CHAPTER 2

LITERATURE REVIEW

2.1 WOOL FIBRE

The textile industry uses substantial quantities of fibres obtained from various animal sources, of these sheep wool is the most important commercially (Rippon 1992). Early sheep were probably domesticated not for their wool, but rather as a source of food and skins. The most important breed for producing premium fine wools is the merino, which originated in Spain during the middle ages. This breed was so highly valued that their export was forbidden until the eighteenth century, when they were introduced into other countries. The most noteworthy of which was Australia, where the breed has been developed to produce highly prized wool with exceptional fineness, length, colour, luster and crimp. A fine wool fibre, viewed under the scanning electron microscope is shown in Figure 2.1.

Figure 2.1 SEM of a fine wool
Raw wool contains 25-70% by mass of impurities. These consist of wool grease, perspiration products (suint), dirt and vegetable matter such as burrs and seeds (Rippon 1992, Garner 1967, Pearson et al 2004, Glaser 1996). These impurities are removed by specific processes such as scouring and/or carbonizing (Pearson et al 2004, Lewis 1992). The wool discussed in this chapter is the fibrous material from which the surface contaminants, described above, have been removed.

Wool is an extremely complex protein, evolved over millions of years for the protection of warm-blooded animals in a great variety of climates and conditions. Wool is produced in the fibre follicle in the skin of the sheep. Because of the multitude of variations possible in, for example, the diet, breed and health of the sheep, as well as the climate, wool fibres vary greatly both in their physical properties, such as diameter, length and crimp, and in their chemical composition (Pailthorpe 1992).

Wool consists principally of one member of a group of proteins called keratins (Hughes et al 2001, Fiadeiro et al 2000, Hogg et al 1994). Keratin fibres are not chemically homogeneous; they consist of a complex mixture of widely different polypeptides (Rippon 1992). Despite the classification of wool as a keratin, clean wool in fact contains only approximately 82% of the keratinous proteins, which are characterized by a high concentration of cystine.

Approximately 17% of wool is composed of proteins which have been termed nonkeratinous, because of their relatively low cystine content (Rippon 1992). The wool fibre also contains approximately 1% by mass of non proteinaceous material; this consists mainly of waxy lipids plus a small amount of polysaccharide material. The nonkeratinous proteins and lipids are
not uniformly distributed throughout the fibre but are concentrated in specific regions of the structure (Rippon 1992).

2.1.1 Chemical bonding in wool polymer

Wool contains eighteen different amino acids and the amino acids are combined together to form a long polymer chain called polypeptide chain. A significant proportion of the polypeptide chains in wool are believed to be in the form of an alpha-helix, this ordered arrangement being responsible for the characteristic X-ray diffraction pattern of α-keratin (Morton and Hearle 1986, Hogg et al 1994). The individual peptide chains in wool are held together by various types of covalent crosslinks and non-covalent interactions (Figure 2.2). In addition to their occurrence between separate polypeptide chains (inter-chain), these bonds can also occur between different parts of the same chain (intra-chain). With respect to the properties and performance of wool, however, inter-chains bonds are the more important of the two types (Rippon 2003).

Figure 2.2 Chemical bonding in wool polymer
2.1.2 **Morphology structure**

Thus, wool is a complex natural fibre composed mainly of proteins (97%) and lipids (1%), with a heterogeneous morphological structure (Heine and Hocker 1995). Wool fibres have approximately the form of elliptical cylinders, with average diameters ranging from 15 µm to 50 µm and lengths determined by the rate of growth of the wool and the frequency of shearing (Makinson 1979). Wool and other keratin fibres consist of two major morphological parts: the cuticle layer (usually referred as scale layer of wool) which is composed of overlapping cells that surround the cortex (inner part of the fibre). The cortex comprises spindle-shaped cortex cells that are separated from each other by a cell-membrane complex (Figure 2.3), which consists of non-keratinous proteins and lipids (Feughelman 1997, Rippon 1992, Makinson 1979, Plowman 2003, Negri et al. 1993).

![Figure 2.3 Schematic diagram of a wool fibre](image-url)
2.1.2.1 Cuticle

The cuticle cells are laminar, rectangular structures which form a sheath of overlapping scales enveloping the cortex (Speakman 1985, Naik 1994, Negri et al 1993). They comprise 10% of the total weight of the wool fibre (Naik and Speakman 1993). The cuticle cells are composed of three distinct layers, called epicuticle, exocuticle and endocuticle (Rippon 1992) as shown in Figure 2.4.

![Figure 2.4 Schematic scale structure of the cuticle](image)

The substructure of the cuticle cells is directly relevant to felting, friction and shrinkproofing processes. The epicuticle, which constitutes about 0.25 percent of the total mass of the fibre, is very inert chemically, being resistant to acids, oxidising and reducing agents, enzymes, and alkalis (Makinson 1979, Negri et al 1993). This membrane does not form a continuous sheet over the whole fibre, but covers the outer surface of each cuticle cell (Naik 1994). The epicuticle membrane is raised in the form of characteristic bubbles or sacs (Allworden bubbles) when the fibre is immersed in aqueous chlorine solutions (Makinson 1979, Rippon 1992). The epicuticle
is known for its hydrophobicity, probably due to the lipid component bound to the membrane (Negri et al 1993, Hocker 2002). The resistance of the surface membrane is thought to be due to the naturally occurring covalent isopeptide crosslinks as well as to covalent attached lipid, predominantly 18-methyleicosanoic acid (Naik 1994, Negri et al 1993, Brack et al 1999, Swift and Smith 2001, Heine and Hocker 1995). This fatty acid is covalently bound to the protein matrix via cysteine residues forming a layer that can be removed by treatment with alcoholic alkaline or chlorine solutions in order to enhance many textile properties such as wettability, dye uptake and polymer adhesion (Negri et al 1993, Brack et al 1999).

Thirty-five percent of the exocuticle A-layer is made by cystine residues, and in addition to normal peptide bonds, the cuticle is crosslinked by isodipeptide bonds (\(\varepsilon-(\gamma\text{-glutamyl})\text{lysine}\)) (Naik 1994, Rippon 1992, Heine et al 1995). The A and B layers are both resistant to boiling in diluted hydrochloric acid and to trypsin digestion, however they can be solubilised by trypsin treatment after oxidation or reduction. The endocuticle is preferentially attacked by proteolytic enzymes, and readily degraded in diluted boiling hydrochloric acid (Naik 1994, Sawada and Ueda 2001).

Therefore, as pointed out by several authors, wool cuticle forms a diffusion barrier to chemicals and other treatment agents (Naik 1994, Schafer 1994, Nolte et al 1996). This diffusion barrier (to dye molecules, for example) is mostly due to the hydrophobic character of the exocuticle A-layer, caused by the large amount of disulphide crosslinks and the bound lipid material. Consequently, the fibre pre-treatment processes modify mainly the composition and morphology of the wool surface (Brack et al 1999, Millington 1998, Pascual et al 2001).
2.1.2.2 Cortex

Next to cuticle cortex occupies 90% of the wool fibre and has the biggest influence on wool’s physical and chemical characteristics. It composed of three typical cortical cells called Ortho cortex (60-90%), Para cortex (40-10%) and Meso cortex (only in low-crimp merino wool). The three cortex cells differ in their characteristics such as accessibility and ease of swelling in alkali, in birefringence and are wound around each other in phase with the fibre crimp. Mercer first used the terms ortho and para in which the ortho cortex is heavily dyed with basic dyes while para cortex is less reactive (Speakman 1985).

The cortical cells arranged in a bilateral manner and the border line between ortho and para cortex proceeds in a helical manner along the fibre axis. This results in a staple crimp the para cortex always being situated in the inner part of the curvature. The cells of ortho and para cortical segments are spindle shaped and have comparable dimensions, being 100 micron in length and 4 micron in diameter. They has finger like projections at the end of the cells that inter-digitize with similar projections from the neighboring cells along the fibres (Marti et.al, 2004). Ortho and para cortical cells differentiate each other in chemical and physical properties. These differing properties are related to wool’s crimp and they impart resilience, loftiness or bulk (Simpson and Crawshaw 2005; Bradbury 1972).

2.1.2.3 Medulla

Medulla or core, which is a network of air-filled cell walls or in some-cases a completely hollow tube. In fine wools the medulla is absent and even in coarse wool only some of the fibres are medullated. The medulla may be interrupted or fragmented (hetero medullation), unbroken (hairy
medullation) and heavily medullated (kemp) as shown in Figure 2.5. Discontinuous (ladder type) medullas of definite patterns are found in Angora rabbit hair (Onions 1962; Wildman 1954).

![Figure 2.5 Schematic diagram of different medullated wool fibres](image)

**Figure 2.5 Schematic diagram of different medullated wool fibres**

2.1.3 Shrinkage of wool

There are five kinds of shrinkage in wool: relaxation shrinkage, consolidation shrinkage, swelling shrinkage, hygral expansion and felting shrinkage (Brady 1997, Rouette and Kittan 1991).

2.1.3.1 Relaxation shrinkage

Relaxation shrinkage occurs when the stresses or strains imposed during the processing of the textile materials are relaxed in water or water plus soap or detergent, without agitation. This form of shrinkage is common to all fibre types and fabric constructions and is non reversible. To obtain a lower relaxation shrinkage the garment must be processed with as less tension as possible or it must be relaxed by corresponding finishing processes.
2.1.3.2 Consolidation shrinkage

The relaxation of residual strains in a fabric is frequently opposed by the many frictional constraints within the fabric brought about by fibre-fibre and yarn-yarn contacts within the fabric. Further shrinkage, called consolidation shrinkage, can be brought about by gentle agitation in addition to simple soaking. This process is non reversible.

2.1.3.3 Swelling shrinkage

When hydrophilic fibres absorb water the longitudinal swelling is negligible while the transverse swelling is appreciable. The transverse swelling can lead to dimensional changes known as swelling shrinkage. The problem is common to all hydrophilic fibres but is reversible.

2.1.3.4 Hygral expansion

Hygral expansion is the change in dimensions that takes place in wool fabrics as a result of change in regain, and hence relative humidity. The dimensional changes caused by hygral expansion are reversible.

2.1.3.5 Felting shrinkage

One of the intrinsic properties of wool, that is peculiar to wool only, is its tendency to felting and shrinkage. Under certain conditions, such as moisture, heat and mechanical agitation, wool shrinks, basically due to its morphological and scale structure. The result is an irreversible shrinkage called felting shrinkage. There are different theories concerning the origin of wool felting (Heine 2002). The hydrophobic character and the scaly structure of the wool surface are the main factors causing the differential frictional
effect (DFE) resulting all fibres to move to their root end when mechanical action such as moisture, heat, and pressure is applied in the wet state (Makinson 1979, Chi-wai et al 2004, Hocker 2002).

The felting shrinkage affects not only the garment dimensions but its look as well. The woven or knitted structure becomes less visible, and the garment becomes thicker and less elastic. The factors contributing to felting shrinkage are fibre friction, fibre elasticity, fibre diameter, yarn linear density, yarn twist, looseness of weave or knit, and finishes, e.g. chlorination and application of polymers in machine-washable wools (Connell 2005).

The felting shrinkage is reduced by the modification of the wool surface either by oxidative or reductive methods and/or by the application of a polymer resin onto the surface (Shaw and Lewis 1976).

2.2 INDIAN WOOL

Indian wool in general is heterogeneous and differs significantly with that produced in the world. The presences of hetero type medullated fibre, high bulk and low crimp are some of the typical characteristics of Indian wools. The most important indigenous breeds of India are Chokla, Nali, Magra, Marwari, Gaddi and Malpura. Central Sheep and Wool Research Institute (CSWRI), India has developed crossbred sheep named Bharat merino, Avivastra and Avikalin from crossbreeding of exotic sheep like Rambouillet and Australian merino with indigenous sheep like Chokla, Nali and Malpura for fine wool production (Arora et al 1978, Gupta 1990). India ranks third in sheep population (62.5 million) and eighth in greasy wool production (55 million Kg) in the world (Anon 2007).


2.2.1 Classification of Indian wool

Nearly 40% of Indian wools are mainly medullated. They are classified based on medullation into true wool (non-medullated) and medullated wool (hetero, hairy and kempy type). Based on the marketing and grading of Indian wool, Singh and Metha (2002) inferred that price of Indian wool is fixed based on its fineness, medullation, impurities, and its economic value. The grading of Indian wool is considered to important for proper selection and utilization for particular end products. Indian wools are classified into five different geno-types based on their gross dimensional properties as shown in Table 2.1 (Sule 2003a). The medium coarse wool is mainly used for various types of carpets, coarse wool for felt and durries manufacturing, crossbred wool for suiting, knitwear, shawl and blanket manufacturing, indigenous wool for hand knitting, handloom and non-woven.

Table 2.1 Classification of Indian wool based on its geno-type and its fibre diameter

<table>
<thead>
<tr>
<th>Type</th>
<th>Fineness (micron)</th>
<th>Fibre types (%)</th>
<th>Region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>True wool</td>
<td>Hetero type</td>
</tr>
<tr>
<td>Fine cross-bred</td>
<td>23-28</td>
<td>&gt; 95</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Medium fine</td>
<td>28-34</td>
<td>65-75</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Carpet</td>
<td>34-40</td>
<td>30-60</td>
<td>10-25</td>
</tr>
<tr>
<td>Coarse blanket</td>
<td>40-50</td>
<td>20-40</td>
<td>2-10</td>
</tr>
<tr>
<td>Manure grade</td>
<td>50-80</td>
<td>10-20</td>
<td>0-1</td>
</tr>
</tbody>
</table>
Indian wool spun on the woolen system, some can be processed on semi-worsted, worsted or DREF spinning system. The Indian woolen industry graded Indian wool into three grades (A, B, C) based on fibre fineness and further classified into three subgroups (A1, A2, A3) in each group based on medullation percent and their end uses (Sule 2003a).

2.2.2 Physical properties of Indian wool

The mean range of fibre fineness, staple length, medullation, burr content and clean wool yield of Indian wool are 30 to 45 micron, 50 to 70mm, 30 to 80%, 2 to 5% and 60 to 80% respectively (Gupta 1990). Some of the characteristics of various Indian wools are shown in Table 2.2. Most of Indian wools are devoid of crimp in the absence of well defined bilateral cortical structure and have less than five crimps per inch. They vary in colour from lustrous white to ivory white. The canary stained wool varies from pale yellow to deep yellow colours (Acharya 1982, Anon 1980). A crossbred named Bharat merino developed by C.S.W.R.I, which has 75 percent exotic fine climatic inheritance and physical and chemical properties of its wool resemble fine merino wool (Parthasarathy et al 1996).

Table 2.2 Physical characteristics of various Indian wool

<table>
<thead>
<tr>
<th>S. No</th>
<th>Breed</th>
<th>Fineness (micron)</th>
<th>Staple length (mm)</th>
<th>Medullation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chokla</td>
<td>28.2</td>
<td>47</td>
<td>24.0</td>
</tr>
<tr>
<td>2</td>
<td>Magra</td>
<td>34.0</td>
<td>58</td>
<td>42.0</td>
</tr>
<tr>
<td>3</td>
<td>Nali</td>
<td>35.0</td>
<td>78</td>
<td>30.3</td>
</tr>
<tr>
<td>4</td>
<td>Marwari</td>
<td>38.8</td>
<td>66</td>
<td>49.8</td>
</tr>
<tr>
<td>5</td>
<td>Malpura</td>
<td>42.0</td>
<td>56</td>
<td>71.8</td>
</tr>
<tr>
<td>6</td>
<td>Bharat Merino</td>
<td>23.8</td>
<td>72</td>
<td>1.20</td>
</tr>
</tbody>
</table>
2.2.3 Mechanical properties of Indian wool

Tensile properties of a wool fibre like stress-strain property, load-elongation, creep and stress relaxation behaviour are known to be dominated by the characteristics of the alpha helices. The alpha helix present in the oriented state which form part of the fibrillar structure with the fibril-matrix bonds. The alpha helix content of non-medullated Indian wool is higher and they are present in a more ordered and oriented form than in fine wool, thus leading to higher modulus and lower creep in the former fibre. The high Tg and torsional modulus of fine wool in the dry state compared to those of non-medullated Indian wool can be attributed to the presence of a much longer amount of bulky side groups in fine wool compared to non-medullated Indian wool (Rama Rao 1990).

2.2.3.1 Stress-strain property

In dry state the stress-strain property of non-medullated Indian wool and fine wool are identical (Sule 2003b). A feature of the stress-strain curve of non-medullated Indian wool is the low yield point at wet state. The greater amount of amorphous region, which allows easy access of water into the fibre structure and lower cystine content of non-medullated Indian wool are the contributing factors to low-yield point. Non-medullated Indian wool showed a higher stress with a high initial modulus whereas medullated wool fibres have a slightly higher elongation and a lower modulus (Gupta et al 1987). Non-medullated Indian wool shows a high tensile stress at low humidity and low strain level, while the retention of tensile stress at high strain and high humidity is more in non-medullated Indian wool than in fine wool. The rigidity modulus decreases with humidity and the rate of decrease is more in non-medullated Indian wool than in fine wool (Rama Rao 1985).
2.2.3.2 Elastic recovery

Elastic recovery of non-medullated Indian wool is must better than that of fine wool fibres and this contribute to their resiliency. Non-medullated Indian wool showed good delayed recovery at 20 and 35% extensions and shows improved total recovery. The work recovery at 20% extension was highest in fine wool followed by crossbred wool while it was lowest in non-medullated Indian wool (Chopra 1978).

2.2.3.3 Glass transition temperature

Alpha form crystallites in fine wool melts at around 215°C with super contraction occurring before melting (Cao and Bhoyro 2001). Non-medullated Indian wool showed a single peak at 240°C and a broad peak at 290°C with indications of a second at 350°C (Blakey et al 1967). The glass transition temperature at standard regain was -10°C for non-medullated Indian wool and -4°C for fine wool. Fine wool is in the visco-elastic state at the lower temperature, while non-medullated Indian wool is moving from the visco-elastic state to the rubbery state (Gupta and Rao 1991).

With the increase in moisture, the bonds are loosened or broken and the bulky side groups which are contributing to high rigidity can now generate more free volume and thus enhance the freedom of motion in other molecular segments. The bulky groups in the segments will require higher thermal energy for motion to commence resulting in high glass transition temperature of Indian wool in the wet state (Rama Rao and Gupta 1991).
2.2.4 Chemical properties of Indian wool

Indian wools are predominant of paracortex therefore they are less reactive than fine wool and have lower urea-bisulphite solubility than fine wools. They are easily affected by alkaline suint due to lower density fibres on sheep body and less wax content and exhibit a high alkaline pH which may range from 7.1 to 10.5 depending upon genotype and clipping seasons. Autumn clipped wool exhibited a high pH (9.3 to 10.5) as compared to the spring clipped wool (7.1 to 9.0) (Anon 1979). The pH, urea-bisulphite solubility, ash content, total sulphur, cystine content and tryptophan of various Indian wools are shown in Table 2.3 (Behera and Shakyawar 1998).

Table 2.3 Chemical properties of various Indian wools

<table>
<thead>
<tr>
<th>Breed</th>
<th>pH</th>
<th>Urea bisulphite solubility (%)</th>
<th>Alkali solubility (%)</th>
<th>Total sulphur (%)</th>
<th>Ash content (%)</th>
<th>Cystine content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chokla</td>
<td>9.3</td>
<td>11.58</td>
<td>9.58</td>
<td>2.98</td>
<td>0.57</td>
<td>9.12</td>
</tr>
<tr>
<td>Nali</td>
<td>10.5</td>
<td>0.60</td>
<td>10.99</td>
<td>2.20</td>
<td>0.94</td>
<td>6.41</td>
</tr>
<tr>
<td>Marwari</td>
<td>9.9</td>
<td>6.02</td>
<td>8.54</td>
<td>2.84</td>
<td>1.18</td>
<td>9.33</td>
</tr>
<tr>
<td>Patanwadi</td>
<td>9.3</td>
<td>4.80</td>
<td>9.39</td>
<td>2.81</td>
<td>0.86</td>
<td>9.23</td>
</tr>
<tr>
<td>Gaddi</td>
<td>8.6</td>
<td>37.46</td>
<td>10.14</td>
<td>3.40</td>
<td>0.58</td>
<td>11.36</td>
</tr>
<tr>
<td>Bharat merino</td>
<td>9.4</td>
<td>33.37</td>
<td>3.00</td>
<td>5.27</td>
<td>--</td>
<td>10.42</td>
</tr>
<tr>
<td>Avikaline</td>
<td>8.6</td>
<td>36.20</td>
<td>3.42</td>
<td>4.72</td>
<td>--</td>
<td>10.90</td>
</tr>
</tbody>
</table>
2.2.4.1 Grease content

Indian wool has low grease content (4%) as compared to 20% in fine wool, because of its low secondary to primary follicle (S/P) ratio. The S/P ratio of fine sheep varied between 15 and 30, while Indian wools between 0.5 and 3.0 (Sule 1966). The scouring yield of Indian wools is comparatively higher and increase with increase in diameter. The inherent alkalinity of Indian wool is sufficient to remove the extraneous matter at 40°C to 50°C in aqueous conditions, since suint content is higher in Indian wool than fine wool (Patel et al 1974). Vegetable contaminant is very common to all Indian wool because of their migratory grazing pattern and it is ranged from 5 to 11% (Singh et al 1983, Patel 1978).

2.2.4.2 Sulphur and cystine content

Indian wools have higher alpha keratose and gamma keratose than fine wools and it is due to it’s highly crosslinking nature. The high-sulphur protein fractions should be rich in matrix (Kulkarni and Moses 1997). Indian wools differ from fine wool in two main aspects, first its sulphur and cystine content and lanthionine content.

The sulphur content of the most Indian wools varies from 2.8 to 3.1%; canary stained wools have even lower sulphur content (2.3%) and fine wool have 3.5%. Indian wool has high lanthionine content (2-3.5%) due to the action of alkaline suint on wool fibre, which makes it resistance to moth attack. The amino acid composition of non-medullated Indian wool was very similar to 64’s fine wool. The exception was cystine, the content of this amino acid being much lower in Indian wool (8.66-8.90 %) than fine wool (11.78-11.98%) (Nandurkar et al 1978).
Possible factor responsible for this are sulphur deficiency in the Indian pastures. Tyrosine content of Indian wools (4 to 5.5%) is generally lower than those of fine wool, and the tyrosine content is related to fibre fineness. The tryptophan content of Indian wool (0.75 to 0.80%) is closely related to fine wool (0.80 to 0.85%) (Anon 1980). The sulphur and cystine content of various Indian wools are given in Table 2.3.

2.2.5 Morphology of Indian wool

2.2.5.1 Medullation of Indian wool

Medullated wool fibres have higher diameter which may be responsible for the higher average fibre diameter of a particular breed of wool if these fibres are present in high proportion. The density of medullated fibres decreases with increase in diameter, but kempy fibres show a reverse trend owing to their ribbon-like cross-sectional shape (Rama Rao and Chopra 1985). Medullated wool show poor resistance to acidic and alkaline attacks and they suffer high strength loss in comparison to non-medullated wool (Gupta et al 1981).

Medullation in the Indian wool fibre significantly influences the stress-strain characteristics. The breaking load, elongation and work of rupture are greater in medullated fibres than in non-medullated fibres (Gupta et al 1981). Medulla in Indian wool imparts flexibility to fibres and facilitates their recovery from distortion unless the walls of the fibres are very thin as in case of kemps. The elastic recovery of Indian wool is similar to those of fine wool at different extensions. Medullated Indian wools have a honeycombed cellular structure. (Sule 2003b, Blakey et al 1967).
2.2.5.2 Scale pattern of Indian wool

The number of scale per inch as well as scale height is higher, but scale index (ratio of scale height and diameter) is lower in Indian wool than fine wool. The scale structures are coronal or annular in fine wool, while flattened and reticulate type found in non-medullated Indian wool (Rama Rao and Gupta 1991). The scale tips project out on both sides of the fine wool, while in non-medullated Indian wool, the scale tips are projected out on one side only and they are not so tapered.

The scale index (scale height/fibre thickness) is about 0.5 in non-medullated Indian wool whereas it is nearly 0.85 in fine wool. Since friction is related to this index, low index in non-medullated Indian wool fibre accounts for the low differential frictional effect reported for this wool. The scale indices for fine wool, non-medullated Indian wool and medullated Indian wool are 0.782, 0.526 and 0.677 respectively (Blakey et al 1967).

2.2.5.3 Bilateral structure of Indian wool

Optical micrographs of oxidized and dyed non-medullated Indian wool show two-phase staining; the dyeing is non-uniform, irregular and typical of para cortex-rich wool fibres. These fibres show preferential dye uptake on the annular region with a small unstained region in the center. The bilateral structure staining in these fibres is not as well defined as in fine fibres and the unstained region is about 15% of the total fibre cross-sectional area. This ring effect becomes more pronounced in coarse fibres. Ortho cortical cell is ranged from 50 to 74% in fine wool and from 5 to 40% in Indian wool. Fine wool shows a distinct ortho-para structure, while in non-medullated Indian wool such a distinct division is not observed (Rama Rao et al 1991).
The paracortical cells of non-medullated Indian wool have larger nuclear residues and the cell membranes are more electron-dense than in fine wool. In medullated Indian wool, medulla is formed by the fusion of the cell membranes but when the medulla becomes larger the tricholiyalin droplets seems to have condensed and at some sites their fibrous form can be seen. These medulla cells are connected at a number of places to the nuclear cell residues of the para cortical cells.

As the medulla increase in size the cortical cells become more elongated. The medulla is not in circular in transverse section (Blakey et al 1967). All medulla however are invariably very heavily stained with methylene blue. Cross section of non-medullated and partially medullated Indian wool is mostly paracortical and this makes fibres resist deformation (Rama Rao and Gupta 1991). Non-medullated Indian wool shows extensive inter-digitations that is one cortical cell penetrates into the neighboring cell, rising to small protrusions at many places along the cell wall boundary. Such a pattern is absent in fine wool.

The maximum size of cortical cell in fine wool rarely exceeds 5 micron, whereas in coarse fibre of non-medullated Indian wool cortical cell width about 8 micron. Non-medullated Indian wool shows a large number of such degenerated elliptical shaped cortical cells. The average elliptical factor defines as the ratio of cell widths in two perpendicular directions, is less than 3 in fine wool where as it is nearly 5 in non-medullated Indian wool. The micro fibrils present in cortex, are arranged in near hexagonal pattern in the center whereas they are continuous but form an irregular contour on the outer region (Rama Rao and Gupta 1992).
2.2.5.4 Cross-sectional profiles of Indian wool

The cross-sectional profile of the wool fibre depends on its thickness, the finer the fibre the more circular its cross section. The factor decreases with increase in major axis and the factor of medullated wool is lesser than that of non-medullated wool. The circulatory factor for fine wool (Rambouillet) and some Indian wool (Bharat Merino, Gaddi, Chokla, Nali, Malpura and Marwari) are 0.894, 0.841, 0.862, 0.849, 0.737, 0.841 and 0.778 respectively. Indian wools are not oval but also elliptical (Chopra and Parthasarathy 1986).

2.2.6 Shrinkage of Indian wool

Indian wools felt less than fine wools as they are coarse and rigid, and have lower differential frictional effect than fine wools. Non-medullated Indian wool that having an average fibre diameter of 26.5 micron and 47.0 % medullation, will definitely be superior in felting properties than Indian coarse wool having 41.4 micron fineness and 79% medullation. Since the aggregate scale interlocking effect of the fibre mass will be predominant in wool, which having finer diameter and high percentage of non-medullated fibres (Mahal et al 1972). The directional frictional effect for non-medullated Indian wool, medullated Indian wool and fine wool is found to be 23, 16 and 39% respectively (Blakey et al 1967).

2.2.7 Canary colouration in Indian wool and their uses

Canary coloured wools are produced during autumn clip (March to September). In autumn season, high heat, humidity and bacterial action make suint into alkaline nature and rupture the epicuticle. The damaged epicuticle is allowing suint pigments and alkali to migrate inside the fibre. The migrated
pigment entrapped inside the fibre and caused permanent yellowish colouration called canary colouration. Canary coloured raw wools have high alkaline pH (9.0±0.7), low UB solubility (6-15%), low alkali solubility, low cystine content (9.5±0.4) and sulphur content (2.2-3.0%), low tryptophan content and high lanthionine content. High lanthionine content of canary coloured wools make them difficult to set during decatizing of fabrics or steam setting of yarns. Canary coloured wools easily absorb smoke and toxic products in cigarette. Filters for window air conditioners made from canary coloured Indian wools found 50% more effective than the corresponding white wools (Sule 1966, Sule 2003b).

2.2.8 Weakness of Indian wool

Indian wools have a lot of hairy and kemp fibres that give a chalky white appearance which decreases its economic value. After dyeing they impart skittery appearance to woolen material. They have a multiple scale structure particularly in coarse fibres. Canary coloured Indian wools pick up dye at a fast rate due to absence of epicuticle. This colour is light fugitive (Sule 2003b).

2.2.9 Angora rabbit hair

Angora wool, the specialty hair fiber obtained from Angora rabbit has special characteristics like excellent whiteness, superb softness, lightness and warmth. It has great economic value in woolen textile industry for manufacture of speciality fabrics. Having special characteristics and rare availability, it is a very costly fiber. The products of angora wool have high demand in elite group of consumers. However, like other speciality fibers rabbit hairs also possess difficulty when processed alone due to its lesser scale height and absence of inter fiber cohesion. It is believed that while in use, part
of this fiber drops away from the products (Berger 1963, Watkins and Buxton 1992). Research works were carried by pretreating the rabbit hair with acetic acid / sulfur dioxide / low temperature plasma in order to reduce the anti static charges and spun in different spinning system to produce 100% Angora rabbit hair yarn (Jin et al 1990, Sui et al 1997, Ji and Han 1998, Danisha et al 2007). Some research work was also carried by blending Angora rabbit hair with wool / cotton and spun in a cotton and woolen spinning systems and the authors observed that there is ample scope to improve processing of rabbit hair in blends further (Arora et al 1983, Singh et al 1984).

2.3 WOOL PROCESSING

Wool is mainly used in the following broad product areas: men’s and women’s woven outerwear, knitwear, underwear, socks, hand knitting yarns, blankets, upholstery, filled beddings, rugs and carpets. All these product areas offer challenge to the wool dyer and finisher to innovate and add value to the final product (Russell et al 2002). A variety of processes are available to improve the appearance, handle, performance and durability of the woolen materials. Chemical processing on wool fabrics such as scouring, carbonizing, crabbing, dyeing, shrink-resist finishing, moth-proof finishing and flame-retardant finishing imparts some functionality, while mechanical processing modifies the handle, drape and surface characteristics. These two broad streams of wool finishing are inextricably entwined in the finishing of wool fabrics to meet the aesthetic, durable and performance level demanded by the consumer.

Generally functional finishes are designed to impart specific functional properties to the fabric such as machine-washability and also to improve the properties of the fabric in relation to its aesthetic characteristics such as tailoring performance. Some of the important finishing processes
which improve dimensional stability and functionality of woolen materials are machine-washable or shrink-resist finishing, flame-retardant finishing, moth-proof finishing, water- and oil-repellent finishing, durable-press finishing, softening finishing, abrasion resistance finishing, wrinkle-recovery finishing and antimicrobial finishing (Lewin and Sello 2000).

Before the more specialized finishing processes are applied, fabrics usually require cleaning like desizing and scouring to remove warp sizing, oils, other additives and dirt. Processes such as bleaching and dyeing are known as wet-finishing processes, since the fabric is exposed to bleaching or dyeing in aqueous solutions (Glaser 1996). Some of the finishing processes in which enzymes can be employed will be described later (section 3.3.3). The conventional processing for wool such as scouring, carbonizing, bleaching and dyeing and different finishing that may be carried out on wool prior to commercialization are discussed in this sub-division.

2.3.1 Conventional processing of wool

2.3.1.1 Scouring of wool

Washing, also denominated as scouring, is the first process that raw wool goes through, and its purpose is to remove the dirt, grease, and other impurities. As already referred, wool fleeces usually contain less than 50% of clean fibre, being heavily contaminated by wool wax, skin flakes, suint, sand, dirt and vegetable matter. To achieve satisfactory wool products, these contaminants need to be efficiently removed by scouring with sodium carbonate and non-ionic surfactants (Tomasino 1992, Dominguez et al 2003). The wool emerges at the end of this process is about 30 percent lighter than its original weight. The grease that is removed (lanolin) is considered a valuable byproduct. Raw wool contains 10 to 25 percent grease, or lanolin, which is recovered during the scouring process (Lewin 2007). Lanolin
consists of a highly complex mixture of esters, alcohols, and fatty acids and is used in adhesive tape, printing inks, motor oils, and auto lubrication. It can also be purified for use in the manufacture of many cosmetics and pharmaceuticals (Glaser 1996).

2.3.1.2 Carbonising of wool

Scouring does not always eliminate vegetable matter such as burrs and seeds. Heavily contaminated wool must go through a process known as carbonising. If burrs are not removed at this stage they can cling to the wool fibres and not be noticed until the process is complete. The process of carbonising is the treatment of the vegetable matter with sulphuric acid and heat. The wool is steeped in the acid solution, which causes the burrs to break up. The wool is then subjected to heat, which converts the disintegrated material into carbon. The burrs are then finally removed, firstly by crushing and then shaken out of the wool by a machine rotating at high speed. Any remaining impurities are thus blown out of the fibre. Following carbonising, the wool should be rinsed and neutralised by a wet process. Such neutralisation should be carried out immediately after baking, otherwise fibre damage will occur during storage of the wool in such an acidic state (Lewis 1992, Anderson 1960).

2.3.1.3 Bleaching of wool

Only a small percentage of the total world production of wool is bleached (Lewis 1992) and this operation is only performed when wool is intended to be white dyed or light dyed, like for baby clothes. Hydrogen peroxide and peroxy compounds damage wool fibres, due to progressive oxidation of disulfide bonds ultimately forming cysteic acid (Gacen and Cayuela 2000).
3.1.4 Dyeing of wool

Dyeing operations are used at various stages of production to add colour and sophistication to textiles and increase product value. Wool textiles are dyed using a wide range of dyestuffs, techniques, and equipment. Until fairly recently, most of the dyes used on wool were acid dyes. Nowadays, acid, chrome, metal-complex and reactive dyes may all be used for the dyeing of wool (Pailthorpe 1992).

2.3.2 Finishing of wool

2.3.2.1 Shrink-resist finishing

There are three types of dimensional changes occurred in woolen material, the first is relaxation shrinkage which is irreversible and is caused by the release of latent strains in the fabric, second is hygral expansion which is reversible change in dimensions occurred, when the regain of wool fibre changes and third is felting shrinkage which is caused by milling the fabric in a locked steam pars (Lees and Medley 1967). Controlled felting is used to produce desirable change in the handle and appearance of the wool fabrics while uncontrolled felting in frequently laundered garments such as socks and under wears is unacceptable.

As a result numerous chemical treatments have been developed over the years for reducing the felting shrinkage of wool. In the late nineteenth century acidified solution of hypochlorite was used to reduce the felting shrinkage of wool (Makinson 1979). By 1972 a number of processes had reached sufficient levels of effectiveness and durability for the IWS standard (International Wool Secretariat) to promote the “SUPERWASH” concept. Superwash is a standard of performance of wool mark products that
will not felt during normal wear life when machine washed according to the washing instructions.

The shrink-resist process can be classified into subtractive, additive and combination of subtractive and additive process, in which the subtractive process modifies the outer cuticle surface of the wool fibre with loss in weight, the additive process masks the surface cuticle by the deposition of polymer, and the third process combined both subtractive and additive process (Lewis 1992).

2.3.2.1.1 Degradative process

The oldest type of shrink-resist treatment involves chemical attack on the cuticle of the fibres by chlorination. Such treatments are commonly called degradative processes. The principal mode of action of degradative antifelting treatments is that they make the cuticle cells softer in water than those of untreated fibres. This softening is the result of oxidation and scission of the numerous disulfide bonds in the exocuticle of the wool. This softening, which results from an increase in the number of charged and/or soluble molecules contained inside the cell membrane, causes a reduction in the directional frictional effect (Makinson 1979).

2.3.2.1.2 Additive process

Chlorination on woolen material leads to slight yellowing which is unacceptable for bleached and pastel garments as well as degradation of the wool fibre, so that the strength and wear-life of the garments are adversely affected. For these reasons, non-chlorination based shrink-resist processes have been developed where cross linking polymers can be applied (Cockett
et al 1980a) without a pretreatment. Four important polymer systems had been developed for shrink-resist treatments for wool fabrics.

Among them the most widely used pre-polymer systems are namely Lankrolan-SHR3 (Diamond Shamrock) and Synthappret-BAP (Bayer). They are commercially applied to woolen garments in which both reactive pre-polymers freely soluble in water and capable of undergoing self cross-linking reaction in alkaline conditions. In Lankrolan-SHR3, the functional groups are Bunte salt groups, which react to form a disulfide bond with wool polymer. In the case of Synthappret-BAP, the functional groups are carbamoyl sulfonates, which undergo hydrolysis and then cross linking in alkaline condition to form a substituted urea. Synthappret-BAP can be applied to woolen materials by both exhaustion and padding method.

Shrink-resist treatments for piece goods are usually based on the application of aqueous solutions or emulsions of reactive pre-polymers by padding. The polymer is then cured during the subsequent drying operation. The most commercially successful treatment for woven and knitted wool fabrics is Sirolan-BAP (Fincher and White 1976). This treatment is applied to the fabrics after wet finishing and drying. The finishing liquor contains 10-30 gpl Synthappret-BAP, 10-30 gpl Impranil-DLH and 3-5gpl sodium bicarbonate (De Boss et al 1980, Fincher and White 1977). During drying, the sodium bicarbonate decomposes to sodium carbonate, which catalyses the curing of the Synthappret-BAP (Cook and Fleischfresser 1985) at 160°C. The Sirolan-BAP process forms polymer bridges between adjacent fibres which prevent fibre migration occurred during felting (Cook 1979).

After the fabric has been dried, it passes through the normal dry-finishing processes such as cropping and decatizing. These processes have a pronounced softening effect on the resin-treated fabric (De Boos and White
1978), probably by breaking some inter fibre bonds in the fabric. Alternatively selected softeners may be co-applied with the polymers (Fincher and White 1977) to improve the hand.

Basolan-SW (BASF) is a soft cationic polymer that may be padded on to untreated or previously chlorinated piece goods to achieve super wash performance. The effectiveness of this polymer is improved by a prior chlorination of the fabric. The polymer is claimed to impart better handle to the treated fabric than alternative process (Cafarella 1985).

Two important silicone emulsions have been developed for the continuous shrink-resist treatment of wool fabric, the first system is a thiol-functional silicone that is cured by oxidation, the second system is combined cationic amino functional dimethyl polysiloxane with a methyl hydrogen polysiloxane and / or polyamide cross linker and a catalyst where appropriate (Makinson 1975, Marsh 1966).


Epoxy functional silicones (Guise and Jones 1977a), cured by using amine cross-linkers and silicone-graft copolymers (Guise and Jones 1977b), have also been conferred shrink resistance. Zuchariah et al (1997) inferred that polymer application on plasma treated wool fabric conferred excellent
shrink resistance and restored the fabric tear strength and handle which are adversely affected by plasma treatment. Jang and Carr (1999) applied an ultra violet curable water based polymer with a photo-initiator to plasma treated wool fabric and it confers shrink-resistance and the fabric handle can be improved by the co-application of a softener.

### 2.3.2.1.3 Combined process

Nowadays the combination of subtractive and additive processes has the highest importance in commercial processes. To date the most successful process for producing truly machine-washable wool is the chlorine-Hercosett process. Some of the important processes are described below.

**The chlorine-Hercosett process:** This shrink-resist process invented by Council for Scientific and Industrial Research Organisation, Australia (Anderson et al 1969) and jointly developed by International Wool Secretariat, England (IWS) is the most widely used process for treating wool tops. The process of continuously treating combed wool on a modified backwash involves six distinct steps (Lewis 1977).

They are chlorination, neutralization and antichlor treatment, intermediate rinse, Hercosett polymer application, softener application and drying / polymer curing. The chlorination treatment is carried out at 15-20°C and pH 1.3-1.7 in liquor containing sodium hypochlorite, sulfuric acid and a wetting agent. The chlorinated wool next passes through a bath containing sodium carbonate to adjust the pH 8.5-9.5 and sodium sulfite (1% oww) at 25-30°C and these chemicals are then removed by rinsing in water at 25-30°C in the successive bowl. The Hercosett-125 polymer is a 12.5% aqueous solution of a polyamide epichlorohydrin polymer (Earle et al 1971), taken in
the next bowl at a rate of 2% (oww) and the bath is maintained at 35°C-40°C and at pH 7.5-8.0 by the controlled addition of sodium carbonate.

Then a cationic substituted stearamide is applied at 0.1 to 0.5% solid on weight of wool at 40°C and pH 7.5. The softener improves the subsequent processing performance and also hand of the wool. The presence of the softener on the surface of the fibres inhibits the formation of polymer bridges between the fibres. Finally the finished wool top is dried at 70-80°C to a moisture content of 8%-12%. After drying the wool may be sprayed with water to bring the wool back to condition and then gilled (Makinson and Lead 1975).

The Kroy-Deepim process: In this method, acid-hypochlorite chlorination is replaced by gaseous chlorine. The web of wool tops is guided by polypropylene mesh belts between spray bars, which spray the chlorination solution onto the wool. The chlorination agent is mainly hypochlorous acid formed by dissolving chlorine gas in water at 10°C. The pH of the chlorinating solution is between 2.0 and 2.5, because hypochlorous acid is formed (Makinson and Lead 1973). The chlorinated wool is then rinsed, passed through a squeezed head and the subsequent treatments are applied on a backwash unit as for the chlorine-Hercosett process (Cockett et al 1980b, Bourn et al 1985).

DCCA process: The most commonly used chlorinating agent for woolen garment is the sodium or potassium salt of dichloroisocyanuric acid (DCCA). Wool garments are usually treated with 2.0-3.5% (oww) DCCA at 20°C and pH 3.5-4.0 using liquor to goods ratio of 30:1. The pre-dissolved product is added over 20-30 minutes to allow for the rapid reaction of DCCA with the fibre. The chlorination treatment is usually completed within 30-40 minutes from the initial addition of DCCA. Occasionally 1.5%-2.0%
potassium permanganate is co-applied with the DCCA, which produces a softer and less yellow garment (Cosnard 1971, Hanekom 1974).

When chlorination is substantially completed, sodium metabisulphite or sodium sulphite (3-5% oww) is added to the bath. Then the bath temperature is increased to 30°C and the garment agitated for 15-20 minutes to reduce residual chlorine and lightly bleach the wool. The Hercosett-125 polymer is applied at 2% (oww) in a bath adjusted to pH 7.5-8.0 with sodium bicarbonate or ammonia. Exhaustion is promoted by slowly raising the temperature of the bath to 30°C. The garments are then removed from the machine, hydro-extracted and tumble dried at 60°C-80°C (Veldsman and Swanepol 1971).

2.3.2.1.4 Other shrink-resist processes

Permonosulphuric acid, its salts and potassium permanganate are still used commercially for the shrink-resist treatments to wool fabrics and garments. Dylan-plus process consists of an oxidative pretreatment with permonosulphate and/or a chlorination followed by a resin treatment confers shrink-resistance to woolen materials (Anon 1983). Interox Chemicals et al patented peroxyphthalic acid and its salts as shrink-resist treatments to wool fabric (1986). The Precision process (Textiles) Ltd of Spain used both chlorine and permanganate to modify the fibre surface which gives good handle and whiteness to the treated wool top (1979).

Anhydrous alkali removes a bound surface-lipid layer called F-layer from the wool fibre surface, increasing the wettability, dyeing rate and shrink-resistance of wool (Leeder and Rippon 1985a, Leeder et al 1985b). Spanish workers reported that treatment of wool fabric and top with bisulphite in presence of an organic solvent and/or cationic surfactant increases the rate
of reaction of bisulphite with wool cuticle and to increase the shrink resistance of the fibre (Erra et al 1983). Treatment of woolen materials with low-temperature plasma (Rya et al 1987), in the presence of oxygen, ozone or after glow (Thorsen 1979, Pavlath and Lee 1975, Ryu et al 1975), fluorocarbons or silanes has been reported to modify the frictional properties of wool fibres and improve the shrink resistance of the wool fibre. This treatment has reduced treatment level, no requirement to cure the polymer and excellent handle and whiteness of the treated top.

2.3.2.1.5 Industrial shrink-resist processes

Industrial shrink-resist process is based on degradative oxidation process followed by the application of an anionic polymer on the oxidized wool fibre. It can be applied to wool fibre in various physical forms. For a number of technical and economical reasons most treatments are applied at the combed top (75%), knitted or woven piece goods (2%) or knitted garment stage (23%). The type of the treatment used depends to some extent on the nature of the end product. If it is made from woolen spun yarn the treatment must be applied to the fabric or garment after milling.

In the case of the products from worsted yarn, the shrink resist treatment can be applied to the wool in top form after combing. Top treatment has the advantage of economy but does require additional expenditure at an early stage of processing and the need for dual stock holding (treated and untreated) down the processing chain. Garment and fabric processing simplifies stock-holding and forward planning because the decision to treat can be made toward the end of the processing chain (De Boos 1988).
2.3.2.2 Durable-press (DP) finishing

Durable-press is a performance claim for a machine-washable minimum-iron garment. It must retain their dimension, shape (including pleats and creases) and their surface appearance during wear and laundering. For a woolen garment to achieve these properties, it must at least be shrink-resistant to prevent felting and be set to maintain its shape (Shaw 1978; De Boos 1988).

2.3.2.2.1 Shrink-resist process for DP finishing

There are three basic approaches to render the wool fabric shrink-resistant either by degradative method or by additive treatments or by both as described in the earlier section 3.2.1.

2.3.2.2.2 Setting for DP finishing

Setting of woolen material (Farnsworth and Delminco 1971) is done by any one of the following methods which gave durable creases in trousers and skirts, however not all the methods are suitable for producing durable-press garments.

1. Wet setting: The legs of the garments are sprayed with setting solution and then press on a steam press using 20-30 sec steam, 20-30 sec bake cycle (Farnsworth 1955, Farnsworth 1960).

2. Hot head pressing: The legs of the garments are pressed at 160-180°C up to 30 sec.
3. **Dry creasing-Lintrak**: A thin line of silicone adhesive is laid into a pre-formed trouser creases.

4. **Dry setting**: Fabrics are pretreated in the mill with diethanolamine carbonate and urea. The dry made-up garment is durably creased by steam pressing (Cook and Delminco 1965).

5. **Autoclave setting**: Garments are interleaved between thin sheets of polyurethane foam, suspended by flexible aluminium plates and steamed for 10 min at 110°C (Davidson 1965).

### 2.3.2.2.3 Commercial DP finishing

Only two sequences are used for commercial production of durable-press woolen garments and are described below.

**The CSIRO process:** This process introduced to Australian wool industry in 1971. The garment is applied with a reactive polyurethane prepolymer (2-3% Synthappret-LKF) to the made-up garment from perchloroethylene. Then the garment is re-pressed in order to remove wrinkles and hang the garment in a steam oven. After a short warm-up period saturated steam is introduced and steamed for two hour (White 1973).

**The IWS process:** This process was developed in 1972 and used a thiol-terminated prepolymer (Oligan-SW) as the shrink resist agent (De Boos 1988). The polymer is applied to the fabric by padding. The padded fabric is dried, cured and then the fabric is finished in the conventional manner. A pressure-decatizing step, to provide maximum smooth-drying properties is usually included in the finishing step. After making-up, the garments are sprayed to a 40% wet pick up with 2.5% monoethanol amine / monoethanol
amine sulphate solution (oww) and the garments are set by steam pressing (20-30 sec steam, 20-30 sec bake) and conditioned (Shaw 1972).

2.3.2.3 Moth-proof finishing

Wool and other animal fibres are subjected to attack by the larvae of certain moths and beetles. The wool digesting insect’s larvae have developed an alkaline reducing region in the gut, which is capable of breaking disulfide bonds. Enzymatic digestion of the separated protein chains then follows. The degradation of wool by larvae will be increased if the article is soiled (Moncrieff 1950).

Moth-proofing is necessary to the most susceptible woolen materials such as carpets, upholstery fabrics, blankets, winter underwear and uniform fabrics. Most moth-proofed woolen materials perhaps as much as 90% is nowadays used in carpets (Mayfield Russell 1979, Mayfield 1982). The most important moth-proofing agents are Martius Yellow, Mitin FF and Eulan series. Moth proofing agents are applied by any one of the following methods (Moncrieff 1966).

2.3.2.3.1 Moth-proof finishing methods

a) Application during dyeing: An appropriate quantity of mothproofing agent is added to the dye bath along with the dyes and auxiliaries (Carter and Duffield 1977).

b) Application during scouring: The mothproofing agent is added during raw-wool scouring or more commonly in yarn scouring in hank form.
c) Application by addition to spinning lubricants: The mothproofing agent is mixed with the spinning oil and water and the mixture is applied to the loose wool in the normal way. The fastness of mothproofing agents applied in this way is low.

d) Application from solvent: Eulan BLS (Bayer) is a mothproofing agent, which is mixed with the water and the mixture dispersed in the solvent (perchloroethylene), it exhausts rapidly onto wool placed in the solvent.

2.3.2.4 Flame-retardant (FR) finishing

Wool is regarded as a naturally flame retardant fibre. It has a high ignition temperature (570°C to 600°C), high LOI (25%-26%) and low heat of combustion (4.9 kcal/gm) (Tesoro and Meiser 1970). Wool is self-extinguishing and instead of burning freely when touched by flame, wool chars and stops burning when it is removed from the source of fire. The foam like ash produced has good insulating properties and can be handled immediately after the fire. These thermal properties are associated with the high nitrogen (16%), sulphur (2.8%) and moisture (10-14%) contents of the wool fibre. Although wool is regarded as a safe fibre, higher degree of flame retardancy can be required to some woolen materials like in protective clothing (Tesoro 1969; Tial 1998).

A flame-retardant chemical may char the fuel, quench the reaction of combustion, absorb heat or emit cooling gases or replace oxygen. Problems in the flame-retardant finishing are odor, yellowing, loss of tensile strength, stiffening, skin irritation and color change or loss to woolen materials. There are two types of flame-retardants applied to woolen materials which are based
on their reaction to wool polymer. They are reactive and additive flame-retardants (Benisek 1972a).

In reactive flame-retardants, the reactive components are chemically built into the wool polymer and additive flame-retardants are incorporated into the polymer either prior to or during polymerization (De Boos 1988). Commercially viable flame-retardants for woolen materials are classified into four groups and discussed below.

2.3.2.4.1 Phosphorous based flame retardants

An alkyl phosphonium halide such as tetrakis-hydroxymethyl-phosphonium chloride (THPC) is applied along with urea and a melamine pre-condensate by pad-dry-cure-wash-dry technique to a level of about 20% finish add-on. The finished fabric had to be rinsed with hydrogen peroxide and neutralized with bicarbonate to remove unreacted chemicals (Crawshaw et al 1971, Dupraz 1971).

A water soluble oligomeric vinyl phosphonate called Fyrol-76 is applied in the presence of N-methylolacrylamide and a persulphate with add-on about 18%. It was effective on wool/cotton, cotton and wool/cotton/polyester fabrics except pure wool fabrics (Friedmann et al 1974).

2.3.2.4.2 Organo-halogen based flame retardants

Chlorendic acid exhausted on wool under acidic conditions at the boil imparted flame-retardant effects which is fast to dry cleaning and several washes. Tetrabromophthalic acid (TBPA) or its anhydride do not discolour
the wool and can be applied at boil to impart flame-retardant effect, which is fast to dry cleaning, but not to washing (De Boos 1988, Shaw et al 1972).

2.3.2.4.3 Zirconium, titanium and other metal complex based flame retardants

The zirconium and titanium complex based treatments are developed by IWS (Benisek 1971, Benisek 1981, Benisek and Craven 1983) during 1970-71 and it is called Zirpro flame-retardant finishing. These flame-retardant finishing is based on the exhaustion of negatively charged titanium or zirconium complexes onto positively charged wool fibres in acid conditions during or after dyeing. The metal complexes most commonly applied are potassium hexafluorozirconate (K$_2$ZrF$_6$) or potassium hexafluorotitanate (K$_2$TiF$_6$) (Benisek 1974, Benisek 1975). Treatment from a long-liquor bath at 60$^\circ$C for 30 minutes is the most common application technique, although application by pad-batch-rinse-dry and other techniques is also possible. A pH below 3 is required for about 70% exhaustion of the complexes at 60$^\circ$C during 30 minutes. This can be achieved by the addition of hydrochloric or sulfamic or formic acids. The Zirpro treatment can be combined with other easy-care finishes for wool (Benisek 2004).

2.3.2.4.4 Sulphur containing flame-retardants

Sulfated wool formed by the action of sulfuric acid on wool and it imparts flame-retardant finish, but with limited wash-fastness. However sulfation with 20% sulfamic acid in the presence of 20% urea imparted flame-resistance to wool knit fabric (Lewin et al 1975).
2.3.2.5 Water and oil-repellent finishing

Although wool is an inherently water-repellent fibre, it is wetted rapidly by oils. Oxidative treatments (e.g. chlorination) increase the hydrophilicity of the fibre surface, but such treatments are used mainly on apparel fabrics, where wetting is not considered an important problem (Lewis et al 2000). Overall oil and water-repellent treatments for wool are of only minor commercial importance and restricted primarily to the upholstery and special industrial market. Repellent finishes are applied to well-rinsed fabrics after completion of all dyeing and wet finishing operations in order to minimize adverse effects arising from residues of surfactants, particularly silicones and other auxiliaries or finishes. Wax dispersions, organo-metallic complexes, aluminum salts and soaps, wax dispersions and thermosetting resins, metal salts and wax dispersions, silicones, alkyl pyridinium chlorides and fluorochemicals are used as water repellent chemicals (Marsh 1966, Hall 1966).

Silicones produce good-repellent effects, improved sewability and a smooth lively hand on wool fabrics. The silicones used are primarily from mixtures of polymethyl siloxanes and polymethylhydrogen siloxanes (Wang et al 2001). Silicones are used for treating rainwear, sportswear and furnishing fabrics. Fluorochemicals are effective and require relatively little add-on (0.3-0.5%) but they are expensive and long-term durability to cleaning requires higher levels (De Boos 1988). Their durability is improved when they are co-applied with Sirolan BAP formulations (Guise and Freeland 1982). Where durability to cleaning, particularly dry-cleaning is not required wax-dispersions containing zirconium salts and alkyl pyridinium chlorides are used. The wax/zirconium repellents are widely used, because of their versatility, efficiency and ease of application. A curing step is not required.
and like the pyridinium salts they provide a soft full hand to the fabric (Hall 1966).

Wool fibre was acylated with dodecenylsuccinic anhydride and octadecenylsuccinic anhydride at 75°C in presence of a solvent. Moisture regains and water retention of acylated wool decreased significantly, whereas water repellency increased. SEM analysis showed the presence of foreign material firmly adhered to the surface of wool (Arai et al 2001). A nano fluorocarbon based finish imparts durable water/oil repellent without change in the tensile strength of pure woolen knitting yarn (Feng and Zhang 2006).

2.3.2.6 Antimicrobial finishing

Microbial degradation of textiles is brought about by extra cellular enzymes secreted by an infecting microorganism such as bacteria and fungi. In wool fibre, the enzymes secreted by the microorganism, break down peptide bonds between the amino acids of the protein chains. The ultimate products of degradation are small water soluble amino acids, which then become available as nutrient for the microorganism (Schindler and Hauser 2005). Non-keratinous components are located in intercellular material of the wool fibre and micro organism also attacks that portions. Severe enzymatic attack on this portions leads eventually to fibrillation and separation of the fibre components and leads to severe degradation of the mechanical properties of wool.

Wool contaminated with natural impurities such as oil, wax and grease are more likely to be attacked. It follows that clean wool stored in dry conditions is most unlikely to be attacked. However the bacteria and the spores of the fungi are omnipresent and light infection, sufficient to cause
discoloration of the wool or resistance to dyeing can occur quite rapidly if semi-processed goods are stored wet even overnight.

Three commercial antimicrobial chemicals namely, Sandicide liquid (Sandoz), Prestofen GDC (GAF) and Mystox B (Catomance) are available to impart antifungal and antibacterial finish to woolen materials (Lewis 1973). These products are applied by spraying, padding or exhaustion at the rate of about 3% on weight of wool. Recently various chemicals have been applied to wool to control microbial and larval attack (Purwar and Joshi 2004, Han and Yang 2005).

Magnesium hydroperoxide and related compounds, and chitin and chitosan based antimicrobial agents are the new generation of environmental friendly antimicrobial agents (Purwar and Joshi 2004). Non-toxic natural dyes have also been tested on the antimicrobial activity of wool with good results (Han and Yang 2005).

Carboxylate groups in wool polymer are employed to form ionic interactions with cationic antimicrobial agents such as cetylpyridinium chloride (CPC) and other quaternary ammonium salts, under the isoelectric point of wool polymer and such interactions were proven effective durable antimicrobial agent for wool fabrics (Ping and Sun et al 2004).

Cyclodextrin is grafted up to 12% on cotton or wool fabrics in the presence of a polycarboxylic acid with phosphorous salt as catalyst by pad-dry cure method. The polycarboxylic acids linked through an esterification (or acidification) reaction with the -OH (or -NH$_2$) groups of both cyclodextrin and cotton (or wool) fibres. The grafted cyclodextrin exhibits very good antimicrobial activity on both wool and cotton materials (Martel et al 2002).
2.3.2.7 Wrinkle recovery finishing

Among the textile fibres, wool has excellent wrinkle recovery, however absorbed moisture plasticized the structure and increases the rate of stress relaxation during wear deformation. Consequently the wrinkle recovery of wool deteriorates under very high humidity conditions. Such conditions, however, are encountered only rarely in wear (Sorenson and Hog 1971). Wrinkle recovery can be imparted by treatments that alter the mechanical or moisture absorption properties of the matrix of wool polymer. The following chemical treatments on woolen materials improve wrinkle recovery.

Solvent treatments that remove liable proteins and lipids from wool have little effect on wrinkle recovery. Incorporation of large organic compounds such as ninhydrin, benzoquinone, phenyl isocyanate into wool reduces water uptake at high humidity (> 80%) and increases torsional modulus and wrinkle recovery (Leeder 1971). Certain substantive metal salts like mercuric chloride also improve the wrinkle recovery of wool (Hunter et al 1977). Cross-linked polymers (Jones and Leeder 1975) and some hydrophobic polymers generally impart improvement in wrinkle recovery by marginally reduce the stress relaxation during deformation. When wool is pretreated with poly-functional phenols or aromatic amines and then annealed in the presence of formaldehyde, high wrinkle recovery values resistance to deannealing treatments can be obtained (Ryan 1971, Leeder and Wemyss 1971, De Boos et al 1975).

Needle and Okumoto (1988) found that wet wrinkle property of wool can be enhanced by the partial reduction of disulphide bonds by tetrakis (hydroxymethyl) phosphonium sulphate (THPS) followed by re-cross linking with diamino hexane and additional crosslinking with formaldehyde. Wool fabric is treated separately with epoxide, silicone polymers, and a mixture of
the two in a simple pad-dry-cure process. The epoxide improves wrinkle recovery by changing the viscoelastic properties of wool fibres and increasing their resilience while silicone polymers, which act largely by decreasing the frictional component of wrinkling through the formation of a thin film of polymers on the fibre surface. Fabrics treated by this method show better abrasion resistance, high tear strength, and better hand than fabrics treated solely with the epoxide (Jones 1973, Chapman 1976, Moon and Kang 2000). Kang and Kim (2001) inferred that application of amino functional and epoxy functional silicone softeners in 1:1 proportion give better wrinkle recovery due to the synergistic effect of both silicone and catalytic reaction of the amine group.

### 2.3.2.8 Abrasion resistance finishing

Chemical treatments such as finishing and dyeing have been shown almost invariably to reduce abrasion resistance of wool fabrics by damaging the fibres. Cell membrane complex relatively minor component of the fibre (6%), at the boundary of the cortical and cuticle cells, is thought to be the weak link in the fibre and studies confirmed that it plays major role in fibre damage during wet processing (Tester 1984, Leeder 1986, Zahn et al 1994).

Solvent treatment is thought to remove lipid material from the CMC and improve the adhesion between cortical cells and thus the abrasion resistance. The following chemical treatments are used to improve the abrasion resistance of wool fabrics. Lightly cross linking of wool fibre with formaldehyde or its derivatives under mild conditions improve the Martindale abrasion resistance (Leeder and Rippon 1983). This mild treatment strengthened the weaker regions in which fracture occurred to cause fibrillation of the fibre and stabilize the non-keratinous regions of the fibre including the CMC and the inter macro-fibrillar cement.
A treatment of the wool fabric in 98% formic acid at room temperature for 24 hours increased the Martindale abrasion resistance by a factor 2-3 (Leeder and Rippon 1983). A pad-batch treatment of wool with a propanol/water mixture containing a cross-linker removes lipid material from and crosslink proteinous material in the CMC (Feldtman and Leeder 1984) and it repairs the processing damage. Cook et al inferred that Synthappret-BAP penetrated into wool fibre through non-keratinous regions and located mainly in the ortho cortex which improves abrasion resistance of wool (1989).

2.3.2.9 Multifunctional finishing

The concept of multifunctional finishing brings together a number of quite dissimilar finishing that when combined impart complementary finishes to wool fabrics. All such multifunctional finishing require appropriate pretreatment of the fabric and the use of compatible processes. The multifunctional finishes are more difficult to achieve and those are based on shrink-resist and flame-retardant finishing. The adhesion, curing and mechanical properties of shrink-resist polymers can be affected substantially by the state of the fibre surface and by co-applied additives (Cook and Fleischfresser 1980, Fincher et al 1973).

Similarly when one or more finishes particularly polymer finishes (Benisek and Craven 1980) are applied to flame-retardant fabrics, the burning behaviour of the wool can be change dramatically. Some of the important multifunctional finishing applied to woolen material is discussed below.

2.3.2.9.1 FR and shrink-resist finishing

One approach is to treat the chlorinated fabrics with a minimum of 25% tetrakis-hydroxymethyl-phosphonium hydroxide (THPOH) by a pad-
dry-ammonia cure-wash off-dry-peroxide oxidation sequence. The flame-retardant finish was fast to washing at 60°C. The fabric has a soft hand but tear strength and abrasion resistance was adversely affected (Van Rensberg 1976, Van Rensberg 1978). Application of Zirpro/TBPA treatment (Benisek and Edmondson 1983) imparted very good fastness to washing on Kroy/Hercosett treated wool (Cockett and Lewis 1980), when compared with the Zirpro treatment. These latter treatments have been used commercially to achieve shrink-resistance and flame-retardant in a two-bath system without intermediate drying (Benisek amd Craven 1980).

A 1:2 ratio of Synthappret BAP and Primal E801 is applied to wool fabrics by padding at 1.5%–2.5% (oww) in the presence of 3-5 gpl sodium bicarbonate. After drying and curing, the fabrics were Zirpro treated using 8% oww potassium fluoro zirconate in the presence of 37% hydrochloric acid (10%) and 4% citric acid (Benisek 1974b). This finish is used for shrink-resistance, flame-retardant, pure wool fabrics for air-craft seat covers and curtains.

In IWS process (Benisek and Craven 1984), the application of Synthappret BAP and Neoprene 400 confers shrink-resist finish and the successive application of Zirpro treatment containing TBPA confers flame retardant finish. An anionic fluorocarbon called Nuva F of Hoechst is co-applied to the fabric with the Zirconium complex and TBPA to confer petrol-, oil-, water repellency and acid resistance. Fluorocarbons can be co-applied with shrink-resist polymers to confer stain- and soil-repellency to wool at the same time as shrink resistance (Guise and Freeland 1982). Co-application of the fluorocarbon with the shrink-resist polymer, improves the stability of the finish to washing, dry cleaning and abrasion.
2.3.2.9.2 Water- and oil-repellent shrink-resist and FR finishing

Water- and oil-repellent properties are often required on machine-washable protective clothing. Chemical shrink-resist finishing adversely affects the natural water-repellency of wool. Fluorocarbons improve the water- and oil-repellency of chemically shrink-resist treated woolen materials, but their fastness to washing is limited (Benisek and Craven 1980). High levels of water and oil repellency have been obtained on Synthappret-BAP: Polyvinylidene chloride (PVDC) treated wool fabrics by simultaneous exhaustion of Zirpro flame retardant reagents and a fluorocarbon (Benisek et al 1983). A Synthappret-BAP:PVDC:Oligomeric vinylphosphonate treatment produced adequate flame-retardant, shrink-resist and oil-repellent finish, but the water repellency was lower than obtained by the Zirpro-fluorocarbon exhaustion treatment (Benisek and Craven 1979).

3.2.9.3 Water- and oil-repellent shrink-resist finishing

Fabrics with these properties form the basis of clothing designed to protect against dangerous chemicals. They are also suitable for upholstery fabrics where improved wear performance and resistance to staining are important. Selected fluoro chemicals can be applied with Sirolan-BAP mixtures (Fincher and White 1977) to produce acceptable level of oil and water repellency after repeated washing, dry-cleaning or abrasion (Guise and Freeland 1982). The durability of the repellent effects is greater than if the fluorocarbon is applied alone or sequentially with the Sirolan-BAP System.

Gasoline, oil, water and acid-repellent flame-retardant wool fabrics are required for protective clothing against dangerous and flammable chemicals, for example for riot police uniforms. Zirpro and fluorocarbon finishes applied to carefully constructed wool fabrics are suitable for this
purpose (Benisek and Edmondson 1983). Water-repellent fabrics can be obtained on Zirpro-treated fabrics with selected silicones, thermosetting waxes or organo-metallic compounds. The water-repellent must be applied after the Zirpro finish for maximum repellency (Gordon et al 1984, Benisek 1974a).

2.3.3 Surface modification of wool by pretreatment

The chemical modification of wool can be regarded as a powerful tool to improve some inferior textile performance of the wool fibre and to impart new physio-chemical and functional properties suitable for technological implementation in order to meet market requirements for better wear and maintenance behaviour of woolen materials and for developing new textile products. Pretreatment of wool fibre modifies many of its physiochemical and mechanical properties as per the processors requirements.

Among them, pretreatments using either oxidising agents or reducing agents are applied to wool extensively in order to make them reactive, which make the post treatment as effective and uniform. For example a reduction pretreatment using sodium bisulphite is given to wool prior to Papain treatment for effective antifelting treatment for wool.

Due to release of absorbable organic halogens-AOX to the effluents by the chlorine-Hercosett process (Heine 2002, Julia et al 2000), the development of clean technologies such as enzymatic process for shrink-resist treatment using different protease enzymes is a priority. Recently chitosan, a biopolymer has been introduced as a shrink-resist chemical and plasma treatment which is also used as shrink-resist treatment as well as pretreatment for polymer applications.
2.3.3.1 Oxidative/reductive treatment

Gaseous fluorine treatment oxidized the wool fibre surface, resulting in cystine bond cleavage and to form cysteic acid with a loss of surface sulphur and confers shrink resistance (Kidd et al 1995). When wool fabric is treated with different oxidizing agents in the following steps imparted shrink resistance. The process sequence is Potassium persulphate → Potassium permanganate → Acid chlorination → Hydrogen peroxide bleaching (Shalini Rawat et al 2001). Treatment of wool fabrics with polar solvents such as n-propanol and concentrated formic acid removes lipid materials from cell membrane complex results in improvement in abrasion resistance. The improvements are stable to mild finishing, but are reduced by treatments in aqueous solutions above 85°C (Feldtman and Leeder 1984).

An oxidative batch wise pretreatment for wool fabric using 6% mono-peroxyphthalate (oww) at 30°C for 30 minutes confers 0% shrinkage with 4% strength loss (Levene et al 1996). Pretreatment of woolen material with soda ash leads to change in the fine structure which gives rise better dyeing properties in terms of higher rate of dyeing and dye bath exhaustion. Jovancic et al optimized a recipe for shrink resistance finish for wool fabric with Basolan-D C by studying their physio-chemical and mechanical properties. The Basolan DC gives optimum results at 2.5%-4.5%(oww) concentration at pH 4.5/30 minutes/20°C with 10% sodium sulphate as additive (1993).

Kan et al (1998a) found the alkali solubility, time of half dyeing (t½) and shrink resistance of wool fabric treated with Basolan-D C alone and combination with low temperature plasma (LTP) and Basolan-MW polymer. The LTP/Basolan-D C combinations show high alkali solubility, low t½ and better shrink resistance than other combinations. Reduction or partial
hydrolysis of wool followed by post succinylation with succinic anhydride raises water absorbability, hygroscopic nature and reduces crystallinity. Introduction of new carboxylic groups and increasing in amorphous region contribute to the raise in hygroscopic nature of wool (Kohara and Nakajima 2004).

2.3.3.2 Enzyme treatment

Enzymes can be applied potentially to all stages of textile production. The most classical enzymatic application in the textile industry is the desizing of cotton fabrics using amylases. In finishing, where several enzymes can be applied, depending on the intended look and final properties. Cellulases are also used in bio-polishing processes to improve the appearance of cellulosic fabrics by removing fuzz fibre and pills from the surface, reducing pilling propensity, or delivering softening benefits (Azevedo 2001, Cavaco et al 1996).

Proteases constitute the most important group of industrial enzymes and their major application is the detergent industry. Addition of proteases to detergents considerably increases the cleaning effect by removing protein stains such as blood and egg, and increases the consumption of surface-active substances thereby decreasing the pollution load (Moreira et al 2002, Grebeshova et al 1999). Protease enzymes are also used in the textile industry for the degumming of silk and for producing sand washed effects on silk garments (Freddi et al 2003). The use of proteases to reduce prickle and improve softness in wool has been investigated with encouraging results (Heine 2002). However wool biofinishing is not yet implemented at an industrial scale and attempts are done to implement enzymes periodically in wool finishing and they are described below.
Enzyme pretreatment on dyed wool fabrics improved softness, handle, drape, pilling resistance and change the colour (Riva et al 2002). Protease enzyme penetrates into amorphous region and causes swelling, and it leads to changes in the disulphide region of cystine than amide components during chemical degradation. So percent content of ordered alpha helix region decreases with conversion of beta sheet form in enzyme pretreatment (Wojciehowska et al 2004). Riva et al is applied bacterium Streptomyces Fradiae (SFP) on wool fibre and it attacked neutral keratin and hydrolyzed some peptide linkages. This enzyme treatment causes weight losses at higher concentrations without change in physio-chemical properties while the uniformity is not better (1993).

Shen et al (1999) inferred that the activity of enzyme on wool depends on the bath buffer, its ionic strength and previous process history of substrate. Levene et al (1996) showed that sodium bisulphite pretreatment enhanced the activity of alkaline bacterial protease enzyme and confers better shrink resistance to wool tops and fabric. Among enzymes Esperase was found to be most active while causing the least damage. Wool yarn spun from Novolan-L enzyme treated wool tops has lower number of neps, lower number of breaking through spinning, low co-efficient of hairiness, where the knits have softer feel with better drape, improved pilling performance and dimensional stability (Mangovska et al 2000).

A pretreatment of wool with lipase/sodium-monoperoxyphthalate/sodium sulphite forms Bunte salt with low concentration of cystine monoxide and cystine dioxide and enhances the efficiency of Papain enzyme (El Sayed et al 2002). Cardamone et al (2004) inferred that pretreatment of woven and knitted wool fabric of various weights with peroxy carboximide, ruptured peptide linkages and cystine disulphide cross-linkages through hydrolysis and oxidation reaction and
further proteolytic enzyme treatment biopolishes and controls the shrinkage without appreciable loss in strength and elastic recovery. The addition of a protease enzyme in a oxidizing or reducing bleaching bath shortens the bleaching time by half for the same whiteness index (Levene 1997). Treating of wool with a haloperoxidase (hydrogen peroxide+halide) and a proteolytic enzyme results in improved shrink resistance.

In presence of hydrogen peroxide, wool cuticle degrading enzyme called Bacillus cereus strain NS-11 modified the cuticle components preferentially without damaging the inner components of wool fibre (Takatuka et al 2003). Lantto et al (2005) found that peroxidases are able to catalyze oxidation of wool fibres corresponding to 35%–40% of the tyrosine residues located on the wool surface or 2% of the tyrosine residues in the wool fibre.

Enzyme pretreatment on wool fabric decreases the resistance of the fibre to dye diffusion and so it increases the adsorption rate constant and decreases in the apparent activation energy for the dyestuff when compared to untreated fabric (Riva et al 2002). Enzyme pretreatment of wool fabric with trypsin increases exhaustion of natural dye like crocin, beta-carotene, curcumin, chlorophyll and carmine without change in fastness property (Liakopoulou et al 1998, Tsatsaroni and Liakopoulou et al 1995, Tsatsaroni et al 1998). Levene and Shakkour (1995) found that a chlorination pretreatment followed by an alkaline protease treatment on wool fibre made it clearly descaled wool fibre with enhanced luster. The handle of the fibre can be retained in the post softening treatment.

Brier (2000) stated that treatment of wool fabric with Perizym-AFW improved shrink resistance, whiteness, pilling behaviour, dyeability and washability. This is called as Lanazym process, which is based on purely
enzymatic antifelting finishing of wool. El Sayed et al (2002) described an enzyme-based process to improve the felting resistance of wool top. In this process, lipase is used in the pretreatment step, glutathione reductase in the reduction step, and Papain in the aftertreatment step. The lipase removes lipids from the outer surface of wool, glutathione reductase reduces the disulfide bonds in wool keratin together with nicotineamide adenine dinucleotide phosphate in the reduced form and Papain smooths the wool scales. Wool fibres treated with this system showed good felting resistance as compared with untreated wool, but still was inferior to that treated with the chlorine/Hercosett process.

2.3.3.3 Chitosan treatment

Chitosan a natural biopolymer, chemically called as beta-(1,4)-2-(amino)-2-deoxy-D-glycopyranose. In aqueous solution at pH < 6.5, it is its protonated form (NH$_3^+$) and behaves like a cationic polyelectrolyte and interacting with negatively charged molecules. It can be applied by reactive bonding to cellulose/protein fibre and by cross linking of chitosan. The chitosan finish includes high absorbency properties, moisture control, non-allergic, non-toxic and biodegradable properties to textiles. The major problem of chitosan is its poor durability on textile fabrics due to its lack of strong bonding with fibre polymers (Martel et al 2002).

Pretreatment of 100% wool fabric or wool/nylon blended fabric with alkaline peroxide improves the adsorption of chitosan. The adsorbed chitosan increases the dyeing rate of wool, fastness property, wettability and shrink resistance (Pascual and Julia 2001). Jovancic et al (2001) found that a peroxide treatment followed by a protease treatment enhanced the adsorption of chitosan on wool. They described that alkaline peroxide bleaching generates new active sites on the wool surface (-SO$_3^-$) and protease treatment
modified the hydrophobic cuticle scales. The cationised chitosan forms strong ionic bonds with sulphonic acid groups and form uniform layer which confers shrink resistance. When wool is treated with chitosan, the charged chitosan spread on the surface of the wool fibre and acted as a predominant dyeing site, thus interacting with the dye and in later stages imparting the dye to the wool fibre in very short dyeing times. The adsorbed biopolymer acted as a predominant dyeing site, thus interacting with the dye molecules and in later stages imparting the dye into the wool fibre (Jocic et al 2005).

The enzymatic treatment enhances whiteness and confers shrink resistance to wool, but an increase in the enzyme concentration leads to a detrimental effect on the physio-mechanical properties. A chitosan pretreatment reduces the damage caused by the subsequent enzymatic treatment (Vilchez et al 2005).

Nurhan et al (2004) studied the effect of enzymatic treatment, bleaching treatment and polymer additive treatment on wool fabric both in separate and different successive forms. They observed that the protease treatment enhances chitosan adsorption on wool and also caused an increasing loss of tensile strength. Citric acid (CA) is used as a cross linking agent in fixing of chitosan by pad-dry-cure treatment on woolen fabrics. Citric acid produced esterification with the -OH group of the wool and chitosan and transamidation with the -NH₂ group of the permanganate oxidized wool and formed a crosslink. The surface crosslinks of the oxidized wool fibre are relatively coarse, which is undesirable for shrink-proofing and yet beneficial for the antimicrobial and antiseptic effects of the woolen fabrics. It had a negative effect on the fabric softness, yellowness, stretching resistance, and elongation percentage (Hsieh et al 2004).
There is no dependency of shrinkage of wool fabric on molecular weight or level of N-acetylation of applied chitosan, but the hydrophobic character of chitosan is increased through the incorporation of long-chain N-acyl groups and it gives improved antifelting behaviour, compared to chitosan itself, at the same level of add-on (Roberts and Wood 2001). Jeong et al (2002) inferred that chitosan finishing on wool fabrics increase the bending rigidity and the magnitude of the changes being dependent on the molecular weight of the chitosan and the decatizing conditions.

2.3.3.4 Plasma treatment

Plasma may be described as a mixture of electrons, ions and free radicals and is produced from an electrical discharge, either under vacuum or atmospheric pressure. Plasma treatments are applied to increase the wettability (surface energy) of a substrate and, in doing so, promote adhesion with whatever is subsequently applied. The effect of a plasma treatment on wool is much the same in that the wettability of the fibre is enhanced considerably, an effect which has implications for improved dyeing, printing and the subsequent application of a variety of different chemical treatments (Kan et al 1998b, Poll et al 2001).

When woolen materials in top or fabric form pretreated with glow discharge in presence of non-polymerising gases like air, oxygen and nitrogen, the outer surface of wool fibre (30-50 nm) modified due to plasma etching and surface oxidation. Polymer etching is responsible for the abrasion of the fatty acid layer from the cuticle and parts of the exocuticle-A, and surface oxidation introduces new anionic groups i.e. sulphonic and carboxylic acid groups. Carboxylate groups are derived from a backbone of the protein chains and sulphonate groups by oxidation of disulphide bonds in the cuticle cells. The hydrophilicity of the wool reduces the hydrophobic effect between
the fibres. A thin film of water can be built up on the fibres during washing, which separates them each other and decreasing the differential frictional effect and therefore diminishing the felt ability of wool (Hesse et al 1995).

The air plasma treatment of wool fabrics promotes the spreading and adhesion of the hydrophilic chitosan on wool fibres and produces a small physical cuticle surface change compare with oxygen plasma treatment (Erra et al 1999). Plasma treatments represent probably the most elegant approach to fibre modification for shrink-resist effects because they are surface specific, totally effluent free and thus environmentally friendly but have still to be commercially proven (Kim and Kang 2002).

2.3.4 Wool/cotton blends and their processing

Wool in various forms (scoured and carbonized stock, top, cut top, and stretch-broken top) has been blended with other fibres on the cotton system in four ways. Intimate blends have been produced by mixing the raw materials in the blow room, wool in the form of sliver and cotton in the form of lap have been blended at the card, slivers composed of different fibres have been blended at the draw frame using both conventional and slip drafting, and wool has been blended with cotton on the cotton spinning frame using a double reeling technique in which one roving bobbin contains wool and the other roving the cotton (Lupton et al 1984).

Adding small quantities of wool either cotton or other fibres improves aesthetic, drape and hand, and gives other characteristics that cannot be obtained using one fibre alone. Fabrics made from intimate blends of wool and cotton have many desirable attributes, in particular warmth, good moisture absorption properties and a soft handle (Rippon 1987). Inoue and Niwa (1997) inferred that wool/cotton plied yarn have high hygroscopicity,
high water absorption property and a low stress relaxation rate at high relative humidity. The tensile stress relaxation of the blend yarn is decreased as the wool content increases. A suiting material was woven from a 50/50 wool/cotton blend made from combed cotton and scoured wool fibres. The scoured wool was cleaned and shortened using the carding cleaner. A small amount of vegetable matter present in the greige fabric was removed in dyeing and finishing. The authors discussed the mechanical processing procedures of the blend and other pertinent fabric properties (Bel and Louis 1984).

Two grades (62’s and 80's) cut-top wool is intimately mixed with cotton at varying blend levels. Subsequently yarns are ring-spun using the short-staple system of mechanical processing and standard crepe fabrics were manufactured from each. They inferred that increasing the wool content of a fabric decreased its tensile properties. Cotton/wool fabrics containing 80’s wool however shrunk significantly more than their counterparts containing 63’s wool (Lupton et al 1984).

Wool/cotton blended fabric is bleached in presence of an activator called Warwick-T under mild condition and it gives an acceptable bleaching effect (Anon 1999). Wool/cotton blended fabrics of different blend composition are treated with both cellulase and protease enzymes at two different concentrations and conditions. The enzyme treatments reduce protruding fibres, improve their softness with tolerable loss in strength (Chikkodi et al 1995). Durable flame-retardant finishes based on a vinyl phosphonate oligomer or THPS was applied to cotton/wool and cotton/polyester/wool blended medium-weight twill fabrics by a pad-dry-cure process. Cotton/wool blend fabrics treated with THPS-urea-TMM had the best flame-retardant properties (Beninate et al 1981). The presence of cotton in the blend lowers the dry wrinkle recovery of wool/cotton blended fabric
compared to that of a wool fabric of similar weight. Pardo et al (1968) improved the dry wrinkle recovery of wool/cotton fabrics by treatment with crosslinking agents such as dimethyloldihydroxy ethylene urea (DMDHEU), with considerable losses in strength and abrasion resistance.

Ibrahim et al (2006) optimized a processing condition for anionic dyeing and easy-care finishing of wool/viscose (60/40) and wool/cotton (30/70) blended fabrics in a single-stage process and it is Fixapret-ECO-50 gpl, triethanol amine hydrochloride-20 gpl, ammonium persulfate-7.5 gpl. They are applied by pad-dry-cure method at 160°C for 3 minutes.. They found that the extent of improvement in both the depth of shade and easy-care properties is determined by the nature of substrate and follows the order as wool/viscose>cotton/wool. Beninate et al (1983) observed that the presence of wool in untreated twill fabrics containing cotton and wool caused burning rates to decrease and oxygen index values to increase as wool content increased in the blends. These effects were also observed in cotton/ wool blends treated with low levels of the THPS-urea-TMM flame retardant, but were less pronounced in fabrics treated at high levels.

Rippon (1987) stated that application of a mixture of a DMDHEU and the Synthappret BAP by a simple pad-dry-cure procedure on fabrics made from a range of intimate blends of wool and cotton, improve wrinkle recovery. He inferred that DMDHEU acts by increasing the resilience of the cotton fibres and Synthappret-BAP by reducing the frictional component of wrinkling that is due largely to the cotton in the blend. A simultaneous treatment with low levels of the reagents also controls shrinkage in laundering and improves the wet wrinkle recovery properties of the fabrics. Wasley and Pitman (1971) treated wool cotton blends (50/50) with mixed emulsion containing DMDHEU and 2% aziridinyl-adeprene L-100 polymer for permanent press effects. O’Connell et al (1968) also reported that excellent
durable press properties can be possessed by a combination of treatments consisting of wool shrink proofing and cellulose crosslinking. Harper and Metha (1985) applied DMDHEU and polymer finishing on cotton-wool (60/40) blends to impart durable-press finishing. The maximum DP rating was observed when 10% DMDHEU and 5% ethylene vinyl acetate copolymer mixture is applied. Singh and Yadav (1998) inferred that application of 5% acrylamide in presence of formaldehyde improves the retention of pleats in both all wool and cotton/wool blended fabrics.

Singh and Chaulkar (1992) inferred that application of acrylamide polymer in presence of formaldehyde improves the shrink-resistance and wrinkle recovery of both all wool and cotton/wool blended fabrics. Cardamone (1999) stated that fabrics made from intimate blend of unchlorinated wool and cotton is attained higher resistance to pilling when finished with soft acrylic resins combined with dimethyl siloxane, synthetic wax, glyoxal and melamine resin. Less pilling is observed when nylon is absent in the blend and chlorinated wool is taken. Stephan (1997) stated that fluorocarbon based finishing on wool blended fabrics imparted soil resistance finish.

2.3.5 Conclusion

Consumer across the globe demanding comfort, easy care, relaxed dressing and value for the money they spend. The various functional finishing like softening, antimicrobial finishing, water-repellent finishing etc., with suitable surface modification such as enzyme treatment, plasma treatment etc., on wool fibre and its allied products offer a wide scope for woolen processors to develop diversified woolen products by incorporating all aesthetic properties based on consumer demands.