

7.1 Introduction

Chapter 5 describes the chemistry of wool as it interacts with radiation, acids, alkalis, oxidants, reductants and metal ions. It also includes some useful reactions that modify particular amino acid residues. This accumulation of knowledge of the absorption and reactivity characteristics of wool has facilitated the development of practical treatments that enhance some aspect of the performance of wool products. Generally, the process descriptions that follow are those in current practice. A more historical perspective of wool process developments can be found in text books, e.g. that edited by von Bergen.¹

7.2 Bleaching

Raw wool can be segregated at the marketing point so that the whitest material is channelled towards products dependent on a good natural colour. Nevertheless, bleaching is a very common process and may be enhanced by fluorescent brightening agents for some fashionable wool products that are in competition with synthetic and cotton textiles. Bleaching processes may be carried out continuously, as in conjunction with raw wool scouring, or batchwise on fibre, yarn and fabric.

Reduction bleaches cause little damage to wool by comparison with oxidative methods. Sodium metabisulphite treatments enhance wool brightness, but the preferred reductive bleaching treatment today utilises stabilised sodium dithionite-based products or, alternatively, thiourea dioxide.² Better whiteness can be achieved using formulations based on hydrogen peroxide at the expense of increased damage, particularly to cystine (CYS). Peroxide used in wool bleaching is usually stabilised by sodium pyrophosphate or chemically-related proprietary products. A typical process³ would be a solution of 20 ml/l (35%) H₂O₂ at pH 8.5, with

0.4 g/l sodium pyrophosphate as a stabiliser. The treatment bath would slowly be raised to 65°C and maintained there for about 3 hours.

Wool bleached as an ancillary process during raw wool scouring is usually treated with lower levels of hydrogen peroxide than in the batchwise processes mentioned earlier.

Typically the final bowl of the woolscouring train would be maintained at 0.5–1.1% peroxide in mildly acidic conditions of pH 4–6 and a temperature not exceeding about 40°C. A fraction of unreacted peroxide is held by the wool and it continues an exothermic reaction even after drying. Caution is therefore essential when wool is baled after scouring and bleaching if thermal damage to the wool is to be avoided.

A modest bleaching effect in conjunction with scouring can also be obtained under reactive conditions. With the last scouring bowl set at about 0.4% sodium metabisulphite concentration and a pH of 5.7–6.3, the operating temperature should not exceed 55°C.

7.3 Prevention of dyebath yellowing

A disappointing aspect of wool bleaching is that the products are less stable in colour than before. Colour reversion in a dyebath is particularly unfortunate. One of the obvious reasons for bleaching in the first instance is to achieve bright, pale shades after dyeing, and should the wool material lose half or more of the original improvement it can be most disappointing. Fortunately, there is now greater appreciation of the reasons for colour reversion, this form of it often being referred to as hydrothermal yellowing.

All wools have detectable amounts of α -keto acids and the quantity is greatly increased when they have been damaged by exposure to sunlight (see Section 5.3). Simpson investigated hydrothermal yellowing and considered these carbonyl groups were major contributors.⁴ Inclusion of hydroxylamine (HA) salts at 0.2% concentration in a conventional mildly acidic dyebath reduces hydrothermal yellowing by at least 50–70%. Simpson considered carbonyl groups were the active agents because they are liable to be quite reactive in boiling water, although the end products of their reactions are unknown.

The chemical explanation for the success of the preventative treatment is almost certainly the well-known general reaction of HA with carbonyl groups to form aldoximes and ketoximes. In the case of wool, this intervention avoids colour-forming reactions, although it must be acknowledged there is no material evidence of how these may involve carbonyl groups. A consolidating point in favour of this theory is that the HA-carbonyl reaction is reversible in mildly acidic conditions. Pretreatments of wool with HA and subsequent dyeing in HA-free acidic dyebaths offer only transient protection against yellowing. Boiling in neutral conditions does not cause

yellowing of HA pretreated wool, because the reverse reaction cannot be catalysed by hydrogen ions.

Acidic dyeing conditions predominate in wool dyeings and HA must be present at an adequate dyebath concentration in order to minimise hydrothermal yellowing.

Simpson also emphasised the importance of high temperatures in hydrothermal yellowing. Dyeing assistants and dyestuff selection which permitted dyeing at 80°C rather than at the boil, in conjunction with HA usage, would completely eliminate hydrothermal yellowing.⁵

7.4 Insect-resist treatments

Wool and other animal fibres are attacked by the larvae of particular moths and beetles. *Tineola bissiella* (Hummel), the common clothes moth, is found worldwide and is used as a laboratory test insect. Other moths found in temperate and sub-tropical regions are also significant pests, notably a number of species within the *Tinea* genera (Linnaeus) and *Hofmannophila pseudoprettella* (brown house moth) (Stainton). Several species of beetle attack carpets, and that generally used in laboratory testing is *Anthrenus flavipes* (LeConte). Damage caused by carpet beetles accounts for more than half the total insect damage to wool products,⁶ so it is essential to test treatments against several insect species. For many years it was thought the mechanism of digestion of wool by insects originated with highly reducing conditions in the larval midgut. Disulphide bonds in the ingested wool were cleaved, allowing complete digestion with proteolytic enzymes.

Powning and Irzykiewicz⁷ revised this theory and suggested that wool is partially broken down by protease releasing some free cystine which is then reduced to cysteine by the enzyme system. Cysteine promotes rapid subsequent proteolysis by reducing more disulphide bonds.

Both chemical modifications of cystine and biological antagonists that inhibit the metabolic enzyme cycle have been considered as potential methods of insect-proofing, but none have gone on to commercial adoption. Environmental constraints have become increasingly important in recent years, so that some of the earliest chemical insect-resist (IR) treatments have now been largely abandoned.

A considerable number of very demanding criteria must be met if a treatment is both to comply with environmental regulation and to be effective through the lifetime of the wool textile or carpet. IR agents must survive many different processes, including resistance to hydrolysis in boiling dye-baths, and possess adequate stability to sunlight and laundering or cleaning. The shampoo-fastness requirements for carpets are less stringent than machine-washable standards for wool garments, where an excess of IR may be necessary to compensate for subsequent losses.

Concerns for the health of mill workers, consumer safety and environmental protection lead to regular revisions of standards. In most countries there is strict control of permissible IR agents and their concentration in mill discharge of treatment residues into sewage systems. Lewis prepared an extensive list of insect-resist agents used at some time on woollen goods.^{8,p128} The most important commercial products are listed in Table 7.1.

Absent from the list are the first widely used IR agents based on formulations of dieldrin. Its high toxicity to mammals and fish, and longevity in the environment, led to a ban on its use in most markets. *Mitin FF* has been used since 1939 and, in spite of a high cost, its excellent fastness to washing and light, and exhaustion properties comparable to acid dyes has meant it retains a place, for example, in the treatments of uniforms.

Increasing pressure to reduce organochlorine residues in the environment has led steadily to replacement of the older products. Permethrin has a lower chlorine content and low mammalian toxicity but is toxic to fish and aquatic invertebrates vital to the nutritional food-chain of fresh-water fish. This has put pressure on development of application methods that generate little waste chemical discharge. *Mitin AL* combines permethrin with a hexahydropyrimidine derivative that has good properties of beetle protection. Wherever feasible, the preferred method of application would be to add the IR agent to dyebath formulations. In the case of wool-nylon blend yarns commonly used in carpets, the IR agent may be taken up predominantly by the polyamide and this portion is ineffective in terms of protection of wool. Some IR agents favour the wool component⁹ and are clearly to be preferred for such products.

Table 7.1 Commercial products for insect-proofing wool

Product/Manufacturer	Chemical name	Year of introduction
Mitin FF (Ciba Geigy)	Sulcoferon	1939
Molantin P (Chemapol)	Chlorphenylid*	—
Perigen (Glaxo/Wellcome)	Permethrin	1980
SMA-V (Vickers)	"	1980
Antitarma NTC (Dalton)	"	1982
Mitin BC (Ciba Geigy)	"	1982
Eulan SPN (Bayer)	"	1983
Eulan SP (Bayer)	Cyfluthrin	1982
Mitin AL (Ciba Geigy)	Permethrin/Hexahydro pyrimidine derivative	1983
Cirrasol MPW (ICI,Aust.)	Cyhalothrin	1985

*Chlorphenylid products from Ciba Geigy and Bayer were withdrawn from the market in 1989.

One method devised to limit IR agent discharge in mill effluent is massive overtreatment of a portion of the wool prior to blending it with a larger quantity of untreated fibre.¹⁰ This approach is particularly useful for Berber-style carpets. Finished carpets may also be treated rather than fibre or yarn. Ingham and Rowan describe foam and spray/vacuum procedures, and a dry process involving talc containing the IR agent dusted onto a carpet prior to steam fixation.¹¹ Such processes do not create any aqueous effluent and essentially solve the potential environmental problem.

Insect-resist treatments may also be applied during processing in woollscouring plants, provided effluent discharge constraints in their particular location can be met concerning residual chemical in rinsings, etc. Very large quantities of wool have been treated, most commonly with synthetic pyrethroids present in the last scouring bowl, which would be maintained at about 70% and pH 4–6 for the purpose.

7.5 Shrinkproofing

7.5.1 General

Apart from dyeing, shrinkproofing processes are the most common chemical treatments applied to wool. In the absence of any preventative treatment, almost all types of woven and knitted wool products will shrink, although the propensity to do so varies widely. Felting is the usual descriptive term for the progressive fibre entanglement of wool products subjected to mechanical action, most particularly during laundering. Felting has been exploited for centuries as a means of manufacturing unique products. Loose wool carded and formed into batting can be compacted and hardened to create felts for a variety of uses, including floor coverings (see Section 10.2). Woollen spun fabrics are often finished with a less drastic felting process described as milling or fulling. For most of the past century, the need to reduce or completely eliminate shrinkage of fabrics as a result of felting has become a necessity. This has required a good understanding of the mechanisms involved in wool fibre entanglement, and the development of a range of treatments appropriate to particular wool products and manufacturing routes. The processes presently favoured for particular wool products are described in Sections 11.1.12 and 11.3.3.

7.5.2 Fibre morphology

It is the distinctive cuticle or scale cell structure of wool fibres that is primarily responsible for felting by fibre entanglement, causing a corresponding shrinkage of wool fabrics, most particularly in laundering. The overlapping cells that make up the cuticle are tightly cemented to each

other and to the underlying cortex. For Merino wool, the exposed length of each cell is 10–20 μm , and the cuticle is 0.5–1.5 μm thick. These scale cells have raised edges and often several ridges or false edges, the pattern varying quite a lot between sheep breeds. The outer membrane of scale cells has often been referred to in past literature as the epicuticle, but it definitely encloses individual cells and not the whole fibre. In the Allwörden test, described in Section 5.8, this outer membrane of each scale cell is inflated by brief immersion of wool fibres in chlorine water. Underlying it is a sulphur-rich layer, the exocuticle, which itself is usually differentiated into an outer ‘a’ layer and a ‘b’ layer. The ‘a’ layer has the highest cystine (CYS) content which may be as much as one residue in five. By way of contrast, the innermost layer or endocuticle has a very low cystine content, of the order of 3% of amino acid residues. More details of the morphology of the wool cuticle are given in Section 3.3.1.

7.5.3 Frictional properties of wool fibres

Makinson¹² has provided a comprehensive description¹² of the several frictional mechanisms likely to be operative in the dynamic situation when a fibre assembly such as a wool fabric is subjected to mechanical action. Noting the uni-directional layering of scale cells with leading sharp edges, one would logically anticipate differential frictional effects (DFEs) according to the direction in which a fibre is pulled over another surface. The term ‘ratchet mechanism’ has often been used to describe how a particular fibre may readily move one way within a fabric but cannot return. It has, however, proved very difficult to assign precise values to frictional parameters because of the irregular asperities on fibre surfaces, and the complex patterns of interfibre contacts. The contrast between air-dry fibres and water-saturated material is very great. The physics of interfibre friction in air-dry situations is described in Section 4.4.5. Viscoelastic properties and fibre swelling, as well as surface characteristics, would be quite different during laundering. Although inter-fibre frictional properties are acknowledged as of crucial importance, the theoretical difficulties generally mean development of shrinkproofing technology has largely moved along on an empirical basis.

7.5.4 Chlorination

Makinson¹² lists about 40 patented variations of wet chlorination and there are probably almost as many wool surface treatments based on alternative oxidants. Similarly there is a comparable diversity of polymers designed to be applied either as a one-step shrink resist process or, more commonly, as an aftertreatment following some form of wet chlorination. A relatively

small number of these processes are in current use and the descriptions that follow are mainly confined to them.

Treatments with chlorinating agents stand well above all others as either sole or preparatory processes in shrinkproofing. There are some very different reactions possible (Section 5.10), but in shrinkproofing technology the primary modification sought is either to alter wool fibre surfaces so as to facilitate polymer adhesion or alternatively to oxidise some CYS in the exocuticle in order to alter fibre swelling (in water) and other viscoelastic properties of the scale cells.

Dry chlorination, i.e. exposure of wool products and typically knitwear to chlorine gas in sealed vessels has been a major technology, probably peaking in volume useage over the period 1930–1950, especially for blankets and hosiery.

Wet chlorination, on the other hand, continues to be used in several variations up to the present day, according to whether a mild preparatory treatment of fibre surfaces is required for subsequent polymer applications, or a more thorough oxidation of the wool epicuticle is sought as a stand-alone shrinkproofing process.

Simple acidified hypochlorite treatments are now limited to a preparatory process for subsequent application of polymers. The nature of the attack on wool differs for free chlorine in water, HOCl and OCl⁻, which predominate at pH 2, pH 5 and pH 8 respectively (see Section 5). In the crucial pH 2–5 range, the speed of the reaction (and therefore the possible diffusion range into the fibres) can be moderated by pH, temperature and inclusion of other chemicals.

A major survivor of all these chlorination processes is the use of the sodium or potassium salt of dichloroisocyanuric acid (DCCA) applied under mildly acidic conditions, typically about pH5. The chemical mechanism by which it works appears to be a slow hydrolysis of the salt to yield hypochlorous acid (HClO) at pH 3–6.¹³ DCCA is essentially a chloroamide, so that its controlled interaction with wool is not very distant from many earlier attempts to moderate hypochlorite activity by inclusion of nitrogen-containing compounds to act as retardants.^{1,p308}

7.5.5 Permanganate

Potassium permanganate (KMnO₄) is a well known strong oxidant. Although it has probably declined to minor commercial usage, it did have its hey-day in wool shrinkproofing technology and the chemical processes underpinning its success are instructive. Normally KMnO₄ would diffuse right through wool fibres and readily oxidise all the accessible CYS. In a concentrated solution of a salt (NaCl or Na₂SO₄) however, wool swelling is suppressed, so that the KMnO₄ reacts mainly with the high densities of CYS

in the epicuticle. At the termination of this reaction, the black near-surface deposits of manganese have to be cleared by a bisulphite rinse, which rapidly dissolves them.

7.5.6 Permonosulphuric acid

Sometimes this acid is described as peroxymonosulphuric acid or more simply as Caro's acid, so that many of the wool treatments derived from its usage are called Caroic methods. There are a number of favoured processes using this acid (H_2SO_5) under the label of Dylan treatments. The treatment in 10% H_2SO_5 is at pH 0.46. Irrespective of whether it is applied as a batch or a continuous top process, it is terminated by a reductive step with sulphite or bisulphite, which is thought to yield a useful improvement to the primary oxidation in terms of shrinkproofing performance.¹⁴

7.5.7 Polymer deposition processes for wool tops

Feldtman and McPhee produced one of the first publications that clearly demonstrated the advantages of an appropriate surface treatment of wool fibres as a preparatory step for a subsequent application of a solution of a polymeric resin.¹⁵ The advent of combined pre-treatment/polymer application processes was a timely opportunity to improve shrinkproofing up to machine-washable standards for many wool products. One of the first to be widely adopted for continuous treatment of tops was the chlorine/*Hercosett* process. An array of tops is passed around a sequence of six or more suction drums, each in its own treatment bath. The sequence of treatments in successive baths is scour-rinse-chlorinate-neutralise-polymer-softener, and finally passage through a dryer. In more modern versions of the process, the neutralise step after chlorination is often expanded to a bisulphite anti-chlor bath, a carbonate neutralising bath and then a rinse bowl, before polymer application. *Hercosett 57* is a polyamide-epichlorhydrin resin, and another successful polymer, *Dylan GRC*, is a similar cationic resin suitable for application to wool tops.

These treatments do not rely on interfibre bonding to combat felting, and scale masking appears to be the principal mechanism involved. Their outstanding success prompted detailed analysis of the reactions occurring at each stage.¹⁶ One of the problems with the process is that the tops harden when dyed, and the extent of hardening is related to the presence on wool fibre surfaces of degraded exocuticle proteins. Most of this material, about 7.5 g/kg of wool treated, is removed in the carbonate neutralising bath.¹⁶ Perfecting this step and the subsequent rinse appears to be the key to reducing the top hardening problem.

7.5.8 Fabric and garment treatments with polymers

One of the concerns about chlorine-based shrinkproofing processes is the discharge of some harmful compounds such as chloroamines in the waste liquor. It would also be desirable to avoid the fibre degradation inherent in chlorination. There is a regular demand for simple, versatile treatments that could be applied, for example, to batches of knitwear garments.

Many of the polymers developed for woven or knitted products do not exhaust from dilute aqueous baths, so that a common method of application is padding the fabric followed by curing. Shrinkproofing is achieved by inter-fibre bonding and, not surprisingly, the potential drawback of these processes is the loss of flexibility and soft handle.

The types of resin that have found popularity include polyurethanes with free isocyanate groups (*Synthappret LKF*, and its bisulphite adduct *Synthappret BAP*, Bayer), self-crosslinking polyacrylates, and a variety of silicones.

Refinements to treatments are constantly being made, with particular attention to improved curing and fabric handle.¹⁷ A detailed study of variations in applications of *Synthappret LKF* and *Synthappret BAP* (Bayer) on a knitted wool fabric afforded an insight into the role of surfactants in optimising the treatments.

Synthappret LKF is a trifunctional polyether-based urethane prepolymer containing terminal isocyanate groups. It is supplied as a solution in perchloroethylene and applied to the fabric by padding from perchloroethylene, followed by curing in saturated steam for an hour. Solvent-based processes of this general kind have been popular because they are versatile and can be applied to batches of garments in drycleaning machines. Their continued use is in doubt due to increasing restrictions on chlorinated solvents. Environmental concerns are based on the belief some solvent escapes into the atmosphere from industrial processes and chlorinated solvents are one class implicated in changes in the ozone layer.

Synthappret BAP is a water-soluble bisulphite adduct of a trifunctional isocyanate-terminated urethane prepolymer and is applied by padding from aqueous solution with bicarbonate as a curing assistant. The curing process typically dries the fabric at 150 °C for about 3 min. in a stenter.

All polymer applications to fabrics depend for their shrinkproofing action on forming interfibre bonds. These must be sufficiently strong to withstand domestic laundering, so that adhesive forces are the most relevant to shrink-resist efficiency. Less commonly, some polymers fail because of cohesive fracture within the polymer itself. With *Synthappret LKF*, failure occurs at the interfacial bond, whereas both mechanisms were observed with *Synthappret BAP*. Interfibre bonding effectiveness can be quantified by measuring the work to break untwisted yarns.

Surfactants have a substantial effect in increasing interfibre bonding and a plausible reason is that they stabilise *Synthappret BAP* solutions and, by delaying precipitation of polymer in the high temperature curing step, a larger number of bonding sites are formed.

7.5.9 Testing regimes for shrinkproof fabrics and garments

Most of the shrinkage tests utilise a programmable front loading washing machine. Usually called a *Wascator*, it has a horizontal rotating drum. The British Standard BS 4923: 1991 also includes test regimes based on a top-loading agitator type of machine. Many countries adopt the same general principles of testing, but the exact choice of test routine is closely linked to labelling regulations and instructions appropriate to each product. For example, under the *Fernmark* licence issued by Wools of New Zealand Inc., eight levels of *Wascator* operation are recognised. The 7A test is appropriate for knitwear with a handwash label, whereas 5A applies to machine-wash knitwear. Woolmark specifications, for example as controlled within Australia by the Australian Wool Corporation, nominate a selection of *Wascator* routines for each type of garment.

7.6 Antistatic properties

Static electrical charging of wool and other textile fibres during mechanical processing is mitigated by operating in a high-humidity environment and choice of suitably conductive process lubricants. Static electricity became more of a problem in homes and workplaces with the widespread introduction of central heating systems, which lower room humidity or dry out carpets with underfloor heating.

Although wool fibres are predominately composed of hydrophilic proteins, the relatively hydrophobic epicuticular layer is prone to developing a frictional static charge at low humidities. The original solution to this problem for floorcoverings was to introduce metal filaments into the wool pile and conductive chemicals or fibres into the carpet backing, but this approach was quite difficult to accommodate in many production routes.

Mild oxidation of wool carpets with peroxide increases the hydrophilicity of wool epicuticle and lowers static-propensity¹⁸ but, probably because of unwanted bleaching effects, this idea has not yet been applied commercially. Chlorination has much the same effect on wool fibre surfaces but there has never been a thorough evaluation of its potential as an antistatic process.

During the development of a chemical antistatic treatment for wool, it was found that a wide variety of topical treatments with anionic and cationic compounds at add-ons of about 1% on weight of wool treated would

provide excellent performance.¹⁹ However, the majority of these chemicals, which are generally similar to or are actually used as detergents, are water soluble and are therefore readily lost during carpet shampooing.

Cationic antistatic agents were generally the most effective, quaternary ammonium salts being the best sub-group of this class. As the amount of quaternary salt is increased from 0 to 1.4%, body-voltages developed in the standard Stroll Test typically decrease from -16000 V to zero at 0.8–1.2%, dependent on the particular compound tested. Positive voltages up to $+3000$ can be developed after excessive treatments. The mechanism of action of topical antistats is believed to be due to their ability to spread evenly on the low-energy hydrophobic surfaces of clean wool and so form an electrically conductive continuum. Discharges of body voltages of the order of $\pm 1500\text{ V}$ are barely noticed by most individuals, so this sets an approximate objective for antistatic performance at the lowest humidities likely to be encountered.

The natural hydrophobicity of wool fibre surfaces has most conspicuously been turned to advantage in a relatively cheap and simple antistatic treatment. An emulsion of trioctylammonium chloride (*Aliquat 336*, General Mills) breaks on wool fibre surfaces.²⁰ Ammonium groups provide the necessary polar properties and strong bonding of the trioctyl structure with surface hydrophobic groups render the process stable to shampooing and wear. Stringent standards for antistatic performance (conductivity specification) also entail applying a conductive latex as part of the carpet backing.

Wear tests equivalent to several years' heavy traffic and a typical repeat shampooing routine show that the treatment is essentially permanent and does not impair soil-resistance. The process has therefore found regular application, notably in contract carpet installations in static-sensitive situations such as hospitals, aircraft, hotels and other public buildings.

7.7 Flame-retardant wool

Wool has relatively good natural flame-retardant properties, but many wool products fail test specifications where stringent safety requirements are enforced. Fabrics and carpets for aircraft interiors, protective clothing, children's nightwear and furnishings of public buildings are some examples.

Sulphamates and phosphates are very cheap, effective chemicals applied to wool products such as fillings and insulation, where there is no washfastness requirement.²¹ Flame-retardants primarily developed for cotton, based on the use of tetrakis (hydroxymethyl) phosphonium chloride, or THPC, reacted with urea *in situ*, provided the first washfast process applied to wool.²² This process was displaced from the mid 1970s by one or other of a family of *Zirpro* processes. These are based on either zirconium or titanium complexes with citrates, oxalates and hexafluoro compounds.²³ Tita-

mium complexes are cheaper and more effective but cause significant yellowing of wool products and the residues are more toxic. Some variants of *Zirpro* processes reduce smoke emission and meet specifications for aircraft furnishings.²⁴

Neither *Zirpro* nor simple inorganic processes based on phosphate, sulphamate or boric acid increase risk due to toxic gas emission. Their effects on the kinetics of decomposition and gas release has been studied by thermogravimetric analysis.²⁵ The weight loss curves for untreated wool are similar in both air and nitrogen up to 440 °C. After the loss of regain water, the initial decomposition begins at about 210 °C, and at temperatures beyond 440 °C, wool in air or oxygen decomposes more rapidly than in nitrogen. Wool samples treated with phosphoric acid, ammonium dihydrogen phosphate, and tris (1-aziridinyl) phosphine oxide exhibited a decrease in both the rate and magnitude of mass loss at temperatures over 440 °C by comparison with an untreated sample.²⁶

A more extensive study which included *Zirpro* and other metal complexes, revealed a markedly different weight-loss curve when comparing a group of phosphorus-based treatments with those based on tin, tungsten, zirconium and titanium complexes. For the latter group, the final decomposition temperature of wool is lowered and rapid loss of mass ensues.²⁷ It is not unusual for flame retardant treatments of textiles to owe their efficacy to one of several different decomposition mechanisms when exposed to a source of ignition.

Fluorozirconate-based processes have been the most popular choice since their refinement in the mid-1970s, and extra attention has been given to understanding their mode of action. It was found that fluoride is not essential for flame-retardance, and indeed is slowly lost by repeated laundering. However, if the F/Zr ratio is less than 2, there must be complex formation between zirconium and wool carboxyl groups. Zirconium dioxide is ineffective as a flame retardant²⁷ because there is no such bonding interaction between zirconium and the wool protein structure.

7.8 Photostabilisers

7.8.1 Stability of wool-base colour

The complexities of sunlight degradation of wool were described in Section 5.4, and these notably include either yellowing or bleaching according to the relative amounts of UV and near-UV radiation. Bleached wool yellows more rapidly than unbleached wool. Of the methods tried to reduce this colour reversion, incorporating thiourea formaldehyde resins into the wool is the most successful, and retains some protection after repeated laundering. The mechanism of protection appears to be quenching of singlet and

triplet excited states in irradiated wool, supplemented by some catalysed photobleaching.²⁸ This process is really only relevant for undyed or very pale shades on wool fabrics, and predominantly these would be fine wool products.

Colour stability of wool carpets and knitwear dyed in pale shades is a significant problem where both photobleaching and photoyellowing are undesirable. A process based on the proprietary chemical *Lanalbin APB* is designed to balance the two effects.²⁹ Note that this is an entirely different solution as it predominantly relates to coarse wools that have not been chemically bleached, and the main problem is to successfully counter photobleaching rather than photoyellowing.

The process can be carried out most economically in the last bowl of a scouring train. Licencing control of the treatment is held by Wools of New Zealand and it is marketed under the brandname *Fernplus APB*. Fine Merino wools are so densely compacted during their growth on the sheep's back that they do not suffer significantly from photodegradation effects such as yellowing. Subsequently, therefore, fine wool products have a minor propensity for the reversionary process of photobleaching.

7.8.2 Protection from photodegradation

Extending the useful life of wool products by curbing the loss of physical strength and elasticity caused by exposure to sunlight is clearly a desirable objective. It is a truism to say this is against nature, for, in the absence of this destructive mechanism, recycling of discarded keratins such as animal hair and feathers would be seriously impaired. For example, discoveries of mammoth hair or similar remnants from other animals are very rare compared to skeletal remains. When they have been subject to the natural elements of sunshine and rainfall, the constituent proteins are reduced to amino acids and their degradation products within about three years.

There is a radical difference in the problem according to the wool product. Fine wool apparel products are rarely exposed to sunlight for long periods, but wool furnishings such as carpets, drapes, and upholstery fabrics constructed from mid-micron and coarse wools are often exposed daily to long hours of sunlight transmitted through window glass. There is also a growing consumer interest in apparel that protects skin from excessive exposure to the full spectrum of UV radiation in sunlight.

Protection of interior textiles such as curtains is therefore not against UV radiation shorter than 305 nm, which is absorbed by window glass, but the very penetrative and abundant radiation band of sunlight, especially 350–385 nm wavelengths. An obvious strategy is to apply a colourless near UV absorber, rather like protecting people from sunburn with a screening chemical. The most appropriate for easy application are those that simulate

acid dyestuffs. Most commonly used in current industrial practice are sulphonated 2-hydroxybenzophenones and a sulphonated 2-hydroxybenzotriazole.^{30,31} Another commercial product is also available.^{31a}

There are two serious difficulties in developing and testing protective treatments against photodegradation for wool. Firstly, there are substantial differences between results obtained with conventional sunlamps, including the whole environment of accelerated testing (temperature, humidity, etc.) and exposure of samples in various sorts of glasshouse environments with natural sunlight. Secondly, the sequence of wool degradation may commonly begin with strength improvement, followed by a fairly stable period, then a rapid deterioration. Also, abrasion resistance measurements or tests of elasticity are unlikely to follow the same trend lines over various exposure times as may be found with the simpler fabric strength tests, so that relevant performance evaluations require some experience.

These assessment variables were described in studies primarily designed to identify dyestuffs that might usefully be recruited to offer photoprotection to wool.³²

Yellow and brown dyes optimally absorb in the low part of the visible spectrum, i.e. 400–420 nm, and because of this, their overall absorption band extends back into the near-UV region most destructive of wool strength. Dyestuff absorption in this critical region can protect wool to the extent that serious deterioration of physical properties can be postponed for periods of the order of 1000 hours of sunlight exposure. Although it is technically possible to include modest amounts of the most protective yellow dyes in a variety of product colourations such as olive, and various shades of tan and brown, there is little evidence that this opportunity has been seriously addressed by carpet and furnishings manufacturers. Another potential industrial innovation is the incorporation of some aluminium in wool (see Section 5.13.4), which has the effect of repairing the loss of elastic properties caused by photodegradation.³³

7.9 Stainblocking

Since 1980 there has been a sustained interest in improving appearance retention and easy-care characteristics of textile products. A prominent objective within that generalisation is to eliminate residual staining of carpet pile that has suffered spillage of food and liquids. Nylon fibre manufacturers have perceived branding of their product with a proprietary stainblocking finish as an important competitive opportunity. Many of the chemical aspects of adventitious staining of nylon and wool pile carpets are similar, so that much of the stainblocking technology is relevant to both fibres and the competitive motivation is equally cogent for wool.

The predominant source of carpet stains are acid dyes included as food and drink colourants. Wine and tea contain polyphenolic tannins that can be even more difficult to combat.

Initially, it was envisaged that the effectiveness of stainblocking treatments could be attributed to repulsion of anionic (i.e. food and drink acid) stains by applying a chemical that contained sulphonic acid groups. More recently, for both wool and nylon a supplementary mechanism has been recognised. Rather than simply and solely relying on a fibre surface repulsion effect, longer and higher temperature treatments result in diffusion of some stainblocking chemicals into the fibres where their intimate bonding interactions with the fibre substrate results in a diffusion barrier for incident stains.³⁴

The dual objective of stainblocking finishes is therefore to firstly repel aqueous and oily spills, secondly to inhibit stain retention of (mainly) acidic colourants, and thirdly to restrict diffusion further into the fibres by forming an interlocked stainblocker/fibre layer.

A major group of stainblocker chemicals are reaction products of sulphonated phenols and formaldehyde. *Syntans*, as these compounds are generally known, have been evaluated for their stainblocking attributes.³⁵ Acrylic polymers incorporating carboxylate groups were included in the review, both types obviously designed to repel acid dye spillage by a charge repulsion mechanism. Increased liquid repellancy is commonly consolidated by a post-application of a fluorochemical. Fluorochemical treatments of woven and knitted apparel have improved to the point where they frequently meet both the stain and water repellancy performance standards for easy-care products, thus obviating the need to apply stain-resist chemicals as well. Wool carpets are subject to more stringent abrasive wear, which damages the surface layer of fluorochemical so that, for this reason alone, chemical stain blocking remains an important modern technology.

A standard test for staining of carpets involves exposure to the Food and Colouring dye F and C Red 40, applied under standard conditions described in AATCC Test Method 175-1998.³⁶ Stainblocking treatments range from application during yarn dyeing, an aftertreatment to that process, or a product treatment such as applying a foam or spray finish to carpets.

7.10 Multi-purpose finishes

Successful development of versatile flame retardant processes based on *Zirpro* treatments has encouraged development of treatments suited to a wider range of protective wool clothing, which may also require washability and oil-, petrol-, water- and acid-repellency.³⁷

Silicone-based shrink-resist polymer treatments are incompatible with

exhaustion of the fluorocarbons required for multi-purpose liquid repellency finishes. This problem can be resolved by applying the Bayer shrinkproofing product *Synthappret BAP* and *Neoprene 400*.³⁸ The latter has a sufficient chlorine content to counteract the inherent flammability of the shrink-resist finish.

Various other combinations are possible, such as flameproofing with tetrabromophthalic acid, co-applied with *Zirpro* chemicals and an anionic fluorocarbon³⁹ such as *Nuva F* (Hoechst) or *FC217* (3M). Securing good adhesion of a fluorocarbon to wool fibre surfaces is the key requirements for conferring repellancy properties against most liquids.

In simpler situations where flame resistance is not a requirement, co-application of the fluorocarbon and a shrink-resist polymer improves their adhesion and fastness to abrasion, washing and drycleaning.⁴⁰

7.11 Polymer grafting

One of the earliest methods of incorporating a polymer within wool fibres took advantage of the natural small proportion of thiol groups in wool to catalyse polymerisation of ethylene sulphide.⁴¹ The main problem with most free-radical catalytic systems is to confine the catalyst in the fibres and avoid wholesale formation of homopolymer in the monomer bath. This was attempted with the well-known ferrous ion/peroxide combination for generating free radicals. A two step process starting with impregnating wool with ferrous sulphate, then including peroxide in the aqueous monomer bath, has been tried with various monomers. In practice it is difficult to avoid some diffusion of ferrous ion back into solution and therefore formation of non-grafted polymer.

During the 1960s, many new, relatively cheap monomers entered the market and were evaluated as graft polymers in wool. Acrylonitrile and some methacrylates crosslinked with butadiene, styrene and several acrylates were prominent candidates.⁴² A lack of solubility in water is not a particular problem if the monomers are first converted to an emulsion which subsequently begins to preferentially crack on wool fibre surfaces as the reaction temperature is increased. This affinity of the hydrophobic surface of wool fibres for water-insoluble monomers is analogous to the success in coating them with a trioctyl antistatic agent (Section 7.6).

Powerful irradiation facilities using Co^{60} X-rays or 500 kV electrons introduce the possibility of intimate polymer grafting on a wider range of free radical sites in wool proteins.^{43,44} Such experiments have generally been disappointing as the free radicals that are first formed transmute rapidly to low activity forms and result in small add-ons of graft co-polymers.

The most sophisticated and flexible approach to polymer formation in wool is the discovery of a catalytic system uniquely dependent on the small

natural thiol content of wool. Copper acetylacetonate and trichloroacetic acid form a water-soluble complex that degrades by reaction with wool thiol groups and generates both $\text{CCl}_3\cdot$ radicals and CCl_3^- ions at temperatures above 60°C . Excess trichloroacetate decomposes to form CO_2 and HCCl_3 , and this concurrent evolution of some gas flushes air (and therefore free-radical inhibitor oxygen) from the reaction vessel.^{45,46} This catalytic and flushing system is economically formed from small amounts of acetyl acetone, copper sulphate and an excess amount of trichloroacetic acid, added individually to wool immersed in water, typically in a dyeing vessel equipped with a close-fitting lid. Both water-soluble and insoluble monomers can be introduced into the dye vessel, the insoluble ones being first converted into an emulsion with a detergent stabiliser in a side tank.

Processes developed from this system include grafting 20–130% poly-methacrylic acid in loose wool, subsequently converted into needlepunched batting in the form of a continuous sheet.⁴⁷ This was mounted in a prototype cation-exchange water treatment plant designed for rapid removal of metal ion pollutants captured by carboxylate groups within a continuous cycle of metal recovery and Na_2CO_3 regeneration.⁴⁸

Potential large-scale utilisation of polymer grafting, specifically aimed towards the carpet industry, was evaluated with up to 1.5 tonne lots of carpet wools treated to exhaustion with 750 kg of various butyl acrylate, methyl methacrylate, styrene and methacrylic acid mixtures in a sealed dyeing vessel. A great advantage of this polymerisation process is that it is readily adapted to suit conventional metal complex dyeing⁴⁸ in a combined process. Other unique features of the process include the complete absence of unwanted homopolymer in the immersion liquor and the total utilisation of available monomer. The latter feature is not just unusual amongst grafting reactions, but very importantly permits normal discharge of the spent treatment liquor to drain. Its success arises from the fact that polymer accretions within wool fibres preferentially attract monomers from the external aqueous phase.

Wool-polymer composites produced in this way process normally from spinning right through to carpet tufting. Performance comparisons with pure wool carpets of the same construction and pile weight are satisfactory,⁴⁹ and the low price of monomers gives a cost advantage.⁵⁰ However, these processes have not been used commercially, a major reason at the time of their development being the promotion by wool interests of 100% wool products. Nevertheless, the prospect remains of preparing novel wool-based materials by applying a proven, facile process. Polymer grafting in straight long-staple wools, such as those from the Lincoln breed, had some brief commercial success for the manufacture of ladies' wigs, where the addition of the polymer conferred advantages in setting structure and waves in the product.

7.12 Removal of vegetable matter by carbonising

Very often burrs, seeds and other vegetable matter are removed mechanically during the carding process. However, some types of vegetable matter and heavily contaminated wools require carbonising. This process involves padding scoured wool with dilute sulphuric acid (5–7% w/w and approximately 65% pick-up). After first drying at 70–90 °C to concentrate the acid, the wool is baked for about a minute at 120–125 °C. This chars and embrittles the vegetable matter so that when the treated wool is passed through rollers it is basically crushed to powder and falls out either directly or on subsequent mechanical processing. Many woolscouring companies readily incorporate carbonising within their regular scouring service to clients (Section 2.7.1).

Without careful control, carbonising may cause serious damage to the wool. In particular, its initial moisture content must be sufficiently low, and the low-temperature drying step carried out carefully. A more uniform distribution of the acid is achieved with the assistance of a detergent. Non-ionic agents containing an alkyl or aryl hydrocarbon group are generally the best choice.⁵¹ Carbonised wool should not be stored without first rinsing and neutralising.

The most notable chemical modification of wool induced by carbonising is described as a peptidyl shift. This is a reversible reaction whereby the peptide bonds adjacent to serine (SER) and threonine (THR) residues are cleaved and are detected as an increase in terminal amino groups at those sites. Prompt neutralisation has the effect of reforming up to 80% of the SER and about 70% of the THR peptide bonds.⁵² Successful management of this step essentially means that carbonising should result in minor main chain peptide cleavage and trivial deterioration of the physical properties of the treated wool.

7.13 Setting

Setting is the general description given to a variety of chemical, and combinations of chemical and physical, processes that are designed to stabilise yarns and fabrics so that they will remain permanently in a particular configuration. Part of the important history of wool science aimed at understanding the factors involved in the physical stability were fundamental studies of the setting properties of individual fibres.

Wool fibres held while extended 30–40% and immersed in boiling aqueous solutions, which may also contain setting assistants, for periods up to 2 hours retain most of the extension when released. When the free fibres are again boiled for an hour, some contraction occurs and the residual

extension is defined as 'permanent set'. A full account of setting properties of wool fibres and the associated physical and structural changes is given in Section 4.3.7.

Introduction of synthetic fibre fabrics produced a great stimulus for development of setting processes applicable to wool fabrics. The synthetic competing fibres are thermoplastic so that durable creases and pleats are readily formed under compression at an appropriate temperature.

Imparting flat finishes to fabrics with short steaming times, as is generally practiced in industrial setting, results in minor setting of individual fibres. Assessment of industrial setting of pleats and creases is commonly studied by removing yarns from the crease area and releasing them in hot water. Poorly-set fabrics give crease angles of 170–180° and well-set examples have crease angles less than 50–60°.

Setting treatments that provide the best permanent set of single fibres are also the best for imparting well-set pleats and creases. The important step is relaxation of molecular stresses by conformational rearrangement of wool fibre proteins. This requires breaking and reforming both hydrogen bonds and disulphide crosslinkages. Reducing agents such as ammonium thioglycollate promote disulphide bond rearrangements, the active agent being the thiol anion. This is RS⁻ in the following equation, and not the parent RSH thiol.⁵³



Accordingly, wool is not readily set in acidic conditions, but sets well in neutral or alkaline solutions where thiols largely exist in their ionised state. A more extensive account of the various chemical reactions between wool and reducing agents is presented in Section 5.11.

In terms of industrial milestones, one of the most famous would be *Siroset*, introduced by CSIRO in Australia in 1959. The most common application of this technology is to spray a reducing agent, monoethanolamine sulphite, on the relevant areas of the garment and steam it for a few minutes. This was a major success for basically permanent setting of creases in men's trousers as well as ladies' pleated skirts.

Following the same general principles, flat-setting of fabrics that have also been adequately shrinkproofed, affords a method for producing washable, minimum-iron garments. They were first introduced in Australia under the *Sironise* label, but since then, many similar product treatment variations have come into the marketplace.

In recent times the setting of permanent creases in wool trousers has moved away from chemical treatments to be replaced by methods based on applying a thermosetting resin along the crease line and on the reverse side of the fabric.

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