WOOL

1. Raw Wool Specification

Wool is the fibrous covering from sheep (1) and is by far the most important animal fiber used in textiles. It appears to have been the earliest fiber to be spun and woven into cloth. In 2000–2001, world greasy wool production was 2.3×10^9 kg from 1×10^9 sheep, which is equivalent to 1.4×10^9 kg of clean wool (2) (Tables 1 and 2). This is down from a peak of 2.0×10^9 kg in 1989–1990.

Wool belongs to a family of proteins, the keratins, that also includes hair and other types of animal protective tissues such as horn, nails, feathers, beaks, and outer skin layers. The relative importance of wool as a textile fiber has declined over the past decades with the increasing use of synthetic fibers for textile products. Wool, however, is still an important fiber in the middle and upper price ranges of the textile market. It is also an extremely important export commodity for several nations, notably Australia, New Zealand, South Africa, and Argentina, and commands a price premium over most other fibers because of its outstanding natural properties. These include soft handle (the feel of the fabric), water absorption (and hence comfort) and superior drape (the way the fabric hangs). Table 2 shows wool production and sheep numbers in the world's principal wool-producing countries.

The principal characteristics of clean wool types are average diameter, measured in micrometers (referred to as microns), and average length, measured in millimeters. Essentially all fine diameter wool is produced by merino sheep or

Table 1. **World Production of Wool (2000/2001), × 10^6 kg**[a]

Source	Fiber diameter (micrometers)	Greasy	Clean
merino	<24.5	932	572
crossbred	24.6 to 32.5	540	308
other (carpet)	>32.5	852	494
Total		*2,324*	*1,374*

[a] Ref. 2.

merino cross-breeds. Over 75% of the sheep in Australia (the world's largest wool producer) are merino sheep, which are also bred in large numbers in South Africa, Argentina, and the former USSR. The softness, fineness, and lightness of fabrics is determined primarily by fiber diameter, and so the price is very sensitive to the mean diameter (3) (Fig. 1).

Medium diameter wool includes sheep breeds of English origin, eg, southdown, hampshire, dorset, and cheviot, as well as crossbreds, eg, columbia, targhee, corriedale, and polwarth, from interbreeding with merinos. Coarse diameter wool comes from sheep chiefly bred for meat, eg, lincoln, cotswold, and leicester.

Raw wool from sheep contains other constituents considered contaminants by wool processors. These can vary in content according to breed, nutrition, environment, and position of the wool on the sheep. The main contaminants are a solvent-soluble fraction (wool grease); protein material; a water-soluble fraction (largely perspiration salts, collectively termed suint); dirt; and vegetable matter (eg, burrs and seeds from pastures).

In buying raw wool, wool processors are concerned about its quality, the quantity of pure fiber present, and its freedom from contamination (4). For the fine and medium wools used for apparel, the major characteristics are average fiber diameter, yield, ie, the percentage content of pure fiber; content and type of vegetable-matter (VM); average fiber length; strength of fiber staples;

Table 2. **Wool Production and Numbers of Sheep in Principal Wool-Producing Countries (2000/2001)**[a]

	Wool production (greasy)		
Country/Region	× 10^6 kg	%	Sheep, × 10^6
Argentina	62	2.7	13.4
Australia	652	28.1	113
China	291	12.5	135
Iran	74	3.2	53.9
New Zealand	258	11.1	45.3
South Africa	50	2.2	17.5
former Soviet Union	128	5.5	49.2
Turkey	70	3.0	30.2
United Kingdom	62	2.7	27.6
Uruguay	57	2.5	13.0
other	620	26.5	508
Total	*2324*	*100*	*1006*

[a] Ref. 2.

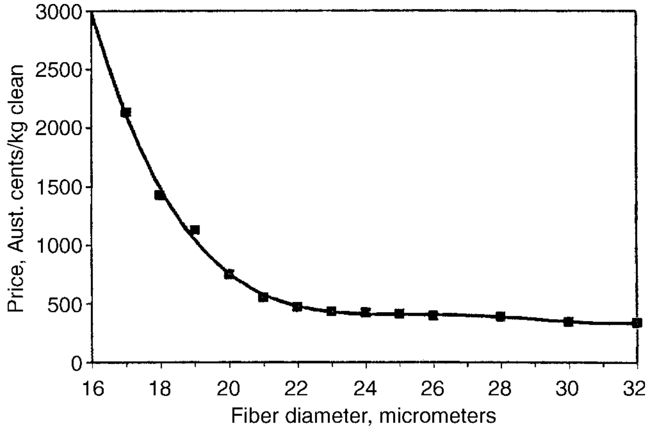


Fig. 1. Dependence of Australian wool prices on fiber diameter (1999/2000) (3).

and the position of any weak spot along the fibers. For very fine wools, the frequency and clarity of waves (crimp) in the staples has a significant effect on price. The range of fiber diameters, color of the clean wool, and the number (if any) of naturally colored fibers present can also be important. For carpet-type wools (long wools), the important properties (5) are yield, fiber diameter, fiber length, color, bulk (the volume occupied by the fibers in a yarn), and vegetable-matter content. Also important for coarse wools is the degree of medullation. This is associated with cells containing air, arranged along the fiber axis. The presence of medulla cells increase light scattering by the fibers, restricting the use of these wools for some purposes.

Until the early 1970s, the characteristics of different wools were largely evaluated visually by wool classers and valuers. With the development of sampling techniques and equipment capable of rapid and economical measurement of yield, diameter, and vegetable matter (6,7), objective measurement and the sale of wool by sample became dominant in major wool-exporting countries. In sale by sample, cores are drawn from each lot and tested for yield, diameter, and vegetable-matter content in accordance with international standards (8,9). Measurements of staple length, strength, and position of weakness are also now in routine commercial use. In addition, a full-length display sample, representative of each lot and obtained by standard procedure (10), is available for buyers to appraise other characteristics. Sale by sample decreased costs by reducing the handling of bulk wool in wool-brokers' stores and selling operations. It also enabled the processing performance of wool to be predicted in topmaking (11) and spinning (12).

2. Fiber Characteristics

New instrumentation for measuring fiber diameter (13,14) has meant that data on the range of diameters present (CV_D) and fiber curvature (related to crimp frequency) are now available. The impact of these is fairly well established

(15). These instruments have also been introduced on-farm so that the fleece quality of each animal can be assessed from a mid-side (16) or whole-fleece (17) sample. In some cases it is possible to gain increased returns from separating out the finest fleeces but bigger gains are possible from accelerating the rate of genetic progress. A remaining objective of research is to facilitate the introduction of a system of sale of raw wool by description in which a sale sample will not be required for inspection.

2.1. Fiber Growth.

Wool fibers are produced from multicellular tube-like structures known as follicles. These follicles are located in the skin layers (dermis and epidermis) of sheep and two types of follicles, primary and secondary, are usually identified. Primary and secondary follicles are described from the order of their initiation and development in fetal skin. The primary follicles develop first, in the unborn lamb. Secondary follicles develop later and in finer wooled sheep derived secondary follicles subsequently form by branching from the original secondaries, with which they share a common orifice (18). Each primary follicle has a sebaceous gland and a sweat gland together with an arrector muscle, whereas secondary follicles usually have only an associated sebaceous gland (19).

2.2. Fiber Morphology.

Wool fibers consist of cells, where flattened overlapping cuticle cells form a protective sheath around cortical cells. A scanning electron micrograph of a clean merino wool fiber is shown in Fig. 2. In some coarser fibers, a central vacuolated medullary cell type may be present.

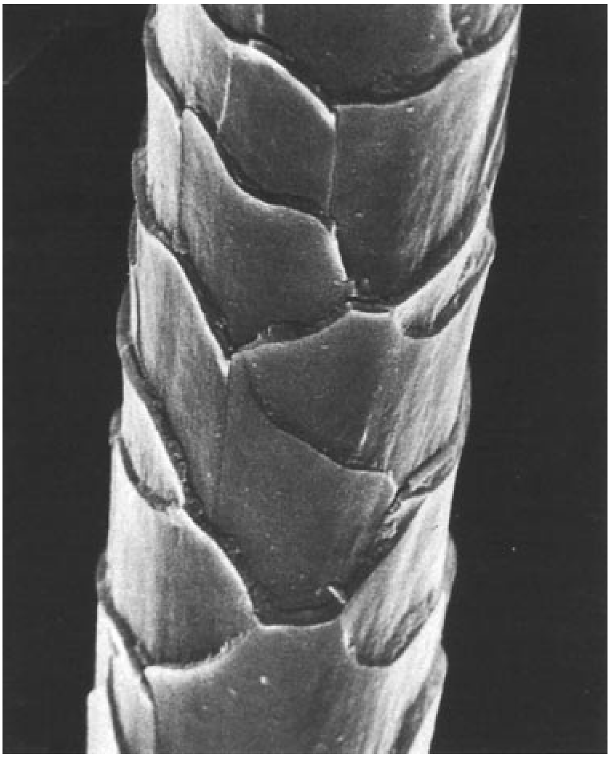


Fig. 2. Scanning electron micrograph of merino fiber, showing overlapping cuticle cells.

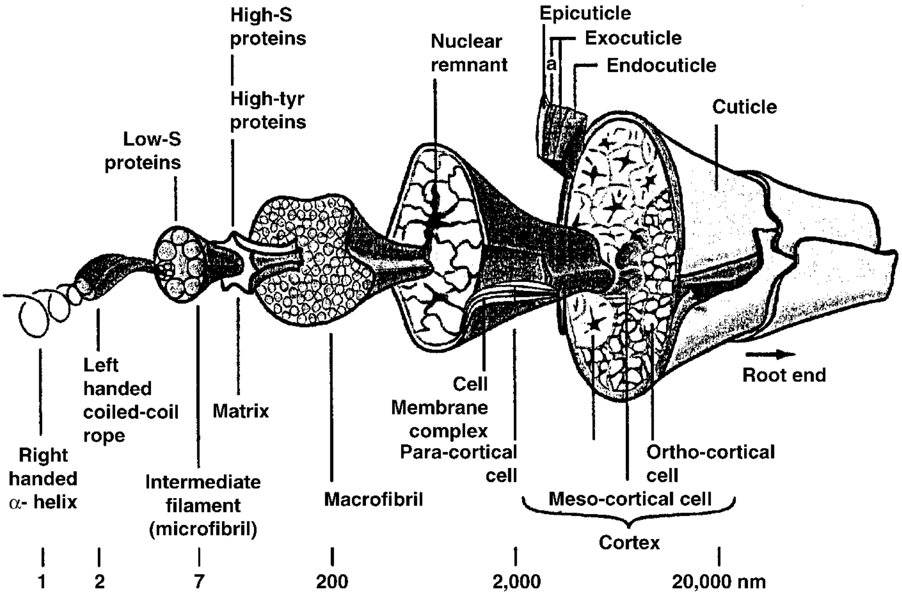


Fig. 3. Schematic of the structure of a fine merino wool fiber.

In fine wool, such as that obtained from merino sheep, the cuticle is normally one cell thick (approximately 20 × 30 × 0.5 micrometers) and usually constitutes about 10% by weight of the total fiber. Sections of cuticle cells show an internal series of laminations (Fig. 3), comprising outer sulfur-rich bands known as the exocuticle and inner regions of lower sulfur content called the endocuticle (20). On the exposed surface of cuticle cells, a membrane-like proteinaceous band (epicuticle) and a unique lipid component form a hydrophobic-resistant barrier (21). These lipid and protein components are the functional moieties of the fiber surface and are important in fiber protection and textile processing (22).

The cortex comprises the main bulk and determines many mechanical properties of wool fibers (Fig. 3). Cortical cells are polyhedral, spindle-shaped, and approximately 100 micrometres long. They consist of a class of biological filaments known as intermediate filaments (23) embedded in a sulfur-rich matrix. The intermediate filaments (originally termed microfibrils), together with the matrix, are organized into large macrofibrillar units and these are often observed in sections of cortical cells. In fine merino wool, two main types of cortical cell, known as ortho- and para-, are arranged bilaterally. Orthocortical cells show different intermediate filament/matrix packing arrangements from those of paracortical cells (24). The arrangement of ortho- and paracortical cells differs among wool types. For example, in lincoln wool an annular (orthocortical core surrounded by paracortex) cellular arrangement is present. Merino fibers possess a characteristic crimp and in these fibers the orthocortex is located on the outer side of the crimp curvature.

A continuous intercellular material is present between cuticle and cortical cells which, despite being a relatively minor fraction of the total fiber weight, is of increasing interest because of its presumed role in the penetration of water and chemical reagents into wool fibers. This region, called the cell membrane complex, is approximately 25 nanometers wide (25). It comprises a continuous phase of intercellular material, together with the apposing cellular membranes of the cuticle and cortical cells.

Over the past decade, major advances have been made in the knowledge of the cellular and molecular processes in wool follicles that lead to the formation of the wool fiber cuticle, fiber surface, and fiber cortex. In the wool follicle, presumptive cuticle cells undergo flattening during their passage up the follicle and are interlocked with the cuticle cells of the inner root sheath (IRS). When examined by transmission electron microscopy (TEM), the developing fiber cuticle cells demonstrate densely stained intracellular laminae forming in the outer regions of the cells. As the laminae develop, they separate to form an outermost layer, the a-layer, and an underlying layer. Together, these layers comprise the exocuticle.

The remaining cellular volume contains an innermost lightly stained endocuticle (20). In the final stages of cuticle differentiation, proteolipid complexes are formed on the presumptive fiber surface. Unusual mixtures of fatty acids are present in these complexes, which lead to the formation of a hydrophobic surface on the emergent wool fiber (26).

During their upward growth in the follicle, fiber cuticle cells remain adhered to the IRS cuticle by intercellular laminae that develop between two cell types (20). This produces a membrane complex that is different in appearance to that formed between differentiated cortical cells. The main differences exist in the presumptive surface of fiber cuticle cells, where the original plasma membrane appears to be disrupted. This process has been observed by using energy-filtered transmission electron microscopy (21), where it appears that the intercellular laminae are precursors to the formation of a new fiber cuticle surface membrane. It seems reasonable to conclude that a specialized hydrophobic membrane must be synthesized, because a plasma membrane is designed to exist only in a physiological environment and could not perform the protective and other specialist functions of the fiber surface membrane. The mechanism involving separation of inner root sheath cuticle and fiber cuticle cells is essentially unknown, but the cleavage plane appears to occur along a densely stained ultrafine band located in the center of the intercellular laminae (21).

Cortical cells form from a central or annular stream of germinal epithelia. During their early differentiation they undergo elongation and alignment processes. The initial sites for the formation of keratin structural components (arising concurrently with cell elongation) are at the outer boundaries (plasma membranes) of cortical cells, often in association with desmosomes (27,28). At high magnification, these initial keratin structures appear to consist of intermediate filaments (IFs) of 7–8 nm in diameter. These show appreciable staining when viewed after application of the heavy-metal preparations commonly used for contrast enhancement in TEM studies (28). After the formation and packing of IFs into lattice structures, a densely stained proteinaceous material appears to occupy the interfilamentous spaces. This proteinaceous material forms a matrix that is generally considered to be composed of high sulfur and high tyrosine proteins. The formation of these various structural components from their constituent proteins follows this two-stage sequential differentiation (29). As differentiation proceeds, the IF matrix aggregates to form structures, often known as macrofibrils, which increase in size and eventually occupy the bulk of presumptive cortical cells (30).

3. Chemical Structure

Wool belongs to the family of proteins called α-keratins, which also include materials such as hooves, horns, claws, and beaks (31). A characteristic feature of these "hard" keratins is a higher concentration of sulfur than "soft" keratins, such as those in skin. Although clean wool consists mainly of proteins, wool also contains approximately 1% by mass of non-proteinaceous material. This consists mainly of lipids plus very small amounts of polysaccharide material, trace elements, and, in colored fibers, pigments called melanin. The lipids are both structural and free.

3.1. Protein Composition. Proteins, or polypeptides, are formed by multiple condensation of α-amino acids via their amino and carboxyl groups to form secondary amide (ie, peptide) bonds (–CONH–). The general structure of all proteins or polypeptides may be represented as (–NHCHRCO–); where R represents the side-chain of the amino acid. The peptide grouping is also known as an amino acid residue, because it is the part of the amino acid that remains after the condensation reaction. Complete acid hydrolysis of wool yields 18 amino acids, the relative amounts of which vary considerably between fibers from different sheep breeds, from different individuals of the same species, and sometimes along the length of single fibers from the same animal (31). These differences are the result of several factors, including genetic origin and nutrition. Studies on the chemical structure of wool have been largely confined to fine merino fibers, although aspects treated herein are relevant to all wool types. Typical figures for two different samples of wool are given in Table 3.

The side groups of the amino acids derived from wool vary markedly in size and chemical nature and play an important role in the physical and chemical properties of the fiber. Those containing non-polar, hydrocarbon groups are hydrophobic and of low chemical reactivity. The polar, aliphatic hydroxyl groups of serine and threonine are chemically more reactive than the hydrocarbon residues. The side chains that have the most overall influence on the properties of wool are, however, the acidic groups of aspartic and glutamic acids and the basic groups of hystidine, arginine, and lysine. These acidic and basic groups give wool an amphoteric character and play an important role in wool dyeing. They are also responsible for wool's ability to combine with large amounts of acids or bases. The individual polypeptide chains of wool are held together and stabilized by both covalent and noncovalent bonds and interactions.

The most important of these is the disulfide bond (Fig. 4). This occurs by reaction of pairs of cysteine residues to form cystine (disulfide) linkages (–S–S–) between different polypeptide molecules, or between segments of the same molecules, as shown. The disulfide inter-chain cross-links have been compared with the rungs of a ladder. They are important because they prevent movement of chains and chain segments and, thus, are responsible for the higher stability and lower solubility of wool fibers compared with most proteins.

Table 3. **Amino Acid Composition of Merino Wool**

	Amino acid content, Residues/100 residues		
Amino acid[a]	Sample 1[b]	Sample 2[c]	Nature of R group
glycine	8.6	8.2	aliphatic hydrocarbon
alanine	5.3	5.4	aliphatic hydrocarbon
valine	5.5	5.7	aliphatic hydrocarbon
leucine	7.7	7.7	aliphatic hydrocarbon
isoleucine	3.1	3.1	aliphatic hydrocarbon
phenylalanine	2.9	2.8	aromatic hydrocarbon
tyrosine	4.0	3.7	aromatic hydrocarbon
serine	10.3	10.5	hydroxyl
threonine	6.5	6.3	hydroxyl
aspartic acid[d]	6.4	6.6	acidic
glutamic acid[e]	11.9	11.9	acidic
histidine	0.9	0.8	basic
arginine	6.8	6.9	basic
lysine	3.1	2.8	basic
methionine	0.5	0.4	sulfur containing
cystine[f]	10.5	10.0	sulfur containing
tryptophan	[g]	[g]	heterocyclic
proline	5.9	7.2	heterolytic

[a]($^{+}H_3N-C(R)-COO^{-}$).

[b]Ref. 32.

[c]Ref. 33.

[d]Includes asparagine.

[e]Includes glutamine.

[f]The amount of cystine is shown as the concentration of its reduction product, cysteine (also termed "half-cystine"). This includes any of the oxidation by-product, cysteic acid, that is present.

[f]Tryptophan is destroyed under the conditions used for these analysis; values of about 0.5 residues % have been obtained by alternative techniques (34–36).

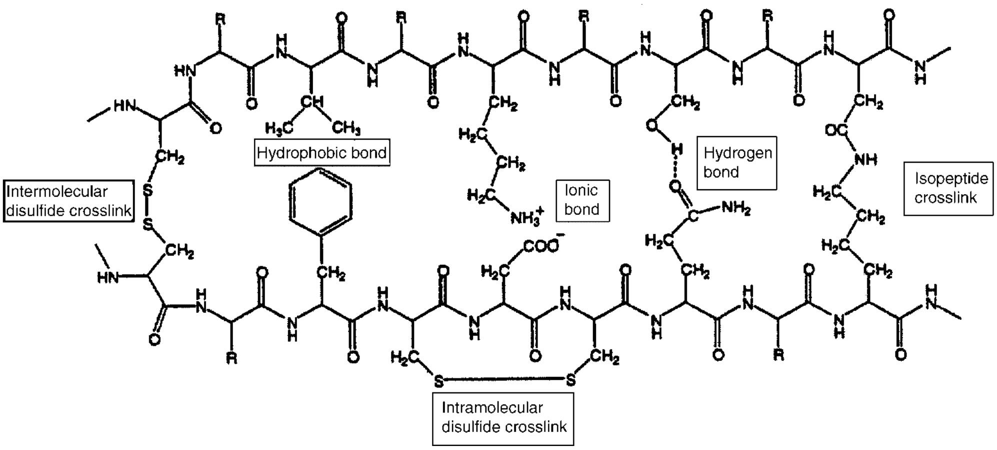


Fig. 4. Types of covalent and non-covalent bonds in wool.

The disulfide cross-links are readily rearranged through a thiol/disulfide interchange reaction under the influence of heat and water, or more rapidly on treatment with alkaline-reducing agents (eq. 1 where W = Wool).

$$\mathrm{WS_1{-}S_2W} + {-}\mathrm{S_3^-} \rightleftharpoons {-}\mathrm{S_1^-} + \mathrm{WS_2{-}S_3W}$$

Thiol/disulfide interchange facilitates conformational rearrangement of the wool proteins, leading to relaxation of molecular stress in the fiber. This property is employed in the permanent setting of wool fabrics. Another type of covalent cross-link present in wool is the isopeptide bond, formed between the side chains of lysine and either aspartic or glutamic acid (Fig. 4). Noncovalent bonds or interactions also make an important contribution to the properties of wool. These secondary bonds can occur within a single protein chain, or between different chains. They include hydrogen bonds between –CO and –NH groups in the polypeptide chains and the amino and carboxyl groups in the side chains, and also between suitable donor and acceptor groups in the amino acid side chains. Strong electrostatic interactions (ionic bonds, or “salt linkages”) also occur between ionized carboxyl and amino groups in some of the side chains. Ionic bonds contribute to the dry mechanical properties of wool fibers. Hydrophobic interactions can occur between nonpolar groups in some of the side chains and these contribute to the mechanical properties of keratin fibers, particularly when wet. They are also important in wool setting.

Structure of Wool Proteins. The structure of wool proteins has been the subject of much research. Methods to solubilize, separate, and determine the amino acid sequence of these proteins have been reviewed (31,37). It is estimated that wool contains about 170 different types of polypeptides varying in relative molecular mass from below 10,000 to greater than 50,000 (37,38). Morphologically, wool fibers are biological composites, with each component having a different physical and chemical composition (Fig. 3). The groups of proteins that constitute wool are not uniformly distributed throughout the fiber, but are aggregated within the various regions.

Except for a small amount of the amino acid methionine, the sulfur in wool occurs in the form of the amino acid cystine. Only approximately 82% of clean wool consists of keratinous proteins, which are characterized by a high concentration of cystine. Approximately 17% of the fiber is protein material of relatively low cystine content (<3%); this has been termed nonkeratinous. As a result of the lower cystine content, the nonkeratinous proteins have a lower concentration of disulfide cross-links compared with the keratinous proteins in the fiber. The nonkeratinous material is, therefore, more labile and less resistant to chemical attack than the keratinous proteins. The nonkeratinous proteins are located primarily in the cell membrane complex between the cortical cells and in the endocuticle (Fig. 3). Approximately 13% of the total nonkeratinous material is also located within the cortical cells, where its distribution differs between the cells of the ortho- and paracortex.

The keratinous proteins of wool belong to three groups:

low-sulfur proteins, rich in amino acids that contribute to α-helix formation (glutamic acid, aspartic acid, leucine, lysine, arginine)

high-sulfur proteins, rich in cystine, proline, serine, and threonine
high-glycine, high-tyrosine proteins which are also rich in serine.

The proteins derived from the rodlike intermediate filaments (microfibrils) of the cortical cells contain the helical segments of low sulfur proteins. These are surrounded by a relatively amorphous, nonfilamentous matrix, which consists principally of high-sulfur and high-glycine/high-tyrosine proteins. It has been shown that the amino acid sequences of the helical portions are highly homologous with those of intermediate filament proteins derived from skin and other tissues. For this reason the microfibrils of wool are now generally referred to as intermediate filaments (37). Although the filament proteins of the ortho- and paracortex are similar, the orthocortex contains a higher proportion of intermediate filaments than the paracortex. The orthocortex is, therefore, richer in the low-sulfur proteins that favor α-helix formation. The intermediate filaments contain a rodlike central helical domain in which the sequences show a heptad repeat, interrupted at three positions by short nonhelical segments. The ends of the polypeptides consist of nonhelical domains terminated in carboxyl and *N*-acetyl groups, respectively (37,39). The proportion of matrix (and hence of the high-sulfur proteins) is greater in the paracortex than in the cells of the orthocortex (40). Furthermore, the proteins of highest sulfur content (ultra-high-sulfur proteins) are concentrated in the paracortex (41).

3.2. Wool Lipids. The lipids of wool are located mainly in the cell membrane complex. They constitute less than 1% of the fiber mass but play an important role in many properties, such as the intercellular diffusion of dyes and reagents (25,31). The free lipids are extractable with organic solvents and consist of fatty acids, fatty alcohols, sterols, sterol esters and trace amounts of glycerides, sphinolipids, and glycolipids (26). Although phospholipid is present in the wool follicle membranes, only trace amounts of phospholipid are found in the keratinized fiber (42,43). Cholesterol and its biosynthetic precursor, desmosterol, are the main sterol components of the free lipids. In addition to the free lipids, wool contains some lipids that are believed to be covalently bound to proteins. These components are not readily removed by organic solvents, but those at the fiber surface can be released by alkaline hydrolysis under conditions where damage or modification of the fiber interior cannot occur (44). Covalently bound surface lipids represent approximately 0.025% of the fiber mass and are a distinct component of the fiber that has been termed the F-layer (44,45). This component is very important because it is responsible for the hydrophobicity of the fiber surface. The major component of the F-layer is an unusual branched-chain fatty acid (18-methyleicosanoic acid), which accounts for approximately 60% of the surface lipid material. Removal of the bound surface lipids generates a clean protein surface, which is more wettable, and has higher friction and better adhesion properties than the surface of clean untreated wool (44).

4. Physical Properties

4.1. Fiber Size and Shape. Wool is usually harvested from sheep by annual shearing. The fiber length is, therefore, determined largely by the rate of growth, which in turn depends on both genetic and environmental factors. Typical merino fibers are 50−125 mm long. They have irregular crimp (curvature), with the finer fiber generally showing lower growth rates and higher crimp. The fiber surface is rough as a consequence of the outer layer of overlapping cuticle cells. By far the most important dimension is the fiber diameter. Wool fibers exhibit a range of diameters, which like fiber length is dependent on both genetics and environment. Coarse wool fibers (25−70 micrometers) are used in carpets, while fine merino fibers (10−25 micrometers) are used in apparel because of their soft handle. Fibers from an individual sheep also exhibit a range of diameters. The mean diameter is the prime dictator of price; however, the distribution of diameters is also important. When worn next to the skin, the number of coarse fibers affects comfort as these fibers, rather than buckling, indent the skin and activate nerve receptors (46,47). This gives rise to a sensation of prickle and itch that has been incorrectly assumed, by some consumers, to be an allergic reaction. True allergies are rare, if they exist at all, and the irritation is mechanical and not immunological. Instruments that measure the full diameter distribution as well as fiber curvature have been developed recently (13,14). Individual fibers exhibit curvature in three dimensions; however, by measuring the circular curvature of short segments, a 2-dimensional value can be obtained that correlates with the crimp frequency measured in staples. Crimp contributes to the excellent insulating properties of wool fabrics by improving their bulkiness and, hence, the amount of entrapped air.

4.2. Water Sorption. Wool is hygroscopic and able to absorb and desorb large amounts of water as the relative humidity surrounding the fiber changes. The water is believed to be associated with specific chemical groups in the amorphous regions, with polar side groups and peptide groups of the protein chains considered to be the most important (48). Debate continues, however, on the exact location of this water, its state, and the mechanism by which it enters the fiber (49–51). As a consequence of the lipid outer layer, the surface of wool is hydrophobic. It is dry to touch and not readily wet-out by liquid water. In line with other polymers having functional surfaces, the surface of wool is believed to rearrange in different environments (52). In textiles, the amount of water absorbed is generally expressed as a percentage of the dry weight. This is referred to as “regain”; and is different to “water content”, which is the mass of water in the fiber expressed as a percentage of the total mass of fiber plus water. A pronounced hysteresis is observed in the water sorption isotherm of wool. This is 2% higher on desorption than on absorption, at most relative humidities (53). The saturated regain of wool is about 33%, which is higher than that of most other fibers (54).

Heat is liberated when wool absorbs water; this increases comfort by helping to buffer the wearer against sudden environmental changes. The absorption of water by wool also results in other improvements to comfort during wear. At a given relative humidity, wool has similar water sorption to skin. Wool garments, therefore, act as an excellent buffer during physical activity by transporting perspiration away from the skin, thereby keeping its moisture content close to the comfort level. A new wool-containing product designed for active sportswear (SportWool$^{\mathrm{TM}}$) utilizes the moisture-buffering properties of wool (55). As can be

Table 4. **Effect of Water Sorption on the Physical Properties of Wool Fibers at 25°C**[a]

	Regain, %							
Property	0	5	10	15	20	25	30	33
relative humidity, % (absorption)	0	15	42	68	85	94	99	100
relative humidity, % (desorption)	0	8	32	58	79	92	98	100
specific gravity, kg/m^3	1.304	1.314	1.315	1.313	1.304	1.292	1.277	1.268
volume swelling, %	0	4.24	9.07	14.25	20.0	26.2	32.8	36.8
length swelling, %	0	0.55	0.93	1.08	1.15	1.17	1.18	1.19
radial swelling, %	0	1.82	4.00	6.32	8.88	11.69	14.57	16.26
heat of wetting[b], kJ/kg wool	101	64.4	38.1	20.5	10.0	4.2	1.13	0
Young's modulus, relative[c]	2.69	2.54	2.36	2.02	1.59	1.27	1.05	1.00
torsional rigidity modulus, GPa[d]	1.76	1.60	1.26	0.90	0.50	0.28	0.16	0.11
electrical resistivity, MΩ · m	—	3×10^4	400	8	0.40	0.06	—	—

[a] Unless otherwise stated, data from *Wool Research*, vol. 2, Wool Industries Research Association Leeds, UK. 1955.

[b] Heat evolves when wool, dry mass of 1 kg, at a particular regain is immersed in water.

[c] Ref. 56.

[d] To convert GPa to psi, multiply by 145,000.

seen from Table 4, most physical properties of the fiber are affected by (water) regain.

Wool is sold by weight; thus, allowance for uptake of water must be made. A premium is paid for fine wools and because the diameter changes with regain, diameter measurements must be made under standard conditions of temperature and humidity.

4.3. Thermal Properties. The regular packing of α-helical polypeptide chains within the intermediate filaments forms a crystalline phase that occupies about 70% of the dry volume of the fiber (57). This phase melts irreversibly at a temperature that is both time- and regain-dependent (58). During the dyeing and finishing of wool, no melting of the fiber occurs. Care should be taken, however, when processing blends of wool and synthetic fibers that require higher temperatures. The amorphous matrix phase contains a high concentration of the amino acid cystine and is, therefore, highly cross-linked. As with other amorphous materials, a glass transition, T_g, has been detected in the wool fiber (59,60) which is sensitive to physical aging (61). Water acts as a plasticizer, lowering the glass-transition temperature of the dry fiber from 170°C to below zero when saturated (Fig. 5).

The glass-transition temperature is an important parameter, as the properties and performance of wool are influenced by the environmental conditions (temperature and humidity) relative to the glass transition. The insertion of temporarily, set creases or pleats in wool fabric (equivalent to thermally, set creases

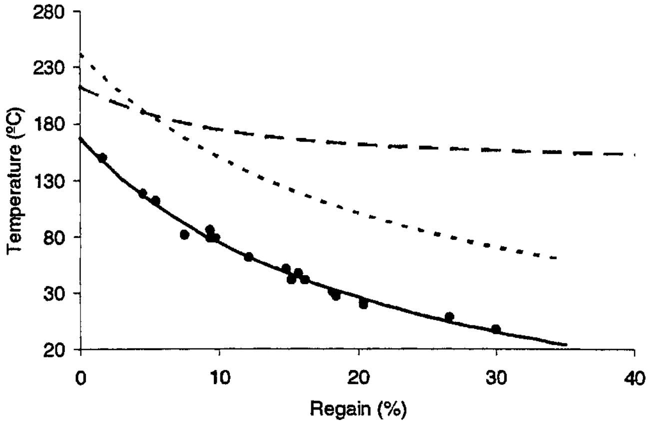


Fig. 5. Glass-transition (—) (Ref. 59), indicative permanent setting temperature (----) and melting temperature (– – – –) of wool as a function of regain (57).

in synthetic, polymer fabrics) is achieved by subjecting wool to bending strain above T_g and fixed by transition to conditions below T_g. This can be done by heating and cooling, wetting and drying, or a combination of both, eg, steam pressing. Wrinkle recovery is poorer when wrinkles are inserted above T_g and recovery is below T_g. This is likely to occur under hot and humid conditions where local wetting (perspiration) and wrinkle insertion occurs simultaneously. When the fabric moves away from the skin, the wrinkle has insufficient time for complete recovery before the fabric dries. This causes the T_g of the fabric to rise to a temperature above that of the environment. The viscoelastic properties (59), physical aging (59), felting (62) and the water absorption isotherm of wool (50) are also influenced by the glass transition.

4.4. Tensile Properties. The tensile properties of wool are quite variable but, typically, at 65% RH and 20°C individual fibers have a tenacity of 110–140 N/ktex (140–180 MPa), breaking elongation of 30–40% and an initial modulus of 2100–3000 N/ktex (2.7–3.9 GPa) (54). Although wool has a complicated hierarchical structure (see Fig. 3), the tensile properties of the fiber are largely understood in terms of a two-phase composite model (63–65). In these models, water-impenetrable crystalline regions (generally associated with the intermediate filaments) oriented parallel to the fiber axis are embedded in a water-sensitive matrix to form a semi-crystalline biopolymer. The parallel arrangement of these filaments produces a fiber that is highly anisotropic. While the longitudinal modulus of the fiber decreases by a factor of 3 from dry to wet (56), the torsional modulus (a measure of the matrix stiffness) decreases by a factor greater than 10 (Table 4 and Ref. 66). The longitudinal stress–strain curves for a wool fiber at different relative humidities are shown in Fig. 6 (54).

Three distinct regions can be discerned, especially for fibers at higher relative humidity. Once the fiber crimp is removed, a near-linear region up to about 2% strain is obtained (pre-yield region). For the wet fiber, this is generally associated with stretching of the α-helices within the intermediate filaments. At lower (water) regain, the matrix phase plays an increasingly dominant role. Between 2% and 25% strain (yield-region) progressive unfolding of zones of

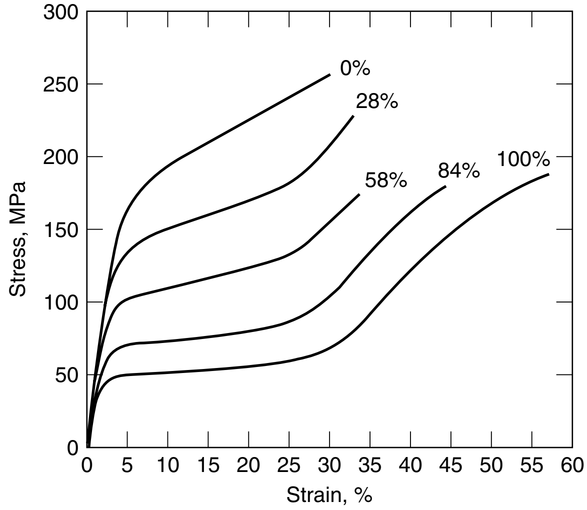


Fig. 6. Stress-strain curves of typical wool fibers at different relative humidities.

α-helices to form a β-pleat configuration occurs. Very little increase in stress is observed during this stage and complete recovery is still possible, provided the fiber is allowed to relax in water. Beyond 25% strain (postyield region), the fiber stiffens and breaks. At a molecular level, the reasons for this are still a matter of debate but include resistance to the unfolding of a stabilized region of the intermediate filaments (63,65) and the rubberlike response of the matrix (64). A recent review looks critically at the different models (67).

For a fiber immersed in water, the ratio of the slopes of the stress–strain curve in these three regions is about 100:1:10. While the apparent modulus of the fiber in the pre-yield region is both time- and water-dependent, the equilibrium modulus (1.4 GPa) is independent of water content and corresponds to the modulus of the crystalline phase (68). The time-, temperature-, and water-dependence can be attributed to the visco-elastic properties of the matrix phase.

5. Wool Processing

The conversion of raw wool into a textile fabric or garment involves a long series of separate processes. There are two main processing systems, worsted and woolen. A significant volume of wool is also processed on the semiworsted system, for carpet use. Some wool is processed on the short-staple (cotton) system. Details of the principal stages in the woolen and worsted systems and discussion of more recent developments can be found elsewhere (69,70).

The majority of the world's apparel wool clip is combing wool and this is processed on the worsted system. This process was so named because the combed wool spinning industry in England developed in the English town of Worsted in the fourteenth century (70). Fine, smooth yarns were produced by "spinsters" who placed the combed parallel array of fibers on top of a distaff (combed wool even today is known as top), drew the strand down to the required linear density, and inserted the twist using a spindle. Prior to the development of worsted spinning, and coexisting ever since with it, the traditional system produced yarns in which the fibers were much more disorientated. Although the texture was not as smooth, there was a high degree of bulk and the finished woven fabrics produced coatings, blankets, and distinctive products such as tweeds and flannels. Woolen spinning is the mechanized form of the traditional system.

Besides scoured (cleaned) wool, the next saleable commodity in worsted processing is top, or combed wool. Generally the combing plant combines the processes of scouring and combing. Most often, a separate commercial enterprise which buys top from the topmaker carries out spinning. Although there are woolen sales-to-yarn spinners, particularly in the knitwear area, the production of woven woolen products in the one enterprise from raw wool is more common. The woolen process is characterized by a much higher degree of vertical integration than the worsted system.

5.1. Scouring. The first stage in wool processing is to remove the fleece impurities by scouring. The impurities consist principally of wool wax, dirt, proteinaceous contaminants, and suint. The latter is a water-soluble component, consisting mainly of potassium and other inorganic salts arising from perspiration. Scouring is carried out by washing the raw wool in an aqueous medium, a solvent medium, or a combination of the two. Aqueous scouring is used to process 99% of the world's wool. This involves washing the raw wool in aqueous solutions (neutral or slightly alkaline) of nonionic detergent or, less frequently, soap and alkali. This is followed by rinsing in water.

The process is carried out in a series of between four and seven tanks (called bowls), in which the wool is transported through the wash liquor by mechanical rakes, or by passing it around perforated drums (71,72). At the end of each bowl, the wool passes through a roller squeeze. Agitation of wool in anhydrous solvents does not cause felting, and several systems (71,72,74) have been operated to take advantage of this property, but none are still in commercial operation.

There are two broad categories of contaminants on raw wool: those that are easily removed and those that are hard to remove. The different rates of removal of these contaminants in the scouring process has led to the development by CSIRO of a new scouring technology, known as Siroscour. This uses the principles of multistage scouring, rather than severe mechanical action, to optimize the removal of contaminants during aqueous scouring. The three separate stages which comprise the Siroscour process are (*1*) a modified desuinting bowl, designed to remove as much dirt as possible; (*2*) a hot scouring stage that removes the easy-to-remove contaminants; and (*3*) designed to remove the hard-to-remove contaminants. In order to achieve optimum performance, separate dirt and grease contaminant recovery loops are incorporated into the Siroscour process, as well as specific bowl designs for optimum scouring efficiency of Australian wools. Comparative trials have shown Siroscour to consistently produce wool of superior whiteness and lower residual content of mineral contaminents (ash content) than other scouring systems (75).

In most situations, wastewater discharged from a scouring machine contains large quantities of wool wax and both water-soluble and water-insoluble material (organic and inorganic). The pollution load of a single modern scouring machine is equivalent to a population of 50,000 people. Disposal or treatment of the wastes to comply with environmental requirements is expensive. In the past, the least expensive approach involved biological treatment by irrigation of large land areas, or maturation in very large, shallow lagoons. The high levels of potassium present in scour effluent require 1000 ha of land for sustainable irrigation. These factors have forced scourers to install large evaporation ponds that cover many hectares. Technology has been developed that enables scourers to recover a large amount of the potassium from the scour liquor. This can be used as a potassium supplement in fertilizer.

Physicochemical methods of wastewater treatment have been investigated. These include: flocculation with inorganic or polymeric flocculants, or with sulfuric acid; and also physical techniques, eg, membrane processes and solvent extraction. Few of these processes have proceeded beyond pilot-scale evaluation, however. One of the most recent processes that has proved to be commercially viable is the Sirolan CF technology developed by CSIRO (76). This is a chemical flocculation process that removes more than 75% biological oxygen demand, 80% chemical oxygen demand and 99% of the suspended solids and wool wax. This is a simpler process with lower operating costs, than other methods involving chemical flocculation. Sludge disposal technologies have been developed that can be used in conjunction with the Sirolan CF process. These include composting, incineration and pelletizing (77). The centrate from the Sirolan CF process contains mainly suint salts. Plant growth trials, carried out by Agriculture Victoria and CSIRO, demonstrated that suint salts, which contain about 27% potassium, are equal or better than inorganic sources of potassium (78).

5.2. Carbonizing. Carbonizing is a process used to remove excessive amounts of cellulosic impurities, eg, burrs and vegetable matter, from wool. It is carried out on loose wool, rags (79) and fabric (80). With loose wool and fabric, the wool is treated with aqueous sulfuric acid and then baked. The cellulosic matter is rapidly destroyed by the hot concentrated acid, by conversion into friable hydrocellulose, whereas wool is scarcely affected by the treatment. For dyed rags, hydrogen chloride gas is preferred as the mineral acid, because it has less effect on the colors. After acid treatment, the carbonized vegetable matter is crushed to facilitate its removal. The wool is then normally neutralized in alkali, although some mills omit this stage to facilitate subsequent dyeing under acid conditions.

Most industrial carbonizing is done on loose wool, the technology having changed little over the past 40 years. Australian carbonizers use surface-active agents to reduce fiber damage in the carbonizing process (81,82). The improved results depend on the use of high acid concentrations and rapid throughput (81).

5.3. Processing on the Worsted and Woolen Systems. The wool is dried after scouring and blended before carding. Carding individualizes the entangled fibers and reassembles them into a "sliver" weighing about 25 g/m. At the same time, up to 90% of the vegetable matter (VM) is removed. Lubrication (83) is used to minimize fiber breakage. After carding, there are three stages of gilling, to align fibers and remove hooked fiber ends before combing. Here, the advancing beard of fibers is inserted into a circular comb, and the leading fibers are then gripped and pulled through a top comb before being reassembled, like overlapping tiles, in the output sliver. The process removes short and entangled fibers and almost all remaining VM. The waste (noil), can be carbonized and fed into the woolen system. The sliver is then given two more gillings and consolidated into top. Some combing plants also produce shrink-resist treated wool top. The current process incorporates chlorination followed by application of a polymer.

The worsted spinner converts top of about 25 g/m linear density into roving of between 200 and 2000 g/km, depending on the linear density of the yarn to be spun. The sequence of processes incorporates four or five drawing stages. The first three or four usually employ gills, whereas the last is commonly carried out on a roving frame in which the attenuated strands are rubbed or twisted to impart cohesion. For finer wool, dyed tops or after blending with synthetic fibers, it is normal to re-comb the wool before the above drawing stages.

Long-staple ring spinning is similar to short-staple (cotton) ring spinning, except that the components are increased in approximate proportion to the length of the fibers. On the spinning frame, the rovings are drafted by a factor of about 20, twist is inserted, and at the same time the yarn is wound onto bobbins. The yarn on the bobbins is usually steam-set in an autoclave to reduce its twist liveliness, then wound onto packages or cones. Detection and removal of thick, thin and colored faults can occur during winding. Following twisting into a two-fold yarn and further setting, the yarns are ready for knitting or weaving. Open-end (rotor) spinning is rarely used for wool and spinning and twisting are very costly operations, because of their low productivity: typically 40 spindles produce 1 kg/h of yarn.

In woolen processing, there are no highly efficient mechanical methods to remove VM. Generally, very clean scoured wool, combed wools, or carbonized wool must be used as inputs. Alternatively, fabrics must be carbonized. A much longer card than in worsted processing and shorter fibers are used. The web of fibers at the card delivery is split longitudinally into about 120 ends, rubbed to impart cohesion, and wound into cylindrical packages called slubbing. Twisting of these slubbings occurs on the woolen spinning frame with a draft of 1.3 to 1.5, to produce woolen singles yarn. This yarn can be woven without any further processing, other than a winding and clearing operation similar to that used in the worsted sequence. Woolen spinning is, thus, a very short sequence of operations compared to worsted processing. Woolen yarns, however, become economically uncompetitive with worsted yarns at relatively coarse yarn counts, because production is tied to the number of ends times their weight.

Woolen yarns cannot be spun as fine as worsted yarns, even when using the same fiber diameter. The fabric weights are greater and they have a harsher feel. For these reasons, woolen products have not been able to follow the modern trend to smoother lightweight clothing as easily as their worsted counterparts.

5.4. Setting. Setting operations form an important part of the processing of wool yarn, fabric, and garments. Yarn is set in steam to stabilize twist and prevent snarling during winding and warping, while fabrics may be set after weaving to prevent the formation of distortions during wet processes, such as scouring and dyeing. Normally, fabrics are flat-set near the end of the finishing routine to impart dimensional stability and to confer the required handle. Finally, garments are set by steam pressing to form their desired shape, for example, to insert pleats and creases.

Two forms of set may be conferred to the wool fiber and these two forms can be distinguished on the basis of stability. Temporary set (or cohesive set as it is generally referred to in the wool industry) is imparted when wool fibers are dried, or steamed for a short time and then cooled while under strain. This set is readily lost when the fibers are gently steamed or allowed to relax in water at room temperature (84). Permanent set, as the name implies, is set that has a considerable degree of permanency. Set that remains after relaxation in water at 70°C for approximately 15 minutes is generally considered permanent, ie, the set is permanent to conditions in excess of those that a wool garment would normally encounter during use, eg, machine washing.

At the molecular level, setting is a process of stress relaxation which results from the rearrangement of the protein macromolecules that form the fiber. Under ambient conditions of water content and temperature, the matrix regions of wool are glasslike (ie, below the glass-transition temperature, see Fig. 5). When fibers are deformed under these conditions, stress relaxation is slow.

If wool is heated or becomes wet, the matrix regions become rubber-like and stress relaxation occurs much more rapidly. Cohesive, or temporary setting occurs whenever the fibers are deformed under conditions where stress relaxation is high (rubbery state), and then cooled or dried to a glassy state before they are released. In the glassy state the relaxation rate is slow, so that the fiber will essentially maintain its new shape indefinitely, or until it is again wetted-out or heated to make it rubberlike.

The protein molecules, particularly those of the cuticle and matrix regions of the fiber, are stabilized by a number of covalent bonds and non-covalent interactions. The most important of these are disulfide bonds, which crosslink the peptide chains (Fig. 4). A unique feature of the wool fiber is the ability, under suitable conditions, for these disulfide bonds to rearrange and form a new cross-linked polymer network. This occurs via a mechanism involving thiol/disulfide interchange (eq. 1). Permanent setting will occur if this rearranged network, cross-linked by reformed disulfide bonds, is at equilibrium with the new shape of the fiber. The rate of disulfide rearrangement is “catalyzed” by the concentration of thiol anions in the fiber (85), as well as by the macromolecular mobility of the protein chains. Hence, the rate of disulfide rearrangement can be increased by increasing the pH, breaking disulfide bonds with a reducing agent to form additional thiol anions, or by increasing the regain or temperature to facilitate molecular mobility. In addition to the rearrangement of disulfide cross-links via thiol/disulfide interchange, other mechanisms are also involved. These include rearrangement of hydrogen bonds and the formation of new types of covalent cross-links that are formed from residues produced by breaking disulfide bonds. The new bonds include lanthionine and lysinoalanine cross-links (86). These cross-links are more stable than the disulfide bonds from which they were produced and make a significant contribution to the stability of permanently set wool fibers. In some circumstances, hydrophobic bonds between suitably located nonpolar side chains can also contribute to the stabilization of permanent set (87). Fig. 5 depicts a curve above which the temperature and regain are sufficient for imparting permanent set to wool within a few minutes. This curve is indicative only, as its actual position can vary between different wool types, previous treatments, and process conditions, because it is influenced by the thiol content and pH of the wool fiber, and also the definition of permanent set.

During wool processing, the regain and temperature are carefully selected and controlled in order to impart either permanent or temporary set. As indicated in Figure 5, permanent setting can be achieved under wet or dry conditions (less than saturation, ie, $<33\%$ regain). The most common form of wet permanent setting is continuous crabbing. This is an operation in which a wet fabric, sandwiched between a hot (up to 160°C) roller and an impermeable belt, is heated to temperatures above 100°C for up to 1 minute, before being rapidly quenched in cold water. The amount of permanent set imparted in a continuous crab is less than that conferred by a traditional batch crabbing operation. The continuous method has greater productivity, however. The effectiveness depends on the pH of the wool and the treatment time and temperature. The rate of permanent setting can be increased by increasing the number of thiol groups within the fiber by impregnating the fabric with a reducing agent. Some dyeing operations can impart large amounts of permanent set to wool. This can be minimized by including in the dyebath a chemical that reacts with the thiol anions. Minimizing permanent set during dyeing is beneficial in maintaining fiber strength (88) and for maintaining yarn bulk (89).

Dry setting operations usually involve the use of steam. As is the case for wet setting, the amount of permanent set imparted in steam-setting depends on the wool pH, water content and the time and temperature of setting. Fabrics are steam-set by decatizing. In this process, the wool fabric, interleaved with a cotton wrapper cloth, is wound onto a perforated drum, through which steam is forced. In continuous machines, the conditions are mild and little permanent set is imparted. In a batch process, in which the fabric roll is placed in a pressure vessel (autoclave), setting temperatures up to 130°C for 3–5 minutes are used. These conditions impart a higher degree of permanent set than continuous methods. The amount of temporary or cohesive set imparted in both batch and continuous machines depends on the temperature of the fibers when the fabric is released from the wrapper cloth. The cooler the fabric, the higher the level of cohesive set. Yarns on packages are normally cohesively set in an autoclave at temperatures up to 90°C, in order to reduce twist liveliness. A vacuum pump is used to remove air from the packages, which ensures even penetration of steam and, thus, a uniform level of set.

Normal pressing operations carried out during garment making impart only temporary set to the fibers. A number of commercial processes are used, however, to set permanent creases into wool garments (90–92). These include autoclave setting and wet or dry pressing in the presence of chemical assistants. Permanent pleats are fixed into skirts by autoclave setting at around 110°C. In the SIROSET (trade mark) process of CSIRO, for inserting permanent creases into trousers, a chemical assistant (monoethanolamine sulfite) is sprayed onto the trousers before steam-pressing.

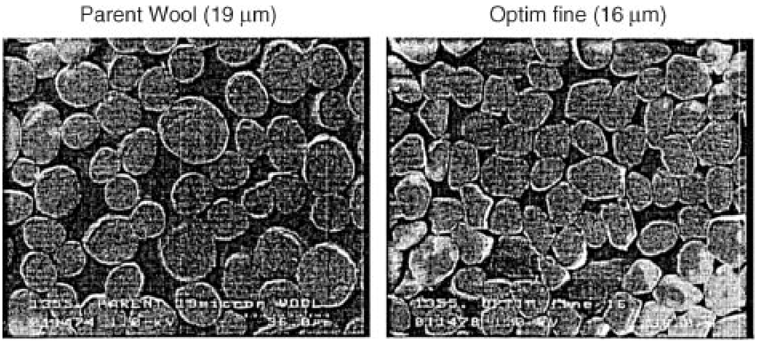
5.5. A New Textile Fiber from Wool.

The most recent application of wool setting is in the manufacture of *OPTIM* (trade mark), a new textile fiber produced from wool (55,93). The production process involves stretching and setting wool to create two new fiber types; Optim fine and Optim max (94). A key aspect of the continuous process is the use of false twist to maintain cohesion within a large fiber assembly during the whole operation.

In the Optim fine manufacturing process a chemical setting agent, such as sodium bisulpfite, is applied to wool. A twisted assembly of the treated fibers is stretched by around 40–50% and then permanently set in the extended state. This procedure gives longer fibers of decreased diameter. Stretching and setting the fibers converts ordered intermediate filaments in the wool from an α-crystallite helical form to a β-pleated sheet structure that more closely resembles silk (95). Typically, the diameter is reduced by about 3–4 μm for a 19 μm parent wool fiber. The use of false twist to control fiber movement applies a large transverse force to the twisted assembly that changes the cross-sectional shape of the fibers so that common measures of diameter that assume a mostly circular cross-section are no longer valid (Fig. 7).

Optim fine fibers are stronger and softer than the parent wool and exhibit an attractive lustre. They are used to produce fabrics with many of the aesthetic properties of silk. The modified wool is ideal for spinning into fine yarns, especially with other high value natural fibers, eg, silk, cashmere and alpaca, where softness, lightness and sheen are desirable attributes.

Optim max utilizes a key benefit of the manufacturing process that allows the extent of set in the fiber to be manipulated in a controlled manner. Optim max fiber is wool that has been temporarily set while stretched, so that the fiber retracts when released in hot moist conditions by about 25% in length. This fiber offers scope for innovation in yarn and fabric design. For example, when Optim max is blended with normal wool, spun into yarn and relaxed in hank form in hot water, the Optim max fibers retract and force the normal wool fibers to buckle. The yarn has an increased volume and this property produces increased "cover" in knitted fabric and decreased weight. When knitted to the same cover factor, a weight saving of 20–30% is possible compared with fabrics made from normal wool yarns.


Parent Wool (19 μm)

Optim fine (16 μm)

Fig. 7. Scanning electron micrograph of cross-sections of normal wool and Optim fine fibers.

6. Shrinkage of Wool Textiles

Two mechanisms of fabric shrinkage are observed for wool; relaxation shrinkage and felting shrinkage (22,96). Relaxation shrinkage occurs when a fabric or yarn made from any textile fiber is first immersed in water. It results from the release of temporarily-set strains imparted during previous processing operations such as spinning, knitting and fabric finishing. Relaxation shrinkage also occurs when a knitted garment or fabric is immersed in water after it has been dried while in a stretched state (for example by line drying). Felting results from the presence of cuticle cells (scales) on the wool fiber surface that point away from the fiber root and overlap like tiles on a roof (Fig. 2). The protruding scale edges result in differential friction between the with-scale and against-scale direction, which under some conditions results in irreversible migration of individual fibers toward their root-ends. Felting is exploited in the "milling" of wool. This is a process of controlled, mild felting used to close-up the structure of fabrics and garments. Milling is also used to produce wool felts, which are composed of a very dense matting of fibers. Felts are used for products as diverse as hats, polishing pads, table covers and piano hammers.

Felting in garments and fabrics that leads to excessive shrinkage is, however, undesirable. It occurs when the wet material is subjected to severe mechanical action, for example, in laundering or tumble drying (22). Shrink-resist treatments are directed at preventing felting shrinkage, whereas minimization of relaxation shrinkage requires careful control during fabric finishing. Felting of loose fibers results in entanglement, whereas in fabrics fiber migration inside and between yarns reduces the fabric area, ie, shrinkage occurs. The mechanisms of felting shrinkage and its prevention have been discussed comprehensively (22). Many factors influence felting shrinkage; these include; (a) yarn and fabric structure (woolen or worsted, knitted or woven, yarn twist level); (b) the method of wash-testing (pH, temperature of wash liquor, presence of detergents, electrolytes or lubricants and the severity of the mechanical action of the washing machine); (c) the properties of the fiber (elasticity, diameter, length). Recently, felting shrinkage has been related to the glass-transition temperature of wool (97). Important points to note are that products made from fine diameter wools felt more readily than those from coarse fibers; and that if a small amount of untreated wool is added to shrink-resist treated wool, the blend will felt as readily as the untreated material.

6.1. Shrink-Resistent Terminology and Testing.

The term shrink-resistant is preferred to "shrinkproofed," although in recent years emphasis has switched to performance-related terms, such as hand-washable and machine-washable. A recent trend is to use the term easy-care, which for knitwear means resistance to felting shrinkage under severe conditions, including tumble drying. It also includes assessment of the fabric appearance after testing. For woven garments, this includes retention of pleats or creases as well as smooth drying performance. All these terms are meaningless unless related to some standard testing sequence and criteria for passing the test.

Relaxation shrinkage tests usually involve mild agitation in water. Felting shrinkage is then determined after more severe agitation. Hence, in practice it may be difficult to say when relaxation ceases and felting starts. The most commonly used methods to test for felting shrinkage is to use multiple wash-test cycles in domestic-type washing machines (front loading in Europe, or top loading in the United States). The Woolmark Company (formally the International Wool Secretariat) has developed test methods for machine washability, together with performance criteria for different garment types and end uses. Woolmark test methods are widely used around the world, although in the United States AATCC methods predominate.

6.2. Development of Shrink-Resist Science and Technology. Felting of wool and its use in fabric finishing has been known for a very long time. Monge observed the differential friction effect in wool fibers in 1790 and Mercer chlorinated wool to improve dye affinity in printing in 1839, but chlorination was soon found to impart shrink-resistance (22). Chlorination was widely used during World War II to produce shrink-resistant wool socks and blankets for the military. From then on, two distinct trends in shrink-resist research and technology emerged. Firstly, better control of the reaction of chlorine or other oxidants with wool; and, secondly, the use of synthetic polymers to bond adjacent wool fibers together. The reader is directed to Reference 98, which gives a good summary up to the early 1950s, and to Reference 22, which continues to the late 1970s and discusses the mechanism of felting. Recent research has been directed toward environmental aspects of the shrink-resist treatment of wool, particularly the reduction or elimination of organochlorine compounds in effluents from treatment plants. In future years, replacements for chlorination processes are likely to emerge.

Figures published by The Woolmark Company in 2002 show that approximately 40×10^6 kg of wool is shrink-resist treated each year. This figure may include some low-level chlorination treatments of fine wools, designed to prevent felting during wet processing or to improve garment appearance or dyeability. The products of these low-level treatments are generally not claimed to be machine-washable. The fact that only 5–10% of all wool is shrink-resist treated indicates that many end uses do not require an anti-felting treatment. More than 90–95% of the treated wool is used in knitwear. The amount treated, however, varies markedly from country to country and also with the type of product, with those worn next to the skin, eg, underwear, being most likely to be treated. Wool can be shrink resist treated at various stages, from loose wool to garments. Approximately 5% is treated at the loose wool stage, mainly for use in bedding products such as futons; 80% at the top stage; very little as yarn; 10% as knitted garments; and about 5% as woven fabrics. The chlorine-Hercosett process for treating loose wool or top is by far the most important method used. In 2002 this method accounted for at least 80% of shrink-resist treated wool.

6.3. Shrink-Resist Treatments. Mechanistically, shrink-resist treatments can be divided into degradative and additive types. Degradative treatments use an oxidizing agent to eliminate or reduce the differential friction effect of the fiber surface by modifying or removing the scales. In some cases, a polymer is also applied to the surface to mask the modified scales. The additive approach prevents fiber migration by bonding fibers together with elastomeric polymers. Some polymer deposition processes involve a degradative chemical pretreatment, to improve the adhesion of the polymer to the fiber surface. Additive treatments must be applied after spinning (usually at the fabric stage), whereas degradative treatments can be used at any stage from loose wool through to garments.

Chlorine-Based Shrink-Resist Treatments. The principal oxidizing agent used in degradative shrink-resist treatments is chlorine. Free chlorine reacts very rapidly with wool; hence, it is difficult to treat a mass of wool fibers evenly. Two different types of chlorination methods are used commercially; continuous treatment and batch treatment. In the continuous method, top or loose wool is reacted with an aqueous solution of chlorine gas for a short time (<30 s). The batch treatment method involves a longer treatment time (5–30-min) with a less reactive chlorinating agent, such as DCCA (*N*, *N′*-dichloroisocyanuric acid). Batch treatments are mainly used on garments and fabrics but can also be applied to loose wool or tops. Generally, in both continuous and batch treatments a reactive polymer, usually cationic, is applied after the chlorination step.

The features and chemistry of chlorination shrink-resist treatments are best illustrated by consideration of the chlorine-Hercosett process for wool top (99). This process uses a dedicated plant, of which there are about 40 around the world. A web of parallel slivers is treated with water and chemicals in a series of bowls (tanks), separated by squeeze rollers. The wool is then dried. Usually, 30–40 slivers (20–30 g/m) are treated simultaneously at a speed of 5–10 m/min. Overall production rates range from 200 to 500 kg/h.

The first stage involves chlorination, either with chlorine gas dissolved in water or with sodium hypochlorite acidified with sulfuric acid. Chlorination is the most critical step of the process and modern plants incorporate features designed to achieve uniform treatment of the web. These include cooling the chlorine solution to 10–12°C, to slow down the rate of reaction with wool; and special application devices, eg, those produced by the Kroy or Fleissner companies, to rapidly contact the web with a large volume of dilute chlorine solution. The second stage of the process is a neutralization, or anti-chlor, treatment with sodium sulfite. In the third stage, the wool is treated with a cationic polyamide/epichlorohydrin polymer, usually Hercosett 57 (Hercules, Inc.). The final stage consists of treatment with a cationic softener and a lubricant to facilitate further processing, followed by drying to cross-link the polymer on the fiber surface. The reaction of chlorine with wool is complex, but the principal effect of the combination of the chlorination and neutralization stages is to remove surface lipid from the fiber. This increases the surface energy and shifts the isoelectric point of the fiber to a lower pH, by converting cystine disulfide residues to cysteic acid (sulfonic acid) groups. Some of the surface protein is also solubilized and removed, which softens the fiber cuticle. These changes allow the cationic Hercosett polymer to spread on the fiber surface. Virtually all the shrink-resistance is imparted by the chlorination step. The function of the Hercosett is to compensate for any weight loss arising from chlorination, prevent further loss of soluble protein during subsequent dyeing and improve the shrink-resistance of any insufficiently chlorinated fibers.

Chlorine-Free Shrink-Resist Treatments. Commercially, the only other oxidizing agent used to any extent is permonosulfuric acid (PMS; $HOOSO_3H$). This is used in the form of its potassium triple salt, containing potassium sulfate and bisulfate. It is employed in batch processes at elevated temperatures, because it reacts more slowly with wool than chlorine (100). The process sequence is similar to that used for chlorine-based treatments. It involves degradative oxidation with PMS, followed by neutralization with sodium sulfite and then application of a resin. Unlike chlorine, however, PMS does not remove the bound lipid or oxidize cystine to cysteic acid. The main product of the reaction is cystine sulfonic acid or Bunte salt groups.

Other chlorine-free shrink-resist technologies under development include plasma and ozone treatments, for sliver; and enzyme treatments for garments and fabrics.

Additive Shrink-Resist Treatments. The principal additive shrink-resist treatment for wool fabrics uses the polymer Synthappret BAP (Bayer AG). This is a poly(propylene oxide) polyurethane, containing reactive carbamoyl sulfonate (bisulfite adducts of isocyanate) groups; ie, $-NHCOSO_3^- Na^+$. An aqueous solution of this polymer is padded onto woven fabrics. The polymer cross-links on drying to form flexible linkages between fibers and yarns (101). Other polymers may be applied at the same time to modify the handle.

7. Easy-Care Wovens

Dry-clean only garments are increasingly becoming a turnoff to the modern consumer. Consumers now demand “total easy-care” garments that can withstand repeated machine washing and tumble drying, while maintaining their “just pressed” appearance with no more than minimal ironing. In addition to dimensional stability, wool-containing fabrics and garments must be specifically engineered so that, after laundering, seams remain flat and without pucker, the fabric remains wrinkle-free without the development of fuzz or pills and the creases or pleats stay sharp.

To produce total easy-care garments from a blend, of wool and polyester, heat setting the polyester component using a hot head press will generally impart sufficient set to the creases and pleats to make them stable to repeated laundering. A minimum of 20–30% polyester is needed for adequate stability. An alternative procedure that sets the entire garment is to impart temporary set to the wool component of the blend by steam pressing the garment, followed by baking the entire garment in an oven to permanently set the polyester. The wool dries out in the oven and maintains the garment shape during setting of the polyester (102). A fabric-based treatment to prevent felting may be unnecessary, provided the polyester content is above 50% and a suitable fabric construction is used.

It is more difficult to produce pure wool total easy-care garments. The challenge is to obtain adequate permanent set rather than obtaining shrink-resistance, because some wool setting processes are not stable to machine washing. The problem of set stability is further exacerbated when the garments are tumble-dried, because the tumbling action tends to flatten the creases and they become temporarily set in a distorted configuration, even if a high level of permanent set has been imparted to the garment. The application of a delay-cure polymer to the fabric, followed by curing in an oven after the garment has been made and pressed, appears to be the latest approach to producing total easy-care wool garments.

8. Dyeing

Commercially, wool is dyed from aqueous solutions, usually under acidic conditions. In the past, methods have been proposed for dyeing wool from organic solvents, in particular concentrated formic acid. More recently, the use of supercritical carbon dioxide has also been investigated. These solvent systems are, however, very unlikely to replace water as the preferred dyeing medium for wool, because of the relative cost of the solvent compared with water and also the specialized, expensive equipment required.

The majority of dyes used on wool are sodium salts of aromatic anions. Water solubility is usually provided by sulfonic acid groups, but in a few cases carboxyl or hydrophilic, nonionic substituents are used. In a typical wool dyeing operation, the ratio of the mass of dyestuff solution to the mass of wool ranges from approximately 10:1 to as high as 60:1, depending on the type of wool substrate and the equipment used. Wool is dyed as loose fiber, sliver, yarn, fabric, or in garment form by batch methods (103,104). In the case of fiber, sliver or yarn, the process involves pumping dye solution through the stationary substrate; whereas in fabric dyeing the material may be transported through the dye liquor or, alternatively, both liquor and fabric may be moved through the machine. Simultaneous circulation of liquor and wool substrate is also used in garment dyeing techniques. In a typical operation, the liquor is heated from around 40°C to a temperature of 98–100°C, where it is held for a period that can range from around 30 min to over 2 hours. The actual time depends on the type of dye and depth of shade. Procedures have also been developed for continuously dyeing wool in loose, or sliver form and wool fabric can be dyed by a pad-batch method (105). These techniques have found only limited use, however, because they are uneconomic unless a large quantity of substrate is dyed to a single color, which is uncommon in the wool industry.

8.1. Dyeing Theory.

Wool is composed mainly of a large number of different proteins, the fundamental structural units of which are α-amino acids (31). It is amphoteric in character because of the presence of basic amino groups in the side chains of lysine, hystidine and arginine; and acidic carboxyl groups in the side chains of aspartic and glutamic acids. In an aqueous, acidic dyebath protonation of the amino and carboxyl groups results in a net positive charge on the fiber. Early workers explained the mechanism of wool dyeing in terms of electrostatic interactions between the positively charged amino groups and anionic dye molecules. The two most popular theories were the Gilbert–Rideal theory and the Donnan theory (106–108). Later studies, however, showed that the affinity and wetfastness properties of dyes on wool are largely determined by other types of interactions; namely, van der Waals' forces and interactions between hydrophobic regions in the fiber and hydrophobic parts of the dye molecules (109,110). Dyes differ markedly in their hydrophilic–hydrophobic character (105,110,111). Ionic forces are of greatest importance for dyes of relatively low molecular weight. With increasing molecular weight, van der Waals' and hydrophobic interactions become increasingly important, which is reflected in a higher affinity for the fiber and better wetfastness properties. Ionic interactions are important, however, for all wool dyes in determining the rate at which the dye is taken up by the fiber from the dye liquor. The dyeing rate can be controlled by varying the amount of acid added to the dyebath, because this determines the size of the net positive charge on the wool, produced by protonation of amino groups.

In early studies on the uptake of dyes by wool, the fiber was treated as a cylinder of uniform composition. The main focus was on the thermodynamics of the dyeing process, in particular the situation applying when equilibrium had been attained. These studies provided little information, however, on the mechanism of the dyeing process itself. Recent work has clarified the relationship between fiber structure and the mechanism of wool dyeing (112,113).

8.2. Dyeing Mechanism. Wool fibers have a very complex morphological structure (Fig. 3). They can be considered as biological composite materials, in which the various regions are both chemically and physically different (31). Fine wool fibers contain two types of cell: those of the internal cortex and those of the external cuticle. Cortical cells, which constitute around 90% of the fiber, are spindle-shaped and are arranged in an overlapping pattern, parallel to the fiber axis. They are separated and held together by a continuous network, the cell membrane complex. This region of the fiber contains protein and also lipid material. The proteinaceous material in the cell membrane complex is relatively lightly cross-linked compared with the proteins in other regions of wool. The external cuticle cells are rectangular in shape and overlap, rather like tiles on a roof (Fig. 2). Dyes enter wool fibers at the junctions where the cuticle cells overlap and in the early stages of the dyeing process they diffuse into the interior along the lightly cross-linked network of the cell membrane complex (31,112,113). Later in the cycle, the dyes transfer, progressively, from the cell membrane complex into the cortical cells. The affinity of the dyes for wool is largely the result of their interaction with hydrophobic proteins located within the matrix of cortical cells.

8.3. Wool Dyes. The dyes used on wool can be divided into the following groups: acid dyes, chrome dyes, premetallized dyes and reactive dyes (103,105, 107,110,111,114–116). Strictly speaking, all types of wool dyestuffs can be described as acid dyes, but in practice this term is confined to leveling acid dyes, half-milling dyes, milling dyes, and supermilling dyes (111,114). This subclassification of acid dyes arises out of the methods used for their application and their fastness properties on wool.

Leveling acid dyes (sometimes called level-dyeing or equalizing dyes) are the simplest type of dyes used on wool. They are of relatively low molecular weights (300−600) and have a comparatively low affinity for the fiber, because they interact largely by ionic attraction. They are applied at around pH 3, obtained with sulfuric acid. Under these conditions, the initial uptake of dye is usually uneven because the exhaustion rate is very rapid. As their name implies, leveling acid dyes have good migration properties and levelling occurs during the stage of the dyeing cycle when the dye liquor is held at the boil, thus producing a very even result. Levelling of the dyes is assisted by the presence of sodium sulfate in the dye bath, because the anionic sulfate ions compete with dye anions for the positively charged amino groups in the fiber. In general, these dyes are not particularly resistant to wet treatments, but are used when level dyeing is critically important.

Milling acid dyes are so named because they are more resistant than leveling acid dyes to extraction from wool during the milling process. They are of higher molecular weight (600–900) and are more hydrophobic than leveling acid dyes, which gives them a higher affinity for wool. The higher molecular weight and lower dependence on ionic attraction means that they diffuse out of the fiber more slowly than levelling dyes, which is responsible for their higher fastness to wet treatments such as milling and laundering. Their migration properties, and hence their ability to level during application, is not as good as that of acid dyes. In order to obtain level results it is important to ensure that the rate of exhaustion is uniform and not too rapid. This is achieved by setting the dyebath at a higher pH (ca pH 4.5–6.0) with a weak acid, such as acetic acid, and also by the addition of a surfactant-type levelling agent, which promotes even uptake on wool. Half-milling dyes fall between levelling acid and milling dyes in molecular weight (500–600), migration properties, and wetfastness. They are applied at a pH in the range pH 4.0–4.5.

Supermilling acid dyes are similar in molecular weight to milling dyes, but contain long alkyl groups that make them more hydrophobic in character. This gives them a high affinity for wool that is virtually independent of ionic interactions with the fiber; consequently, they have very good wetfastness properties. They show good exhaustion under almost neutral (pH 5.5–7.0) dyeing conditions, but their high affinity means that they have poor migration and relatively poor levelling properties. Auxiliary products are often used to assist level application of these dyes.

Chrome dyes are acid dyes (mol.wt. 300–600) that contain groups capable of forming complexes by reaction with a metal salt, usually sodium or potassium dichromate (111,114). The chrome/dye complex has lower solubility, and hence better wetfastness, than the parent dyestuff. Reaction between the dye molecule and chromium salt can be carried out before, during or after application of the dye to the wool. Modern practice is to carry out the chroming step after dyeing. Chrome dyes are relatively cheap, and have good migration and level dyeing behavior and excellent wetfastness properties. Their popularity, except for black and navy blue shades, has declined in recent years. This is because of the need for prolonged dyeing cycles, fiber damage associated with oxidation of the fiber in the chroming step and environmental concerns about the use of chromium salts in the textile industry.

In many applications, chrome dyes have been replaced by metal-complex dyes, which have a very high affinity for wool (111,115). In these dyes, the metal complex is preformed during manufacture of the dye, by reaction of one metal atom with either one (1:1 metal-complex dyes) or two (1:2 metal-complex dyes) dyestuff molecules that contain groups capable of coordinating with chromium or, occasionally, cobalt atoms. In general, metal-complex dyes produce duller shades than acid or milling dyes. The 1:1 metal-complex dyes are applied to wool from strongly acidic dyebaths at around pH 2. They are almost all monosulfonates (mol.wt. 400–500) and have good levelling behavior and wetfastness properties. Some degradation of the fiber can be caused by the low dyeing pH. The earliest type of 1:2 metal-complex dyes were unsulfonated; solubility was provided by nonionic polar groups, such as sulfonamide or methylsulfone. More recently, monosulfonated, disulfonated, and some carboxyl-containing types have become available. These dyes range in molecular weight from 700 to around 1000. They are applied at pH values ranging from pH 4.5 to 7.0, depending on the degree of sulfonation and molecular size of the dye.

Reactive dyes have molecular weights in the range 500–900 and usually contain two or three sulfonic acid groups (105,116). These dyes also contain groups that react covalently with wool, which gives them outstanding wetfastness properties. They are characterized by bright colors and moderate migration and levelling properties, provided careful attention is given to ensuring that the exhaustion rate is not too rapid. This is achieved by careful control of the dyebath pH and by using special amphoteric leveling agents. Their ability to react with the fiber means that uneven uptake of these dyes is very difficult to rectify. Reactive dyes are relatively expensive and, currently, their most important application is on wools that have been treated to withstand shrinkage in machine washing. They are, however, becoming increasingly important as alternatives to chrome dyes for dyeing all types of wool. At present, reactive dyes offer the only viable alternative to chrome dyes for products where very high wetfastness properties are required.

8.4. Fiber Damage in Dyeing.

When wool is dyed for prolonged times at the boil, the fiber can be damaged as a result of hydrolysis of the component proteins. Methods of dyeing wool substrates at temperatures below the boil (85–90°C) have been developed. One such method, the CSIRO Sirolan-LTD process employs a special chemical (Valsol LTA-N APS Chemicals) that increases the rate of exhaustion and diffusion of dye into the fiber, thus enabling satisfactory dyeings to be obtained at temperatures below the boil (117). Wool dyed by this method suffers less degradation than wool dyed for a similar time at the boil. This leads to benefits in the processing performance of the dyed fiber and in improved quality of end products (118). Permanent setting of wool fibers during dyeing has been identified as a major factor that also contributes to deterioration of the quality of dyed wool (117). This effect is separate from hydrolytic degradation. Setting occurs via a mechanism involving thiol/disulfide interchange (eq. 1). Methods of inhibiting the permanent setting of wool fibers during dyeing have been developed (89). These involve addition to the dyebath of auxiliaries (antisetting agents such as Basolan AS; BASF) that block thiol groups and, thus, prevent thiol/disulfide interchange. Improvements in the properties of a range of products made from wool are obtained by reducing the amount of permanent set that occurs during dyeing.

9. Printing

Printing provides the means of transferring bright multicolor designs onto textiles. The amount of wool fabric printed is very small compared to cotton and synthetics. This is partly because the pigment printing systems widely used for cotton and synthetics have a severe adverse effect on the natural handle of wool. Furthermore, although the printing of wool using dyes maintains the natural qualities of the fiber, it requires a more complex processing sequence involving several stages, some of which are technically challenging.

The usual route for printing wool with dyestuffs is: fabric preparation/print/dry/steam at 100°C (to fix dye to fabric)/wash off (to remove thickener and unfixed dye)/dry. Globally, an estimated 20 million meters per annum of high-quality printed wool fabric is produced, with the center of excellence being in Northern Italy.

Fabric preparation is considered to be the most important stage for obtaining good color yields, levelness and brightness on wool fabric (119,120). Currently, this is done almost exclusively by an oxidative chlorination process. The most popular commercial methods use either a batch treatment with dichloroisocyanuric acid (DCCA), or a continuous fabric treatment with gaseous chlorine (the Kroy process). Chlorination has a profound effect on wool, especially near the fiber surface. The number of anionic groups is increased, with cystine residues oxidized to cysteic acid and accessible peptide bonds cleaved to form carboxyl groups. These reactions increase the wettability of the surface of wool, which facilitates spreading of the dye formulations. Chlorination also reduces the degree of cross linking of wool, which increases the rate of dye diffusion into the fiber. Chlorination can have several adverse effects, however. At higher levels (4% on mass fabric of DCCA), there are problems in obtaining level treatments. Yellowing, especially after steaming, can also occur. These problems can be minimized by treating fabrics continuously in open width in a machine such as the Kroy chlorinator. With all chlorination processes soluble protein and free oxidation products must be removed from the wool before drying. This is done by neutralization with a reducing agent, such as sodium bisulphite or sodium dithionite.

The effluent from the chlorination of wool contains adsorbable organohalogen compounds (AOX), which are now regarded as undesirable products to release into the environment, particularly in Europe. Several AOX-free methods for preparing wool for printing are currently being investigated. Plasma (121) and corona discharge (122) treatments have been investigated as potential prepare-for-print methods for wool, as they oxidize the surface of wool fibers and have the advantage of being dry processes. Although the wettability of fabrics prepared using these methods is high, the color yields of prints are significantly less than prints on chlorinated fabric and the fabric handle is inferior. An alternative approach is the CSIRO ‘Siroflash’ process. This method involves continuous ultraviolet (uv) irradiation of dry wool fabric with the type of commercial uv source used for curing polymer films. This is followed by a conventional oxidative bleaching treatment with hydrogen peroxide (123). This process is surface-specific, giving a white fabric with good handle properties and similar color yields to DCCA treatment.

Most wool is printed directly onto the prepared fabric. Automatic flat-screen printing remains the most popular method over the rotary screen process used for most cotton printing, because of the shorter run lengths normally processed for wool fabrics. The dyestuffs most commonly used for wool printing are acid milling, metal complex, and reactive dyes. A simple dye paste is prepared using a suitable thickener, urea (to swell wool fibers during steaming) and the dyestuffs. Various additives may be included in the paste recipe, such as antifoam, glycerol to prevent screen blocking, an acid donor (to maintain a low pH), wetting agent and a dye solvent such as thiodiglycol (120).

During the steaming stage, large aggregates of dye molecules break down into smaller entities which can then penetrate the swollen wool fibers, allowing fixation to take place. Typical steaming times are 10–15 min for reactive dyes and 30 minutes for acid milling and metal complex dyes. Saturated steam is essential for optimum penetration and fixation of dyes, especially for dyes of high molecular weight such as those based on copper phthalocyanine derivatives. Both continuous and batch steamers are used commercially. Chlorinated fabrics are highly prone to yellowing during steaming, which can be detrimental to printed pale shades.

The aim of washing off is to remove the thickener and any residual chemicals and unfixed dye from the fabric, without causing staining of any pale or unprinted areas. Fabrics printed with metal complex or acid milling dyes are usually washed off in water at 30–40°C, whereas reactive dyes require higher temperatures (60–80°C), with addition of ammonium hydroxide (120).

Discharge printing of wool remains popular, despite its technical difficulties (119,120). In this style of printing, a pre-dyed fabric is printed with a reducing agent that destroys the background shade. Included in the print paste is a dye which is resistant to the discharge agent. The result is bleaching of the color in the printed areas and replacement with the illuminating color. It is often impossible to reproduce the designs and effects of discharge printing with direct printing. The reducing agents used in discharge printing are zinc, calcium or sodium formaldehyde sulfoxylate, or thiourea dioxide. The technique is limited by the choice of dyes that are resistant to the reducing agent.

Other techniques, such as resist printing, cold batch printing and transfer printing have been applied to wool with some success, but these now occupy only a small share of the current wool printing market (119,120).

Digital inkjet printing is a recent development for printing textiles (124). It has the advantage that any design can be transferred rapidly from a personal computer onto a fabric, without the requirements to perform a color separation and make a separate screen to print each color. It is also more cost effective for producing the short runs of printed fabric designs that are typical for wool compared with other methods. The wool fabric is prepared for printing using a conventional method, padded with a mixture of a thickening agent and urea and dried before digital printing. The padding process assists penetration of the dye into the wool fabric and avoids flushing of the prints during steaming.

10. Other Treatments

10.1. Yellowing.

In common with many other polymeric materials, yellowing of wool is an undesirable property that can be caused by several different mechanisms. For wool, the most important of these are exposure to sunlight and heat.

The rate and extent of photoyellowing of wool exposed to direct sunlight is a serious shortcoming when compared with fibers such as cotton and synthetics. Photoyellowing is caused by the ultraviolet (uv) components of natural sunlight (285–380 nm), whereas exposure of wool to sunlight filtered through window glass, which absorbs most of the UV, causes photo-bleaching (125). Photoyellowing of wool by sunlight only occurs in the presence of oxygen and it has been proposed that it is a photo-oxidative process involving the formation of singlet oxygen (126,127). More recent work, however, has shown that in common with cotton, polyester, and nylon, wool in the wet state is capable of producing hydroxyl radicals (OH) on irradiation with uv light at 366 nm and blue light at 430 nm (128). This reaction appears to be catalyzed by trace metals such as iron and copper. It has been proposed that the photoyellowing mechanism for wool may involve a free-radical chain reaction involving formation of hydroperoxide intermediates (as is the case for most other polymers), rather than a singlet oxygen mechanism (128). There is now general agreement in the literature that yellow chromophores formed in irradiated wool are derived (at least in part) from tryptophan residues (129,130).

The use of some water-soluble benzotriazoles (a well-known class of uv absorber) can be effective against both photoyellowing and phototendering. The effectiveness of these reagents relies on intramolecular hydrogen bonding and proton transfer, and intermolecular bonding of the compounds to wool fibers was found to be highly detrimental to their performance. Optimization of the photochemical properties of soluble benzotriazoles has resulted in a suitable formulation (Cibafast W) for use on both bleached and unbleached wool (131). Unfortunately, uv absorbers cannot be used on wool together with a fluorescent whitening agent (FWA) because they absorb the uv wavelengths necessary to excite fluorescence. FWA treatment is essential to achieve a high level of whiteness on wool, because even wool that has been bleached retains some of its natural cream color. An important problem for wool is the very rapid photoyellowing that occurs following treatment with FWAs (132). The poor light-fastness of bright white and pastel colors severely limits the range of possible shades for wool products. This is reflected in wool's limited market share in fashion and summer knitwear, sportswear, hosiery and baby wear. Wet photoyellowing of whitened (FWA-treated) wool is extremely rapid and can cause unacceptable yellowing after a single laundering and drying cycle in direct sunlight. When wet FWA-treated wool is exposed to sunlight, hydrogen peroxide is formed (133). The rate of photoyellowing of FWA-treated wool is significantly increased by doping with hydrogen peroxide. This indicates that blocking the formation of peroxide (via the superoxide radical anion) could improve the photostability of whitened wools.

Treatment of wool with a FWA, followed by posttreatment with thiourea/formaldehyde by a pad/cure method, confers a high level of protection against photoyellowing and also improves the initial fabric whiteness (134). Unfortunately, this process is not commercially viable; partly because of environmental concerns about thiourea and formaldehyde and also because much of the benefit is lost after laundering. An alternative approach is to physically separate the FWA from the wool fiber by incorporating the whitener into a suitable polymer that can be applied as a surface treatment to wool fabrics (135). The photostability of the treated fabrics is somewhat better than for conventional FWA treatments (being similar to bleached wool) but the initial whiteness is significantly lower than that of FWA-treated wool.

Two comprehensive reviews on the photo-degradation of wool keratin have been published recently by Smith (129) and by Davidson (136). There is also an excellent review dealing specifically with the problem of sunlight yellowing of wool treated with FWAs (126).

Thermal yellowing of wool can be a problem during wool processing, in particular during extended dyeing at the boil, in setting with superheated steam (decatizing) and in drying for extended times, particularly under alkaline conditions (137). The thermal yellowing of wet wool is far more rapid than for dry wool, which is similar to the behavior observed for photoyellowing. Thermal yellowing of wool during dyeing is influenced by pH, temperature and time; chlorinated wools being especially sensitive. Yellowing during dyeing can be counteracted by adding a bleaching agent, based on sodium bisulfite or hydroxylamine sulphate, to the dyebath (138). Addition of hydrogen peroxide to the dyebath after exhaustion of the dyestuffs can also be effective.

10.2. Bleaching and Fluorescent Whitening. The natural pale cream color of wool is due to absorption of light above 320 nm. This is the result of natural pigments and also photodecomposition products in the fiber. Reduction of the natural cream-yellow color of wool is sometimes necessary for improving the brightness of dyed shades, particularly pastel colors, and also for improving the whiteness of undyed wool fabrics. Commercially, wool bleaching is carried out using either an oxidative or a reductive system, or a combined oxidation/reduction process. Oxidative bleaching in the dyebath is also possible (138). In general, oxidative bleaching with hydrogen peroxide gives superior whiteness over reductive methods.

A batch treatment with hydrogen peroxide is used for most bleaching applications. An activator (eg, an alkali) is normally added to increase the rate of bleaching. Typically, wool is bleached at pH 8–9 for 1 hour at 60°C with a stabilized solution of hydrogen peroxide (0.75% w/w). It is generally accepted that, under alkaline conditions, the active bleaching species is the perhydroxy anion (OOH^-), the formation of which is encouraged by higher pH (139). Peroxide bleaching of wool under mild acidic conditions (pH 5–6) can also be carried out using a peracid activator such as Prestogen W (BASF), or citric acid (140). As wool sustains some damage in the presence of alkali, this method is useful for bleaching delicate fabrics. An undesirable side-effect is the rapid decomposition of hydrogen peroxide to water and oxygen;, a reaction catalyzed by transition metal ions. A stabilizer, which sequesters these ions is used to prevent this side reaction occurring. The most common stabilizers for alkaline wool bleaching are phosphates, particularly tetrasodium pyrophosphate. However, recent concerns over phosphates in effluents from textile treatment have led to the development of alternative stabilizers based on silicates (141). An alkaline peroxide bleaching process using the silicate-based product, Stabicol BAC (Allied Colloids) has been developed (138).

Heavily pigmented fibers, such as Karakul wools, require a more severe approach known as mordant bleaching. In this method, the wool is treated with a metal salt and then with hydrogen peroxide. In the first step, the melanin pigment in the wool preferentially absorbs the metal cations; and in the second step, the cations catalytically decompose the peroxide to produce highly aggressive hydroxyl free radicals, which selectively attack and bleach the melanin (142).

The two most popular chemicals used for reductive bleaching of wool are stabilised sodium dithionite and thiourea dioxide. Most reductive bleaching of wool is carried out using stabilized dithionite (2–5 g/L) at pH 5.5–6 and 45–65°C for one hour. Thiourea dioxide is more expensive than sodium dithionite, but is an effective bleach when applied (1–3 g/l) at 80°C and pH 7 for one hour. Whiter fabrics are produced when oxidative bleaching is followed by a reductive process. This is often referred to as full bleaching.

To obtain a high level of whiteness, comparable to white cotton and synthetics, wool must be treated with a fluorescent whitening agent (FWA) after bleaching. The normal procedure is to carry out a full bleaching process and include the FWA in the reductive bleaching bath. FWA-treated wool absorbs ultraviolet light and emits blue fluorescence, which makes it appear much whiter than bleached wool. Commercial FWAs for wool are usually based on a sulfonated stilbene, distyrylbiphenyl or pyrazoline derivative.

Wool fabrics that have been bleached or treated with FWAs yellow rapidly when exposed to sunlight, especially when wet. This is a major problem when bright whites and pastel shades are required. Despite a significant amount of research into the chemistry of photoyellowing processes progress in this area has been limited (126).

10.3. Insect-Resist Treatment. Wool is a protein fiber but, because it is insoluble and highly crosslinked, it is not widely used as a food resource. Only a few keratin-digesting animals have developed specialized digestive systems that allow them to derive nutrition from the potential protein resource. These animals, principally the larvae of clothes moths and carpet beetles, perform a useful function in nature by scavenging the keratinous parts of dead animals (fur, skin, beak, claw, feathers) that are unavailable to other animals.

The principal insects that attack wool are the common clothes moth (*Tineola bisselliella*); the case-bearing clothes moths (*Tinea metonella, T. dubiella, T. translucens*; and *T. pellionella*); the brown house moth (*Hofmannophila pseudospretella*); the variegated carpet beetle (*Anthrenus verbasci*); the black carpet beetle (*Attagenus piceus*) and a few others. The taxonomy of the Tineid species has been comprehensively reviewed (143). These insects have different temperature sensitivities and tend to be found in different climates. Studies in Australia have shown that the native Tineids are rarely involved in domestic infestations. The introduced species, such as *T. translucens*, are the major textile pests and these are often associated with the nests of introduced urban bird species such as sparrows and swallows (144), while *T. bisselliella* is widely distributed and is common in domestic infestations.

All keratinous materials stored for long periods, including stored greasy wool in bales, animal skins, furs and horns, are liable to attack. Strategies for protecting goods vary with the product type. Buildings used to store wool may be fumigated or sprayed periodically. Small articles of clothing may be isolated from the environment in sealed bags, often with the use of heat (sunlight), cold (refrigerated storage) or volatile repellent agents (mothballs), with varying degrees of success.

The only practical means of protecting wool textile products is treatment with an insecticide during manufacture (145). Wool products most commonly treated are carpets, furnishings and insulation. Except for insulation, the most convenient point for treating wool goods is during dyeing, which is attractive because it avoids the needs for an additional wet processing step. Also, because under ideal application conditions the pesticide will be adsorbed inside the highly swollen fiber. This ensures that the pesticide will have maximum resistance to desorption from the dry fiber; and also have optimum fastness to washing, drycleaning and skin contact. An additional benefit of locating the pesticide inside the fiber is that there is little contact action against nontarget pests, as the active agent is most efficiently released only in the insect gut when the fiber is completely degraded.

Unfortunately, it is impossible under practical dyebath conditions to ensure 100% transfer of pesticide from dyebath to fiber. It is also extremely difficult and expensive to remove residual insect-resist agent from dyehouse effluents (146). Even if the pesticide is removed by absorption or flocculation, the fate of the adsorbed material also needs to be considered (147). As a result, there is inevitably some environmental contamination. With the current generation of insect-resist agents, discharge of residual pesticide from dyebaths is a cause of significant environmental concern in large processing centers. Insect-resist agents must have a broad spectrum of activity because of the variety of moth and beetle species that must be controlled. They must also be reasonably stable to the dyeing conditions used in their application and be durable on wool for long periods. It is also essential that the agent is relatively hydrophobic so that it exhausts effectively from the dyebath onto wool. Unfortunately, this combination of properties is likely to lead to adverse effects on aquatic insects and invertebrates. To minimize environmental damage an allowable environmental concentration for permethrin of 10 ngnogram/L has been set in the UK (148,149). To meet this requirement, the UK carpet dyeing industry has introduced a range of best practice operational procedures. These include dyeing at low pH and high temperature; avoiding dyes and dyeing assistants that may decrease the efficiency of application of the insecticide; containing spillages; and avoiding the discharge of effluents from tape scouring machines. Additionally, a number of manufacturers are using alternative application procedures, where little or no aqueous effluent is produced (147,150–152).

Prior to the introduction of synthetic pyrethroids, insect-resist agents were based mainly on speciality materials, such as polychloro chloromethyl sulfonamido diphenyl ether (PSCDs) (Eulan U33, Eulan WA New). The production of these compounds has been discontinued, however, because of a combination of environmental toxicity (149) and cost. One speciality insect-resist agent based on sulcofuron (Mitin FF), released in 1939 (153), retains a small market share for specific applications where cost is less important and where high resistance to wet conditions is required. It has also been used on wool insulation where it also has low volatility and provides resistance to rotting (154).

The principal active agent used for insect-resist treatments since the late 1970s has been permethrin. Although other broad-spectrum agricultural insecticides (including other synthetic pyrethroids) have been examined, permethrin remains dominant as it is a nonirritant with a good human health profile, especially when strongly adsorbed into the wool fiber. Pyrethroids with a safer environmental profile, such as cycloprothrin, have also been examined (155). These, however, require higher application levels, which increases the cost of the treatment. Newer commercial insect-resist agents under development are based on lufenuron (an insect growth regulator) (147,156) and on bifenthrin (a synthetic pyrethroid). The latter agent includes a synergist to counter the resistance to synthetic pyrethroids that is being observed in Australia (147).

Resistance is an inevitable result of using a single protective agent for more than two decades. Resistance to pyrethroids is common among other agricultural pests and pyrethroid-resistant strains of the Australian carpet beetle and the case bearing clothes moth have been found in domestic infestations in northern Australia (157). In the future, it is unlikely that specialty insect resist agents for the protection of wool will be developed, as the market is too small to support the testing required to demonstrate the safety of modern, biologically active agents. The focus remains, therefore, on the use of commercial insecticides for protecting wool against insect damage.

A diverse range of nonpesticidal approaches has also been studied (144). Attempts to find triggers for such behaviors as egg-laying and recognition of food were inconclusive. Although it has been long known that otherwise unrelated clothes moths and carpet beetles have developed unique reducing systems in the gut that allow them to digest wool, specific inhibitors of these systems have not yet been identified.

10.4. Flame-Resist Treatment.

Wool is regarded as a naturally flame-resistant fiber, which is partly due to its high nitrogen content, high sulfur content and high (water) regain under ambient conditions. It has a high ignition temperature (570–600°C), high limiting oxygen index (25–26%), and a low heat of combustion (4.9 kcal/g) (158). In most cases, when wool fabrics are ignited they will rapidly self-extinguish, due to the formation of a high volume, insulating ash or char. Unlike thermoplastic materials, wool does not melt or drip when ignited. In many end-uses, no additional fire-retardant treatment is needed.

If higher standards of flammability are needed, such as in aviation, furnishing fabrics or protective clothing, durable protective treatments are available. These treatments evolved from the observation that wool treated with a chrome mordant, such as that used in chrome dyeing, has a markedly improved flame resistance (159). The chrome mordant, however, discolors undyed wool. It was shown, subsequently, that titanium or zirconium compounds give similar improvements in fire retardancy (160), with reduced discoloration of the wool. The Zirpro Process, developed by IWS (now, The Woolmark Company) has been used extensively for wool in aircraft interiors to meet FAA requirements. It is also used for protective clothing and for stage curtains and carpets in public buildings and similar areas, where high flame resistance is required by legislation (161,162). Other wool finishes (dyeing, insect resist, shrink resist) have been developed that are compatible with the Zirpro Process.

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