformly distributed substrate and therefore overcomes some of the unlevelness caused by poor packing and poor liquor circulation in hank dyeing. Horizontal package machines also have the flexibility to keep liquor ratios constant with varying batch sizes by blocking individual tubes, and this also saves water.

In fabric dyeing, the limited liquor circulation found in winch machines has restricted their use to applying acid levelling and fast acid type (half milling) dyes, but with modern jet machines it has been proven that acid milling, 1:1 and 2:1 metal complex dyes can be applied level to wool fabrics. In wool garment dyeing, protection of the garment face is important. Garments are normally dyed inside-out in a side paddle machine. Its gentle

action ensures that the fabric surface is protected whilst maintaining a liquor circulation sufficient to achieve a level appearance.

8.6.3 Process control

Process control specifies that the starting temperature, the rate of temperature rise and the time at top temperature have to be 'controlled' in order to achieve a level dyeing. The word 'control', of course, has always depended upon state-of-the-art technology and fortunately has progressed from cracking the steam valve, through the use of cam controllers, to the sophisticated microprocessor controls in use today. The benefit of the cam type control and the modern microprocessor control is that they can keep a record of the whole dyeing process, which is useful when examining the levelness and handle of the dyed substrate. The microprocessor has the added benefit of being able to follow a precise, pre-programmed method. Computer programs are now available that predict cycle time, heating rates, pump pressures and flow rates required to assess if a particular dye recipe is likely to be level.

8.6.4 Levelling auxiliaries

Levelling auxiliaries have always been used in wool dyeing. Glaubers salt is the long standing traditional levelling agent. It promotes migration with acid levelling type dyes but its use is not recommended with large molecular weight acid milling and 1:2 metal complex dyes because it also promotes aggregation, which can lead to the precipitation of dyestuff. Generally, the levelling auxiliaries in use today consist of the dye substantive cationic type, which can complex with dyestuffs and will therefore reduce the rate of dye uptake and promote migration of adsorbed dye. Fibre-substantive amphoteric types are also employed. This type of product actually accelerates the rate of dye uptake but improves coverage of the inherent variations within the fibre (such as tippiness) and, with some dyes, this gives an increase dye yield.

8.6.5 pH control

pH control once consisted of applying gallons of sulphuric or formic acid in order to achieve exhaustion of acid levelling, 1:1 metal complex and chrome dyes. The use of such acids has reduced for two main reasons:

- i) The low pH values obtained (1.0–3.8) are below the isoelectric region of the wool fibre and can impart wool damage.
- ii) The move to more neutral dyeing dyes has required higher application pH levels in order to guarantee levelness.

Even sulphuric acid type acid levelling dyes and 1:1 metal complex dyes are now normally applied with formic acid, whilst the monosulphonated acid levelling dyes that were traditionally applied from formic acid are now often applied from acetic acid. pH control is critical with neutral dyeing dyes. In certain situations, such as yarn hank dyeing, where levelness is difficult and circulation is limited, acid donors are applied. These products allow dyeing to commence at a higher pH (say 7.0–8.0) but gradually break down to liberate acid during heating and boiling, thereby lowering the pH and allowing the dye to gradually feed onto the fibre.

Traditional acid donors such as ammonium sulphate are still used but the more modern acid donors such as the *Sandacid* (Clariant) products give a much more reliable, gradual fall in dyebath pH because, as organic esters, they hydrolyse at a known rate in water.

Control of all these factors in both the laboratory and under bulk conditions has not only led to improved levelness but also to improved laboratory-to-bulk, and bulk batch-to-batch reproducibility.

8.7 Dyeing fibre blends

When dyeing blends of wool and other fibres, the dyeing process must ensure that the resultant dyed fibre meets the consumer requirements of shade, levelness and colour fastness, and that the integrity of each fibre is not compromised. Polyester fibre is normally dyed at 130°C but this temperature damages the wool fibre. In practice wool/polyester blends are dyed in pressure vessels at 115–120°C for a period of up to 20 minutes. A fibre-protective agent is added to help maintain the quality of the wool. The disperse dyestuffs applied to the polyester component must achieve adequate build up and give minimal cross staining of the wool to ensure adequate colour fastness.

When dyeing blends of wool and cellulosic materials under weakly acid conditions, the wool has a high affinity for direct dye. The main requirement is to prevent the cellulosic dyestuff from cross-staining the wool. With direct dyestuffs this is achieved by applying an anionic blocking agent, which is taken up by the wool fibre prior to the addition of dyestuff.

When polyurethane elastomeric fibres are used to build a degree of comfort stretch into a garment, it is important to select wool dyestuffs that do not give excessive cross-staining of the elastomeric component, otherwise colour fastness levels will be reduced.

Generally, the application process employed is a compromise between the methods employed for each of the blend components. An exception is when dyeing blends of wool and nylon. These two fibres have similar dyeing properties with most classes of wool dyestuffs and, in practice, the wool application method can be employed. There are different types of nylon

used in wool blends and they can have differing affinity for the wool dyestuff. Generally the nylon component of the blend dyes slightly darker than the wool. With monosulphonated acid dyes, this shade depth difference is enhanced and blocking agents are required to reduce the uptake of dyestuff on the nylon. By controlling the application level of blocking agent, the shade depth between the wool and the nylon can be controlled. This is important when dyeing carpet fibres to ensure that the nylon fibre does not grin, i.e. predominate in visual appearance, particularly in heavy traffic areas, where the wool fibre wears more quickly than the nylon.

8.8 Treatments to improve colour fastness

Washable fabrics made of both wool and wool blends are required to be fast both to long liquor washing and contact colour fastness tests. The fastness of acid milling and 1:2 premetallised dyes can be improved by the addition of a cationic fixing agent. The cationic fixing agent forms a complex with the dyestuff and the fibre. The resultant contact fastness to water and perspiration can illustrate a marked improvement, whilst the washing fastness can be improved by around 1 point. Some cationic fixing agents are able to react with wool to form a permanent bond. This type of fix gives a more durable fastness improvement. Light fastness of wool is particularly important when used in carpet and upholstery furnishing fabrics. The wool fibre can exhibit a rapid fade when exposed to daylight, and in pale shades this can lead to an unacceptable level of light fastness. Generally, such wools are dyed with dyes that have a good light fastness but additional products can be applied to improve light fastness properties and these have been discussed in Section 7.8.1.

8.9 Environmental issues

Ecological issues were initially driven by environmentalists but they have since become more generally endorsed by consumers. The underlying concepts are becoming more widely accepted and this is perhaps best illustrated by society's changing attitude to recycling. The colouration industry is being affected by these changes. New and proposed laws are impacting upon day-to-day dyeing activities. Headlines containing such terms as 'heavy metals', 'AOX', 'banned azo dyes', 'consent limits', 'air pollution', etc. are common and concern issues that must be thoroughly addressed by processing companies and standard-setting agencies alike. The hazards presented by all these factors can be categorised into four groups related to the hazards associated with processing, effluent, finished articles and fabric disposal.

8.9.1 Processing

In any manufacturing process, care must be taken to protect the local environment by controlling gas emissions and odours. Employees in the dyeing process must be protected from application hazards, including dyestuff dust and exposure to acids, alkalis and other toxic compounds. Further along the chain, workers who process dyed fibre must be protected from hazards such as residual chemicals.

8.9.2 Effluent

The effluent hazards of heavy metals, AOX, as well as C.O.D., B.O.D. and colour are important. All these factors are carefully monitored by the environmental agencies in order to determine the effluent treatment requirements. Generally, each area has different consent levels; the cost of ensuring that these consent levels are met can be excessive and are normally passed on to the dyehouse. Heavy metals are very difficult to extract, even by reverse osmosis, and as such must be dumped as sludge.

8.9.3 The finished article

The products applied during dyeing must not present a hazard to the consumer. This includes not using banned dyes such as some of the azo types (see Section 8.9.7) and limiting the amount of extractable heavy metals resident upon fabrics. Free formaldehyde is also an issue.

8.9.4 Disposal

Care must be taken to ensure that a product can be disposed of safely at the end of its useful life. (An example of this is CFC gases in fridge freezers.) In textiles, heavy metals are a concern because they can leach out of fibres in landfill sites and survive disposal by incineration.

The processing risks are covered by the health and safety at work acts, the finished article risk is covered by consumer law, whilst effluent is covered by the work of the environmental agencies. In Germany, legislation focuses on an 'emission protection ordinance' which covers emissions, either gas or effluent, from the processing plant, and the 'ordinance on materials and articles', which covers the product.

Eco labels have also come to the fore; these set down minimum standards applying to finished articles and in some cases effluent.

8.9.5 The use of water in wool dyeing

In wool processing and effluent treatment, water remains the standard solvent. It has always been perceived to be freely available and inexpen-

sive. The wet processing of wool requires an abundant supply of soft water. However, the amount of water available is finite and ever-increasing demand is leading to variations in supply quality as water is pumped from one area to another. The cost of treated municipal water supplies continues to increase and the textile industry is now incurring additional costs because this water often requires further softening to be suitable for dyeing. The cost of the disposal of water is also increasing and it is important for industrial efficiency to monitor what is discharged in terms of content and volume.

One of the most important wool dyeing environmental issues under debate is the restriction on the use of mordant dyes. This restriction is prevalent throughout the western world, with a typical effluent limit of 1 mg/l total chromium. The concern is that chromium, and especially hexavalent chromium, will enter the water supply or the food chain. Afterchrome dyes need a minimum amount of chrome to produce the desired shade. Insufficient chrome gives poor reproducibility and, in practice, a slight excess is required. This excess of chromium still has to be applied because lower levels do not achieve the fully-chromed shade. C.I. Mordant Blue 79, for example, requires a minimum of 1.8% chrome and, in practice, a low chrome addition of 2% on weight of fibre is recommended. However, even at low chrome levels, 1 g/l of hydrated sodium dichromate, which equates to over 300 mg/l of chromium, must be applied.

Even when special application methods are employed that involve reduction of chrome VI to chrome III and encourage the chrome to complex with the carboxyl groups within the fibre, and allowing for further effluent dilution from rinsing, it is still indeed a challenge to reduce the chromium level from >300 mg/l to 1 mg/l during the dyeing process. Metal complex dyes are also of concern and the dyer must achieve high levels of dyebath exhaustion to ensure that the effluent discharge is within the specified limits.

If one considers dyeing 100 kg of wool to a 2.5% navy shade with 1:2 metal complex dyes at a liquor ratio of 10:1 followed by rinsing with 2000 litres of water, the chromium contents during dyeing would be as follows:

- weight of dyestuff applied – 2500 g
- dyebath exhaustion – 96%
- dyestuff remaining in exhausted dyebath – 100 g
- the dye powder typically contains 3% chromium on weight of powder
- this leaves 3 g of chromium in the exhausted dyebath
- this 3 g will go to effluent with 3000 l of water, which is 1 mg/l

The residual level of chromium discharged just satisfies the water authority discharge requirement. However, dyeing deeper shades, or using less

rinse water, or achieving lower exhaustion will cause the discharge to exceed the limit.

Recent studies have assessed how dyehouse water can be re-cycled in order to reduce the levels of effluent discharge. In the case of the metal complex dye illustrated previously, the rinse water will be fairly clean and will not present an effluent hazard. Most of the contamination is in the exhausted dyebath and, if this water is re-used in subsequent dyeings, there will be an effluent reduction of colour, heavy metal and even pH chemicals. The extent to which the amount of heavy metal discharged to effluent can be reduced by this technique then becomes dependent upon the amount of free, unbound metal present in the commercial dyestuff.

8.9.6 Extractable heavy metal limits on garments

The issue of chromium is not just related to effluent discharge. It is clear that residual unbound chromium present on the fibre is also a potential hazard. Various Eco standards quote maximum permissible residual metal limits,

| | | |
|---------------|-----------|-------------------------|
| e.g. Oeko-Tex | 100-I | 2 ppm Cr (4 ppm Cobalt) |
| | 100-II-IV | 1 ppm Cr (1 ppm Cobalt) |

These figures are a measure of the amount of free metal that is extracted in a perspiration solution under standard test conditions (*Oeko-Tex* Standard 100⁴), which are intended to simulate potential exposure of the wearer of the garment concerned. These standards apply not just to afterchrome dyes but also to other metal complex dyes. Generally, the amount of extractable metal increases with increasing depth of shade. The 1:1 metal complex dyes usually satisfy the *Oeko-tex* label in pale shades, the 1:2 metal complex dyes satisfy the label in all shades, whilst the chrome dyes satisfy at least to medium depths. *Oeko-tex* is only one label; other labels are similar and all results rely on best practice in terms of application and exhaustion.

8.9.7 Banned azo dyestuffs

Another issue which is perceived as being a hazard to the consumer relates to cleavage of certain azo dyes into amines that can be considered to be potentially carcinogenic. The German ban relates to certain azo compounds, including dyes, in some consumer goods. The only dyes affected are those that are likely to break down to produce one of 20 carcinogenic amines. It is not illegal to manufacture and sell such dyes and the emphasis is on the processor or dyer to avoid using prohibited azo colorants.

C.I. Acid Red 114 is an example of a dye which will cleave to produce o-toluidine. Only articles that are likely to come into more than temporary contact with the human body are affected. Prohibited dyes can be used for other applications.

Environmental issues must be considered when selecting dyestuffs and dyebath auxiliary products. If the wrong products are selected, then there will be a cost penalty incurred to treat affected effluent or to correct faulty garments. Great emphasis has been placed on researching new application techniques and new products that can assist in reducing the environmental impact of the dyeing operation. It is expected that this trend will continue and that issues such as metal-free dyeing and fibre protection will remain as important challenges to the wool dyer.

8.10 Fibre protection

Wool is renowned as being a quality fibre and, as such, it carries a premium price. The value of the fibre demands great care during processing to ensure that the inherent properties of the fibre are maintained. During loose fibre dyeing, the degree of fibre damage must be minimised in order to reduce the amount of waste in carding and to prevent an excessive number of end breaks during spinning. The dyer must ensure that the dyeing time at the boil is kept to a minimum, but it is also an option to dye at temperatures below the boil. Acid milling and metal complex dyes are successfully applied at temperatures of 80–90 °C in conjunction with a low temperature dyeing auxiliary. The auxiliary⁵ promotes dyestuff exhaustion and diffusion, and produces fast, well penetrated results.

A particular property of wool is the structural changes that readily occur in boiling water. Thiol and cystine disulphide bonds can undergo interchange reactions that essentially set wool fibres in their conformation in compacted loose wool and yarns. A full description of permanent setting of wool can be found in Section 7.13. Colourless chemicals capable of reacting with thiol groups have been suggested as a means of restricting permanent set developing during dyeing.

Fibre reactive dyes have also been shown to reduce permanent set because thiol groups are a favoured point of their attachment to the wool substrate. The major advantage of restricting permanent set development in loose wool dyeings is the superior spinning properties as compared with afterchrome wool dyeings for example.

8.11 Summary

The wool dyer's job has changed. It no longer involves carefully cracking open steam valves and tweaking dyeings with skilful shading additions. The

dyer must select the correct dyestuffs and the most appropriate dyeing technique to ensure that the dyed substrate will be processed with maximum productivity through efficient use of bulk machinery and a substrate that will suit the intended purpose for the lifetime of the product in terms of fastness and environmental characteristics. It is likely that the wool dyer will, in future, rely on modern computer programs that can determine the dyebath conditions required to ensure levelness, that can predict an eco profile for a chosen recipe and recommend a dyebath chemical system that can help protect the fibre during dyeing.

References

- 1 Liebetrau P, *Oriental Carpets*, Collier-Macmillan, 1984.
- 2 Duffield P A, *Wool Dyeing*, (D M Lewis, ed.), Soc. of Dyers and Colourists, 1992.
- 3 Frauenknecht J, Hextall P C and Welham A, 'Sandolan MF dyestuffs', *Textilveredlung*, **21**, (1986), 331.
- 4 www.oeko-tex.com.
- 5 Clariant, 'Lanasan LT liquid', Clariant Technical Information, 17th April 2001.