Ecofriendly finishes for textiles

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The challenges facing the textile finishing industry have intensified during the last decade. Current awareness of the negative environmental impact of chemical processing of textiles, combined with increased strict legislation on industrial effluents, has led to the search for advanced, non-polluting processes for treating natural and manufactured fibre fabrics. In this paper, an overview of ecofriendly finishing treatments, which include formaldehyde-free finishes, enzymatic softening, use of silicones, low-temperature plasma and antimicrobial/antibacterial finishes, has been given. Application of breathable coatings has also been demonstrated.

Keywords: Antibacterial finishing, Enzymatic softening, Glyoxal, Moisture vapour permeable coatings, Plasma treatment, Polycarboxylic acids, Silicones

1 Introduction

Today, with the increasing awareness of environmental concerns, an important legislation on eco-toxicological considerations has been introduced. It is related to such important issues as health and safety during storage, application and use, and safe disposal of chemicals into landfill and water or release in air during chemical processing of textiles. These have imposed changes in chemical finishes and finishing methods. So, integrated pollution control is necessary for developing ecofriendly processes in this new millennium. The driving force in the recent technology has been the economy and ecology, and finishers are therefore trying to produce textiles more efficiently, with less water and less pollution.

In this paper, a comprehensive review of the various finishing treatments leading to wrinkle-free fabrics with good and soft handle through formaldehyde-free finishes, bio-finishing and breathable coatings is given. Developments in plasma treatment and antibacterial/antimicrobial finishes have also been highlighted.

2 Easy Care Finishes

2.1 Cotton

In the 1980s, the market for easy care and durable press finishes was dominated by N,N' -1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU), using magnesium chloride as the acid catalyst to initiate chemical crosslinking of cellulose chain molecules. Crosslinking occurred within the accessible regions (i.e. the amorphous regions of the fibre) providing an increase in the fibre resistance to deformation and improved elastic recovery from deformation.

One approach to limit the problems of formaldehyde release has been to use glyoxal-based derivatives such as 1,3-dimethyl-4,5-dihydroxyethylene urea (DHDMI). This is a zero formaldehyde based crosslinking agent for cotton that reacts through the ring hydroxyl groups in the 4,5-positions of cellulose. However, such derivatives are more expensive and somewhat less effective than DMDHEU at the same add-on level, possibly due to hydantoin formation, and hence more active curing systems are often required.

DHDMI imparts a moderate level of wrinkle resistance to cotton fabric in presence of MgCl₂, zinc nitrate or zinc fluoro borate as curing catalyst (Table 1). Zinc fluoro borate was by far the most effective curing catalyst in terms of wrinkle recovery angles observed before and after multiple launderings carried out on the DHDMI finished fabric. Zinc salt catalyst with DHDMI gives first order reaction whereas with magnesium salt, it gives zero order reaction. With zinc salts catalysis, the reactivity of the ring hydroxyl group is increased by the N-methyl substituents present in DHDMI.

The stability of DHDMI at room temperature makes it suitable for use in finishes that are to be postured some months after the fabric has been padded with the treating solutions and dried. The use of polymeric additives such as acrylate copolymers or crosslinkable silicones in 10% DHDMI formulations...
Table 1—Comparison of some formaldehyde-free DP finishing agents with DMDHEU

<table>
<thead>
<tr>
<th>Agent</th>
<th>Catalyst</th>
<th>DP rating</th>
<th>Wrinkle recovery angle deg</th>
<th>Tear strength retained %</th>
<th>Breaking strength retained %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHDMI</td>
<td>Zn(BF₂)₃</td>
<td>3.4</td>
<td>254-271</td>
<td>43-51</td>
<td>59-73</td>
</tr>
<tr>
<td></td>
<td>Zn(NO₃)₂</td>
<td>3.2-3.3</td>
<td>249-265</td>
<td>64</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>MgCl₂</td>
<td>2.8-3.3</td>
<td>227-247</td>
<td>62-66</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>MgCl₂-CA</td>
<td>2.5-3.0</td>
<td>241-244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTCA</td>
<td>Na₂H₂PO₄</td>
<td>4.0-4.7</td>
<td>285-300</td>
<td>51-67</td>
<td>49-59</td>
</tr>
<tr>
<td></td>
<td>Na₃HPO₃</td>
<td>4.0-4.2</td>
<td>286</td>
<td>63-66</td>
<td>59-72</td>
</tr>
<tr>
<td></td>
<td>Na₂H₂PO₄</td>
<td>3.5-4.4</td>
<td>282-304</td>
<td>51-59</td>
<td>50-55</td>
</tr>
<tr>
<td></td>
<td>Na₃HPO₄</td>
<td>4.0</td>
<td>267-285</td>
<td>65-73</td>
<td>55-76</td>
</tr>
<tr>
<td>CA</td>
<td>Na₂H₂PO₄</td>
<td>3.3-4.0</td>
<td>240-268</td>
<td>62</td>
<td>50-61</td>
</tr>
<tr>
<td></td>
<td>Mixed</td>
<td>3.8-4.0</td>
<td>247-264</td>
<td></td>
<td>55-64</td>
</tr>
<tr>
<td>DMDHEU</td>
<td>MgCl₂</td>
<td>4.3-4.8</td>
<td>261-280</td>
<td>49-57</td>
<td>44-60</td>
</tr>
</tbody>
</table>

DHDMI—1,3-dimethyl-4,5-dihydroxyethylene urea; BTCA—1,2,3,4-butanetetracarboxylic acid; and CA—citric acid.

produce a marked increase in DP performance. The moisture regain and affinity for CI Direct Red 81 shown by DHDMI-crosslinked cotton was same as for untreated cotton. But the affinity of the cotton for direct dyes is greatly decreased when cotton cellulose is crosslinked with conventional N-methylol agents.

An alternative approach has been based upon the use of glyoxal or polycarboxylic acids:

2.1.1 Glyoxal

Glyoxal⁷-⁹ in presence of an acid catalyst, such as boric acid, ammonium chloride and aluminium sulphate, on heating gives monoaetals and diacets of glyoxal with cellulose (Fig. 1). Free aldehyde groups present due to the single-ended attachment of glyoxal as in I in Fig. 1 were found to be removable by oxidation with chlorous acid or reduction with potassium borohydride. Since glyoxal molecule can form four linkages to cellulose, glyoxal may be regarded as tetrafunctional. Magnesium chloride was used as a catalyst in early studies for applying a very high glyoxal concentration (10% by wt.). In the absence of active hydrogen compounds as co-reactive additives, the fabric weight gain was only 1.4%. With active hydrogen compounds (alcohols, phenols, amides or thiols) as co-reactant, much higher fabric weight gain could be obtained. But problem with MgCl₂ is that it produces fabric yellowing and severe fabric strength loss. The use of aluminium sulphate as the curing catalyst leads to the high levels of wrinkle resistance. Excess of glyoxal appears to serve as a chelating agent and diluent for aluminium ions, thus moderating the tendency of the catalyst to degrade the cellulose.

2.1.2 Mild Cure Process

The addition of polyhydric alcohols in the pad bath results in low cure process with improved fabric whiteness and increased DP ratings. Alpha-hydroxy acid was added as catalyst activator to suppress the strength losses in treated cotton. This means the curing temperature for crosslinking could be lowered to 115-125°C. The order of effectiveness of various acid catalysts is as follows:

Succinic < lactic < malic < glycolic < citric < tartaric acid.

The extent to which a straight-chain glycol increased DP performance depended primarily on the molecular chain length of the glycol. The optimum length was approximately six atoms, excluding the terminal hydroxyl groups. The role of the glycol is as a crosslink modifier (product II in Fig. 1) which alters...
the polarity and flexibility of the three-dimensional crosslink network in cellulose. Performance of ethylene glycol (EG) and diethylene glycol (DEG) with respect to DP rating is shown in Table 2.

2.1.3 High-temperature Curing Processes

The advantage of high-temperature curing is that 15-60 s residence time of the fabric in the curing oven is sufficient to achieve cellulose crosslinking, and also to heat-set the polyester to final fabric dimensions in polyester/cotton blends. Aluminium chlorohydrate [Al₃(OH)₂Cl₂H₂O] appears to be effective as a high temperature (170°C) catalyst in presence of α-hydroxy acid.

A mixture of aluminium sulphate and magnesium sulphate has also been recommended as a non-yellowing catalyst for the application of glyoxal at temperatures such as 190-205°C in the presence of reactive siloxanes. A silanol-terminated silicone softener appeared to exert a synergistic effect with glyoxal and aluminium sulphate in improving the DP ratings. At a high level of DP performance, equal to that imparted by a conventional treatment with DMDHEU, the glyoxal-finished fabric had higher tearing strength and slightly lower breaking strength than the DMDHEU-treated 65:35 polyester/cotton fabric. A further process improvement consists in adding a buffer such as sodium carbonate to the formulation. This raises the pH of the final finished fabric sufficiently to eliminate the need for an afterwash to remove acidic catalysts.

In another study, glyoxal-glycol finish has been used at curing temperatures of 145-160°C on all-cotton fabrics. The catalyst was aluminium sulphate buffered with aluminium dihydroxycetate stabilized with boric acid. Curing periods of 15-20 s were sufficient to impart a high level of DP properties while using 1,6-hexanediol as the crosslink modifier. The addition of small amounts of phosphoric acid to the formulation was beneficial in preventing deactivation of the catalyst by fabrics containing traces of alkali left from the scouring operation. The effect of the buffer was to improve the fabric strength retention and whiteness obtained.

Rafai et al. 10 have reported the treatment of cotton fabric with glyoxal/starch or hydrolyzed starches/ MgCl₂·6H₂O catalyst/water system. Starch and hydrolyzed starches are used along with glyoxal with the possibility of their contribution in fabric resilience. It is believed that hydrolyzed starch may modify the crosslinking reactions and the structure of the crosslinks, thereby improve fabric resilience.

2.1.4 Inorganic Phosphates as Crosslinking Agents

The phosphorylation of cotton cellulose can be carried out by heat curing of fabric impregnated either with a 1:1 mixture of mono- or di-sodium phosphate or preferably sodium hexameta phosphate. When the phosphorus content of treated fabric exceeds 1.6%, the fibres are found to be insoluble in cupriehylenediamine hydroxide solution, and the cellulose appears to be crosslinked.

2 Cell-OH + NaH₂PO₄ → Cell-O-P(O) (ONa)-O-Cell

Crosslinking of cellulose fabric can also be achieved by phosphorylation with a mixture of urea and mono- or di-ammonium phosphate. A moderate level of DP along with flame retardant properties is imparted using pad-dry-cure method at a sufficiently high degree of phosphorylation. High levels (approx.12%) of monosodium or monoammonium phosphate and, in some instances, very high levels (12-24%) of urea are required.

2.1.5 Durable Press (DP) Finishing with Polycarboxylic Acids

Citric acid was found to be the most effective polycarboxylic acid, in the absence of added catalyst by pad-dry-cure treatment, although it produced more fabric discoloration than the other agents. The crosslinks

<p>| Table 2 — Comparison of ethylene glycol (EG) and diethylene glycol (DEG) as co-reactants for glyoxal in DP finishing of cotton at 125°C (ref. 7) |</p>
<table>
<thead>
<tr>
<th>EG conc. %</th>
<th>DEG conc. %</th>
<th>Mole ratio</th>
<th>Wt. add-on %</th>
<th>DP rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.5:1</td>
<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td>2.6</td>
<td>0</td>
<td>1:1</td>
<td>4.6</td>
<td>3.5</td>
</tr>
<tr>
<td>5.2</td>
<td>0</td>
<td>2:1</td>
<td>7.5</td>
<td>4.2</td>
</tr>
<tr>
<td>10.3</td>
<td>0</td>
<td>4:1</td>
<td>7.4</td>
<td>3.9</td>
</tr>
<tr>
<td>20.6</td>
<td>0</td>
<td>8:1</td>
<td>7.2</td>
<td>4.0</td>
</tr>
<tr>
<td>41.3</td>
<td>0</td>
<td>1:1</td>
<td>7.9</td>
<td>3.8</td>
</tr>
<tr>
<td>0</td>
<td>8.8</td>
<td>1:1</td>
<td>13.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0</td>
<td>17.7</td>
<td>2:1</td>
<td>17.0</td>
<td>4.5</td>
</tr>
<tr>
<td>5.2</td>
<td>4.4</td>
<td>1:0.5:1</td>
<td>10.1</td>
<td>4.1</td>
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<tr>
<td>5.2</td>
<td>8.8</td>
<td>1:1:1</td>
<td>13.2</td>
<td>4.4</td>
</tr>
<tr>
<td>5.2</td>
<td>13.3</td>
<td>1:1:1:1</td>
<td>15.6</td>
<td>4.4</td>
</tr>
<tr>
<td>5.2</td>
<td>17.7</td>
<td>1:2:1</td>
<td>16.1</td>
<td>4.5</td>
</tr>
</tbody>
</table>

4.8% glyoxal + either or both glycols, 0.77% Al₄(SO₄)₄·12H₂O + 0.37% tartaric acid + reactive silicone softener (1% solids) and water.
were formed in cellulose by acid-catalyzed esterification with citric acid itself, furnishing the protons needed for the autocatalysis.

Polycarboxylic acids with 4-6 carboxyl groups per molecule in the presence of alkaline catalysts were found to be more effective than with acids having only two or three carboxyl groups. Sodium carbonate or trimethyl amine was added as a catalyst. These salts act as buffers and greatly diminished acid-induced tendering during high temperature curing. The wrinkle-resistant finished fabrics obtained were recyclable. In the presence of heat, the transesterification of ester crosslinks by neighbouring cellulose hydroxyls causes the crosslinks to be mobile.

The newer catalysts which are more effective than sodium carbonate or tertiary amines are alkali metal salts of phosphorus containing minerals acids. The order of decreasing effectiveness is as follows:

\[ \text{NaH}_2\text{PO}_2 > \text{Na}_2\text{HPO}_3 = \text{NaH}_2\text{PO}_3 > \text{NaH}_3\text{PO}_4 > \text{Na}_2\text{H}_2\text{PO}_4 > \text{Na}_3\text{H}_2\text{PO}_6 = (\text{NaPO}_3)_6 > \text{Na}_2\text{HPO}_4 = \text{Na}_3\text{PO}_4 > \text{Na}_2\text{CO}_3 \]

Sodium hypophosphite is, however, most expensive. Thus, other catalysts are used in the mixture.

Welch and Peters\(^{14}\) have reported the use of sodium bromide as a co-catalyst for DP finishing of cotton fabrics with polycarboxylic acids which permits a decrease of as much as 75% in the amount of sodium hypophosphite required as a curing catalyst. This lowers the chemical costs and the amount of phosphorus compounds that need to be recovered from spent treating solutions which, in many states, cannot be disposed of in rivers or lakes. Tertiary alkanolamines and their phosphoric and metaphosphoric acid salts also help in decreasing the amount of hypophosphite catalyst needed\(^{14}\).

A feature of triethanolamine as a crosslink modifier is that it increases the strength and flex abrasion resistance retained by the fabric during DP treatment. In this respect, triethanolamine is superior to glycerol or pentaerythritol. The sodium salts of alpha-hydroxy polycarboxylic acids can serve as direct replacements for sodium hypophosphite or other phosphorus compounds as curing agents for 1,2,3,4-butane tetracarboxylic acid (BTCA).

In presence of weak bases as esterification catalyst, the reactions proceed by intermediate formation of cyclic anhydrides of BTCA (Fig. 2) as the actual esterifying agents\(^{16}\). Catalyst increases the rate of anhydride formation as well as the rate of crosslinking. It was found that loss of weight corresponds to water loss as anhydrides were formed on heating BTCA and cis-cyclopentanetetracarboxylic acid (CPTA).

Performance of various polycarboxylic acids has also been compared with conventional methyol derivatives as DP finishing agents with sodium hypophosphite catalysts. Most of these acids imparted high DP performance initially, as evidenced by DP ratings of 4.3-4.7 and conditioned wrinkle recovery angles of 285-300° (Table 1). However, the resulting finishes differed considerably in durability to alkaline laundering. The acids arranged in order of decreasing durability, together with the maximum number of machine washings and tumble drying cycles withstood, were as follows:

Butane tetracarboxylic acid > Mellitic = Tricarboxylic > Thiodisuccinic > Citric >>> Maleic > Succinic acid.

The tear strength retention was 60-68% with tri- or tetra-carboxylic acids compared to 54% for DMDHEU finished fabric. This is attributed to the buffering action of sodium hypophosphite catalyst and the absence of Lewis acid catalysts. Thus, BTCA

![Fig. 2 — Reaction of polycarboxylic acid with cellulose (ref. 16)](image_url)
is found to be the most effective of the polycarboxylic acids studied with respect to the level of DP performance, speed of curing, laundering durability, retention of fabric whiteness and free from odour. Recently, malic acid activated by BTCA or small amounts of BTCA with high concentrations of citric acid as a DP finishing agent have also been found to be very effective.

Saraf has reported the use of two commercial non-formaldehyde crosslinking agents, Natrium-NFO and Natrium-CRA, for cotton and polyester/cotton blends. At 15% Natrium-CRA bath concentration, the wrinkle recovery angle of cotton was found to be 240°C when cured at 170°C for 1 min.

### 2.1.6 Use of Functional Polymers

Efforts have been made to add chemically modified starch products to the crosslinking formulation in order to minimize the great loss in the tensile strength of the finished fabrics. In this context, poly(acrylonitrile)-starch graft copolymers based on hydrolyzed and oxidized starches were synthesized. The effect on fabric performance was found with DMDHEU. Crease recovery angles and tensile strength of the cotton fabric finished in the presence of polyacrylonitrile-starch graft copolymer based on hydrolyzed and oxidized starches increase by increasing the concentration of the grafted starch. However, dry crease recovery angle of cotton fabrics finished in the presence of grafted starch products was low.

### 2.2 Finishing of Jute with Glycols and Acrylic Acid

Jute fabric has been modified by using ethylene glycol (EG), diethylene glycol (DEG), polyethylene glycol (PEG-400 and PEG 1500) and polyvinyl alcohol (PVA) in the presence of Al$_2$(SO$_4$)$_3$ as the catalyst by pad-dry-cure technique. Treatments of oxy-jute (copper number 12.6) with 8% DEG in the presence of 5% Al$_2$(SO$_4$)$_3$ as the catalyst followed by drying at 95°C for 5 min and curing at 125°C for 5 min produced fabrics with 260° (W+F) wrinkle recovery, 3.2 cm bending length and improved flexibility. While 8% PEG 1500 produced fabrics with 238° WRA and improved effects in tenacity and elongation-at-break and hence in resilience. 

Ghosh & Das also reported the modification of jute fabrics using acrylic acid (AA) as a finishing agent in the presence of K$_2$S$_2$O$_8$ and Na$_3$PO$_4$ catalysts separately or in suitable combinations, employing pad-dry-cure technique. Treatment with 10% acrylic acid at 30°C and pH 7 produced optimum effects: a batching time of 45-60 min at 30°C followed by drying of the batched fabric at 95°C for 5 min and curing of the dried fabric at 140°C for 5 min produced jute fabrics with 238° (W+F) wrinkle recovery and 2.6 cm bending length while untreated jute fabric had 143° (W+F) wrinkle recovery and 3.8 cm bending length. Na$_3$PO$_4$ catalyst allowed esterification of AA with cellulose, hemicellulose and lignin constituents of jute, and K$_2$S$_2$O$_8$ catalyst facilitated radical polymerization of acrylic acid, leading to some degree of crosslinking of the polymer chain of jute.

### 2.3 Finishing of Silk Fabrics

Finishing of silk fabrics with a mixture of glyoxal and urethane compounds has been reported by Kawahara et al., for improving the crease recovery, drape and tear strength. In addition, good durability against ultraviolet rays and laundering has been demonstrated from glyoxal and urethane mixture finishing agent. Tsang and Dhirag have also given a brief account of various finishes used for silk fabrics. A non-formaldehyde crease-resistant finish for silk has been developed by using citric acid as a crosslinking agent. The finished silk had a dry wrinkle recovery angle of more than 280° compared to 265° for the untreated control. The finished fabric retained 84-98.5% of its breaking strength and there was an increase of 40-80% in its tear strength. The whiteness retention was about 65%.

Durable press finishing with BTCA produced excellent results. Both the dry and wet resiliency of finished silk were remarkably improved. The finished fabric had a dry wrinkle recovery angle (WRA) of 301-311° and wet WRA of 252-263° compared to 265° and 217° respectively for the untreated control. After 50 cycles of home laundering, almost all the finished fabrics retained a DP rating higher than 3.5 compared to 1.9 for the control which was washed once. The dyeing behaviour of crease-resistant silk finished with BTCA and citric acid has also been studied using acid, direct and cationic dyes. Whether dyed before or after finishing, the fabric had good dyeability with improved resilience.

A new easy-care finishing method for silk fabrics with epoxy resin EPTA has been introduced. Silk
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fabric was padded twice with 100g/L EPTA aqueous solution, dried at 40°C and then treated with 8 g/L Na₂CO₃ at 75°C for 15 min. The wet crease recovery angle was improved from 200° (untreated) to 282° after finishing. The breaking strength of finished silk increased by more than 10% and the whiteness decreased by about 2.8%. Finished silk fabrics have good laundering durability; after 20 cycles of home laundering, the wet resiliency retained was 95% of that of the unwashed fabrics durability.

Shiozaki and Tanaka have analyzed the reactivity of epoxide onto silk and demonstrated that the modifications with epoxide onto silk improve moisture absorption, chemical resistance, and wash and wear properties. The four epoxides used were glycidol, ethylene glycol diglycidyl ether, tolyl glycidyl ether and resorcinol diglycidyl ether. From the amino acid analysis of the silk treated with epoxides, it may be concluded that the epoxides react with the side chains of the silk fibroin, such as lysine, histidine, arginine and tyrosine, thereby suggesting that most of the weight gain due to the fibre treatment is distributed uniformly throughout the cross-section and does not occur near the fibre surface. They also reported that epoxides form crosslinks between the adjacent silk fibroin molecules and the hydrogen bonds between the hydroxyl groups of epoxide molecules attached to the side chains of the silk fibroin.

Chemical modification of silk fibres by graft copolymerization of vinyl monomers and by reaction of epoxides and dibasic acid anhydrides, for example phthalic, succinic and glutaric anhydride, have also been reported. The graft copolymerization reaction of vinyl monomers onto silk fibres may be achieved by various methods, such as radiation, chemical- or photo-induced initiation. The use of chemical redox systems in aqueous media has played a major role for both scientific and technological purposes. The study of photo-initiation systems has begun recently. Their primary advantage is that some properties of the grafted polymer are imparted to the fibrous substrate without seriously affecting its basic structure and morphology.

3 Role of Softeners in Wrinkle-free Garments

Durable press fabrics suffer decreased tensile strength, tear strength and abrasion resistance, and often have a stiff, harsh and uncomfortable feel. A quality fabric softener/lubricant will readily mitigate these deficiencies, adding value to a wrinkle-free garment. One function of a softener is to modify the hand or feel of a fabric to reach the desired effect. The softener must also lubricate the fibres to increase abrasion resistance and tear strength. The softener also functions as a sewing lubricant, as high needle speeds can generate enough heat to melt and fuse synthetic fibres. Sewing damage, such as broken or fused yarns, causes garments to be rejected by the customer.

There are four basic classes of softeners, viz. anionic, cationic, non-ionic and blended systems. The general characteristics of these softeners are discussed below in greater detail.

3.1 Anionic Softeners

The anionic softeners are generally sulphated or sulphonated compounds used primarily to lubricate yarns or fibres through processing. Generally, the anionic softeners are good lubricants, provide soft handle and show good stability to alkaline conditions. Most of them show good heat stability and some have good yellowing resistance. However, anionics tend to provide inferior softness compared to the cationics and non-ionics. Furthermore, they have limited durability to laundering or dry cleaning. The major limitation comes from their negative charge, which causes incompatibility in resin finishing baths and makes them most sensitive to water hardness and electrolytes.

3.2 Cationic Softeners

The cationic softeners are nitrogen containing compounds which include fatty amino amides, imidazolines, amino polysiloxanes and quaternaries. This class of softeners provides a very soft, silky hand and improves the antistatic properties of a fabric. They tend to improve strength properties, such as tear and abrasion, and the sewability of a textile, especially when a polyethylene softener is present in the system.

Cationic polyethylene softeners are effective in processing napped or raised pile fabrics where fibre-to-metal friction (μF/M) reduction is essential. In napping softeners, the cationic materials such as fatty amino amides and imidazolines are typically blended with an efficient polyethylene lubricant. Palmitic and stearic acid based saturated fatty groups are preferred to reduce yellowing and to avoid rancidity, which
may occur with oleic or tallow fatty acid types. To achieve maximum lubricity and strength properties, many formulations are made with a significant portion being polyethylene. Typically, a blend will contain 2 parts polyethylene lubricant to 1 part aminoamide or imidazoline. Cationic softeners, as a result of their positive charge, will be attracted to a cotton or synthetic fabric and can be readily exhausted from a long bath or a dyebath. They tend to be compatible with most resin finishes. However, the cationic softeners have a tendency to change the shade or affect the fastness of certain dyestuffs. The development of a fishy odour on a fabric can be another problem with certain systems.

3.3 Non-ionic Softeners

Non-ionics are the most widely used softeners which include polyethylenes, glycerides such as glycerol monostearate, ethoxylates such as ethoxylated castor wax, coconut oil, corn oil, and ethoxylated fatty alcohols and acids. The non-ionic softeners offer excellent compatibility in resin baths and are easy to mix into a formulation. They generally have little or no effect on the shade of dyed fabrics. Most are resistant to discoloration and yellowing.

3.4 Silicone Softeners

Silicones have been used as textile softeners since 1960. Initially, polydimethylsiloxane (PDMS) was used. But in the late 1970s, the introduction of aminofunctional polydimethylsiloxanes opened new dimensions for textile softening. They confer high lubricity to the fibres owing to their low surface energy. Methyl groups are the most important of the organic substituents used in commercial silicones, the vast majority of which are polydimethylsiloxanes (PDMS). Silicones have some unique properties including thermal/oxidative stability, low-temperature flow ability, low viscosity change with respect to temperature, high compressibility, low surface tension (spreadability), hydrophobicity, dielectric properties and low fire hazard.

Silicone softeners currently available can be classified into the following three groups (Fig. 3):

- Non-reactive silicone softeners
- Conventional reactive softeners
- Organo-functional silicone softeners.

3.4.1 Non-reactive Silicone Softeners

Non-reactive silicone softeners are based on polydimethylsiloxanes. The viscosities useful for textile applications are generally in the range of 10,000-12,500 centistoke. Polydimethylsiloxanes impart desirable properties to fabrics due to their flexible polymer backbone, stable bonds and low intermolecular forces. However, the softening effect is not very durable to washing since there are no reactive sites in the polydimethylsiloxane polymer.

3.4.2 Reactive Silicones

These are polydimethylsiloxane polymers modified with silane hydrogen or silanol functional groups. Two mixed polyorganosiloxanes are also made, e.g. poly(methyl hydrogen siloxane). Conventional reactive silicones form a crosslinked siloxane network on the fabric surface in the presence of water and an organometallic catalyst. The crosslinked polymers provide durable softeners better than PDMS. Silanol functional polymers are also the basis for silicone elastomers and textile finishes to improve hand and performance of durable press fabrics.

3.4.3 Organo-functional Silicones

Aminofunctional groups which are bound to polydimethylsiloxane backbone improve the orientation...
and substantivity of the silicon on the fibre. The improved orientation of aminofunctional silicones leads to an extremely soft hand, which is frequently described as ‘Supersoft’. In this, organo-reactive groups such as amines, epoxides and alcohols are introduced in the PDMS.

New Amino Functional Silicones: Amino group (primary to tertiary) in polydimethylsiloxanes was substituted. The structure of the amino group in PDMS is as under:

<table>
<thead>
<tr>
<th>Amino</th>
<th>Abbreviation</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>NH-methyl</td>
<td>-NH₂</td>
</tr>
<tr>
<td></td>
<td>NH-butyl</td>
<td>-NH-(CH₂)₃Me</td>
</tr>
<tr>
<td></td>
<td>NH-lauryl</td>
<td>-NH-(CH₂)₁₁Me</td>
</tr>
<tr>
<td></td>
<td>NH-cyclohexyl</td>
<td>-NH-C₆H₁₁</td>
</tr>
<tr>
<td>Tertiary</td>
<td></td>
<td>-NEt₂</td>
</tr>
</tbody>
</table>

On comparing the effects due to primary, secondary and tertiary amines, it is evident that whiteness, water absorbency and soil release improve with the increasing degree of substitution from primary to secondary to tertiary.

Improved whiteness arises from the chemical structure of the amino functional groups. The thermal yellowing is due to oxidative decomposition of the amino group, forming chromophoric groups. The degree of improvement in whiteness on changing from primary to tertiary amino groups parallels the slowing of thermal degradation, as the number of alkyl substituents increases. Only the silicones substituted with secondary amines show values as good as the silicones based on the amino ethyl and aminopropyl groups which have been commonly used so far. An optimal combination of treatment effects can be obtained with secondary aminofunctional silicones. All silicones substituted with secondary amines, except for the NH-butyl silicone, produce a soft hand that is similar to that produced by the usual NH-ethylene amine modified silicone. NH-ethylene amine substituted silicones have a relatively strong water repellent effect. This effect is lower for silicones substituted with secondary amines. Differences in soil release properties are minimal between the silicones with secondary amine substituents.

Czech et al. demonstrated the effect of “Magnasoft TA-15” additive (which is based on dialkyl oxalate) on yellowing properties of amino modified silicone softeners. This chemical modification results in the formation of a stable emulsion of amide modified silicone with non-yellowing attributes and a distinguishable change in softening properties. In addition, aminosilicone emulsion modified with TA-15 exhibits film forming and elastomeric properties. A new product Magnasoft Plus (amino-silicone) and polydimethylsiloxane-aminopolyalkylene oxide block copolymer, provides good softness along with soil release on polyester/cotton blends. Magnasoft HSSD with both pendant alkyl amine and polyether based polydimethylsiloxane terpolymer has been evaluated as a softener for soil release on wrinkle-free garments in conjunction with fluorocarbon soil release agents.

Softeners for terry towels available in the market are classified on the basis of their durability as permanent hydrophilic and semi-durable hydrophilic.

Permanent hydrophilic: These softeners are usually organo-modified silicones. These products offer an excellent handle along with hydrophilicity, which can last for the lifetime of the fabric (15-20 washes).

Semi-durable hydrophilic: Softeners classified under this category are normally a combination of silicone and cationic components. Towels finished with such softeners sometimes specify that it will show improved hydrophilicity after one wash. These softeners offer an adequate-to-excellent handle and low hydrophilicity.

Resil Chemicals²² have introduced a range of silicone products, for example RESIL Hydra range is a new generation of softeners catering to the special requirements of a terry towel finish—excellent hydrophilicity, soft fluffy handle, durability and non-yellowing—leaving the towels look fresh wash after wash.

Silicones have also been used to improve the all-round properties of silk fabrics. Table 3 shows the results of the crease recovery properties of silicone finished fabrics. It is observed that the recovery angle is high in amino silicone compared to fatty amide, polysiloxanes and silicone softeners. The improved recovery angle is because amino silicones are crosslinked with the fibre. The recovery properties of the silicone finished fabrics after washing does not show any marked difference in the recovery angle.

Shenai⁴⁴ used non-ionic surfactants with considerable water solubility made from the mixed type of poly(organo-siloxanes). A very useful
Table 3—Effect of silicone finishes on silk fabrics

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Crease recovery angle deg</th>
<th>Bending length cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Warp</td>
<td>Weft</td>
</tr>
<tr>
<td>Untreated</td>
<td>79</td>
<td>66</td>
</tr>
<tr>
<td>Fatty amides silicones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%</td>
<td>83</td>
<td>94</td>
</tr>
<tr>
<td>4%</td>
<td>86</td>
<td>96</td>
</tr>
<tr>
<td>5%</td>
<td>89</td>
<td>99</td>
</tr>
<tr>
<td>Amino silicones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%</td>
<td>91</td>
<td>100</td>
</tr>
<tr>
<td>4%</td>
<td>93</td>
<td>105</td>
</tr>
<tr>
<td>5%</td>
<td>95</td>
<td>108</td>
</tr>
<tr>
<td>Amino-epoxy silicones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%</td>
<td>91</td>
<td>104</td>
</tr>
<tr>
<td>4%</td>
<td>95</td>
<td>108</td>
</tr>
<tr>
<td>5%</td>
<td>97</td>
<td>113</td>
</tr>
<tr>
<td>Reactive polysiloxane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>92</td>
<td>100</td>
</tr>
<tr>
<td>3%</td>
<td>93</td>
<td>104</td>
</tr>
<tr>
<td>4%</td>
<td>95</td>
<td>107</td>
</tr>
<tr>
<td>Polysiloxane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>89</td>
<td>101</td>
</tr>
<tr>
<td>2%</td>
<td>91</td>
<td>103</td>
</tr>
<tr>
<td>3%</td>
<td>94</td>
<td>109</td>
</tr>
<tr>
<td>Softener based on micro-emulsion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3%</td>
<td>87</td>
<td>97</td>
</tr>
<tr>
<td>4%</td>
<td>87</td>
<td>98</td>
</tr>
<tr>
<td>Organic functional silicone elastomer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td>92</td>
<td>101</td>
</tr>
<tr>
<td>5%</td>
<td>98</td>
<td>109</td>
</tr>
</tbody>
</table>

In the environment, there is no evidence that silicones adversely affect eco-systems nor has there been any experience of toxic or mutagenic effects on animals or aquatic life. PDMS is ecologically inert and has been found to have no effect on aerobic or anaerobic bacteria. It does not inhibit the biological process by which waste water is treated. Silicones are a minor part of the waste water discharged. They are highly resistant to biodegradation by micro-organisms, but they undergo very effective degradation via natural chemical processing and PDMS breaks down into lower molecular weight silanol. No adverse effects were seen for seed germination. Their molecular size prevents them from passing through the biological membranes of fish or other animals. PDMS fluids exhibit insignificant biological oxygen demand (BOD). Thus, the new aminofunctional silicone softeners have many advantages over initial PDMS like low yellowness, high softness, require low concentration and environmentally safe. In addition, they have the ability to blend with other organic softeners while retaining their original performance.

3.4.4 Environmental Consideration for Silicone-based Softeners

In the environment, there is no evidence that silicones adversely affect eco-systems nor has there been any experience of toxic or mutagenic effects on animals or aquatic life. PDMS is ecologically inert and has been found to have no effect on aerobic or anaerobic bacteria. It does not inhibit the biological process by which waste water is treated. Silicones are a minor part of the waste water discharged. They are highly resistant to biodegradation by micro-organisms, but they undergo very effective degradation via natural chemical processing and PDMS breaks down into lower molecular weight silanol. No adverse effects were seen for seed germination. Their molecular size prevents them from passing through the biological membranes of fish or other animals. PDMS fluids exhibit insignificant biological oxygen demand (BOD). Thus, the new aminofunctional silicone softeners have many advantages over initial PDMS like low yellowness, high softness, require low concentration and environmentally safe. In addition, they have the ability to blend with other organic softeners while retaining their original performance.

4 Biofinishing

Processing of cellulosic fabrics and garments with cellulase enzymes, generally referred to as biofinishing, started in the late 1980s. Superior hand and novelty finishes on rayon, linen and cotton knits can be achieved with cellulases.

Cellulases are multi-component enzyme systems commonly produced by soil-dwelling fungi and bacteria. The most important organisms are Trichoderma, Penicillium and Fusarium. Cellulases consist of at least three enzyme systems working synergistically together as illustrated in Fig.4. Endoglucanases or endocellulases hydrolyse cellulose randomly along the chains, preferentially the amorphous region. Celllobiohydrolases or exocellulase attack the chain ends and produce primarily celllobiose coupled with the binding domains associated with the enzyme. The celllobiose and any small chain oligomers produced by exo-cellulases are then hydrolysed by the third enzyme β-4-glucosidase into glucose.
Enzymes are active at atmospheric pressure in the temperature range of 30-60°C. Based on their sensitivity to pH, they are classified as:

- Acid stable (pH 4.5-5.5)
- Neutral (pH 6.6-7)
- Alkali stable (pH 9-10)

Biofinishing consists of a cellulase enzyme treatment to give a partial hydrolysis of cotton fibre, with a weight loss of around 3-5% and strength loss of 2-7%. However, Kumar et al.\textsuperscript{54} have reported the strength loss (25-30%) of cotton knit and viscose rayon for high surface polishing under acidic conditions at 60°C. With proper control of pH and temperature, standard whole acid cellulases can be used to finish delicate cellulose fabrics (Fig. 5).

The effect of existing dyes and the crosslinking agent on the reactivity of cellulase has been studied in depth. It seems that the planar structure of vat dyes with larger molecular sizes than indigo dye plays an important role in inhibiting the action of cellulase. Cotton/wool blends (90:10 and 70:30) have also been treated with both cellulase and protease enzymes at two different concentrations for improving the surface properties.

Enzymatic softening of cotton and cotton blend fabrics results in:

- less fuzz and pilling,
- better fabric feel,
- increased gloss or lustre, and
- increased durable softness.

In the case of knitted goods, this treatment is highly recommended because of tension-free processing conditions along with agitation coupled with abrasion of the garment to obtain the most effective enzymatic treatment.

The effect of enzymatic treatment on woollen fabrics has also been studied by Pant and Taya\textsuperscript{55}. Bending length of wool decreased when the concentration of enzymes was increased. Protosol caused comparatively less decrease in stiffness than the other two enzymes. Thus, the fabric became soft and supple after treatment with enzymes. Crease recovery angle of fabric increased on increasing the concentration of enzymes. Maximum improvement in crease recovery was found when fabric was treated with trypsin and degummmase enzymes whereas protosol caused comparatively less increase in crease recovery. Thus, the crease recovery property of wool fabric improved when the fabric was treated with enzymes. As the concentration of protosol was increased, great loss in tearing strength of wool fabric was observed. When the fabric was treated with degummmase, there was some loss in strength but it was not as severe as in case of protosol-treated sample. Trypsin also reduced the strength of wool fabric, but it was slightly more as compared to that in case of degummmase.

In another study\textsuperscript{56}, cotton and wool fabrics were treated with low-temperature oxygen plasma or enzymes or both for studying their mechanical and dyeing properties. Plasma pretreatment of wool caused an increase in strength and a higher rate of weight loss in the subsequent protease treatment. When the wool was dyed with a levelling acid dye, the equilibrium dye uptake did not change with plasma or protease pretreatment, but the dying rate increased with the plasma pretreatment. However, with a milling acid dye, both increased greatly in the following order:


From these results, it was assumed that plasma attacks the surface of the fibre while the enzyme affects mainly the inner part of the fibres.

Shrink-resistance properties of wool treated with serine proteinase Bactosol SI have also been investigated\textsuperscript{57}. The independent variables were the concentration of Bactosol SI and the pH of the treatment bath. The percentage area shrinkage, degree of whiteness, loss of weight, and ball-penetration-resistance loss were the responses. The results showed that the enzyme concentration and the pH value of the treatment bath had a large influence on reducing the wool shrinkage and on the degree of whiteness. The treatment time also had a marked influence, mainly on the mechanical properties of the knitted wool fabric.
Enzymatic hydrolysis to improve wetting and absorbency of polyester fabrics has also been reported by Hsieh and Cram. Six hydrolyzing enzymes (Table 4) to improve the hydrophilicity of several polyester fabrics were used. Five of the six lipases improve the water wetting and absorbent properties of regular polyester fabrics more than the alkaline hydrolysis under optimal conditions (3N NaOH at 55°C for 2 h). Compared to aqueous hydrolysis, the enzyme reactions are highly effective under more moderate conditions, including a relatively low concentration (0.01 g/L), a shorter reaction time (10 min), ambient temperature of 25°C and no buffer. Improved water wettability is accompanied by full strength retention compared to the significantly reduced strength and mass due to alkaline hydrolysis. Interestingly, the wetting and absorbent properties of sulphonated polyester and microdenier polyester fabrics are also improved by lipase.

4.1 Finishing of Lyocell

A concern encountered with use of lyocell fibres has been the fibrillation of fibre surfaces under mechanical stress or when swollen with water. They have a tendency to fibrillate because of the high orientation and lack of lateral cohesion. If controlled, this fibrillation can provide a soft finish for lyocell fabrics, but under continued laundering the fibrillation will become worse and may adversely affect the appearance and hand of a textile material. Fibre processing parameters can, therefore, be adapted to minimize the fibrillation problem in the spun fibres. Fibre-reactive dyes, crosslinking resins and enzyme treatments have been investigated as methods for reducing the degree of fibrillation in lyocell fabrics.

In one of the process, the fabric samples were enzyme treated with a commercial whole cellulase in a Launder-O-meter machine at 50°C for 60 min, both with and without steel balls for agitation. The liquor-to-fabric ratio was 20:1 and an acetate buffer was used to maintain the pH at 4.8. A buffer control with no enzyme was run in addition to three enzyme concentrations (1.05, 5.31 and 16.04%). Enzyme-treated fabrics showed minimal fibrillation compared to those submitted to simulated laundering conditions without enzymes. Neither enzyme concentration nor agitation affected the low-stress mechanical properties but did influence the tensile properties. The lowest enzyme concentration was less detrimental to the tensile properties, while inhibiting fibrillation.

Production trials and monitoring in garment processing facilities have shown that fabric breakdown is significantly reduced when engineered component cellulases are used as compared to conventional whole cellulases. This is particularly evident on delicate fabrics and lyocell blends. Process conditions used were: liquor ratio of 10:1, pH 5.0, treatment temperature of 58°C and treatment time of 45-60 min. The enzyme dosages were adjusted to achieve a high degree of defibrillation. On 100% lyocell, the handle attributes of the engineered component cellulases treatments were assessed higher than that of the whole cellulase, but the differences were small at the dosages tested. Much clearer differences were seen in the lyocell/cotton and lyocell/linen blends. The panelists consistently rated treatments by engineered component cellulases as softer and bulkier compared to the whole cellulase, irrespective of the dosages. This suggests that hand preference may be directly related to the composition of the enzymes and not to the enzyme dosage. These three enzyme compositions influenced the fabric hand properties differently due to the possible differences in their mode of action.

5 Plasma Treatment

The application of the plasma treatment has been demonstrated for the surface modification of various textiles. A lot of environmental and production problems can be solved by using a non-equilibrium low-temperature plasma. The plasma processes are dry ones and do not require water or non-aqueous solution. Promising applications of gas discharge plasma for the activation of chemical reactions in liquids have also been reported.

<table>
<thead>
<tr>
<th>Lipase</th>
<th>Supplier or manufacturer</th>
<th>Source</th>
<th>Form</th>
<th>Activity</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ICN</td>
<td>Hog pancreas</td>
<td>Powder</td>
<td>30.8 units/mg</td>
<td>2.8% moisture, 0.9% fat</td>
</tr>
<tr>
<td>B</td>
<td>ICN</td>
<td>Porcine pancreas</td>
<td>Powder</td>
<td>16 units/mg</td>
<td>Diastase-free 12% protein</td>
</tr>
<tr>
<td>C</td>
<td>Sigma</td>
<td>Wheat germ</td>
<td>Powder</td>
<td>7.6 units/mg</td>
<td>95% protein</td>
</tr>
<tr>
<td>D</td>
<td>Sigma</td>
<td>Candida rugosa</td>
<td>Powder</td>
<td>250,000 units/mg</td>
<td>95% protein</td>
</tr>
<tr>
<td>E</td>
<td>Geneencor International</td>
<td>Pseudomonas mendocina</td>
<td>Liquid</td>
<td>250,000 units</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>F</td>
<td>Novo Nordisk</td>
<td>Aspergillus oryzae</td>
<td>Liquid</td>
<td>100,000 units</td>
<td>&gt;90%</td>
</tr>
</tbody>
</table>
The plasma technique is based on ionised gases produced by electrical discharges. In fact, the coupling of electromagnetic power into a process gas generates the plasma medium comprising a dynamic mixture of ions, electrons, neutrons, protons, free radicals and metastable excited species which enable a variety of surface processes, e.g. surface activation for creating reactive etching, dissociation of surface contaminants (scouring/bleaching) and deposition of coatings for specific applications. In all, the plasma treatment is a highly surface specific of the material (<1000 Å) which does not affect the bulk properties. The mean depth of plasma active species action in polymers\textsuperscript{63} is given in Table 5.

Depending on the gas pressure, two significantly different forms of discharges are known:

**Corona Discharge:**
- generated at gas pressures equal to atmospheric pressure
- electromagnetic field at > 15 kV
- frequency range of 20-40 kHz

**Glow Discharge:**
- generated at gas pressure in the 0.1-10 MPa range
- electromagnetic field in the 0.4-8.0 kV range
- broad frequency range of 0 – 2.45 GHz.

Strictly speaking, both forms should be regarded as a source of low-temperature plasma. In industrial applications, a steady-state glow discharge capable of operating at one atmosphere would allow many plasma-related surface modification processes to be done on the production line, rather than in expensive vacuum systems that force batch processing.

Different gases can be used to achieve specific chemical modifications to the textile surfaces. Properties enhanced include wettability, adhesion, crosslinking, biocompatibility, protection and anti-wear, and chemical affinity or inertness\textsuperscript{64,67}. Relative free-radical intensity of the plasma-treated fibres, measured by ESR, increases in the following order:

Cotton > Wool > Silk > Nylon 6 ≡ PET

The natural fibres, especially cotton and linen, showed larger free-radical intensity than the regenerated cellulose and synthetic fibres.

The *in-situ* plasma polymerization for grafting of polymers onto the textile surface has also received considerable attention for improving wettability. Chemical grafting with various monomers onto plasma-activated surface of celluloses and other fibres has been reported for accomplishing specific properties.

### 5.1 Shrinkproofing of Wool\textsuperscript{68-74}

The most important factor for the renewed interest in plasma technology came in 1987 from the new legislation in Germany restricting the concentration of AOX compounds in the discharged effluents to 0.5 mg/L. The glow discharge treatment of wool in non-polymerizing gases like air, oxygen and nitrogen provides hydrophillicity of the fibre surface and has an excellent shrinkproofing effect in combination with ecofriendly resin. The new zero-AOX shrinkproofing treatment consists of oxidative step and subsequent application of a new resin based on collagen proteins\textsuperscript{68} which are crosslinked with the fibre surface by means of trifunctional epoxy Araldit PT 810 and glycidyl acrylate. Almost complete shrink resistance of wool fabric and top is accomplished using the collagen/Araldit resin with plasma pre-treated material (Fig. 6).

Wakida \textit{et al.}\textsuperscript{69}, Kan \textit{et al.}\textsuperscript{70,72} and Rakowski\textsuperscript{71} have also made in-depth studies on the shrinkproofing, dyeing and printing of plasma-treated wool. Wool and poly(ethylene terephthalate) fabrics and film were treated with low-temperature plasmas of helium/argon or acetone/argon\textsuperscript{69} under atmospheric pressure (Fig. 7) for 10-180 s. Although argon itself cannot independently generate a plasma under atmospheric pressure by applying high frequency voltage, it is easily generated by adding a small quantity of helium or acetone to argon gas. Wettability values of wool and PET fabrics treated with the plasmas under atmospheric pressure are shown in Table 6. The helium/argon plasma treatment was much more effective in increasing the
Untreated reference
P: Plasma-treated
C: Caroat-treated fabric
CAC: Carnal-treated fabric after application of the araldit/collagen resin
RAC: Plasma-treated fabric after application of the araldit/collagen resin

Table 6 -- Effects of low-temperature plasma treatment under atmospheric pressure on water penetration of PET and wool fabrics.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Time of water penetration s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>&gt;3600</td>
</tr>
<tr>
<td>Acetone/argon plasma</td>
<td></td>
</tr>
<tr>
<td>10 s</td>
<td>1167</td>
</tr>
<tr>
<td>30 s</td>
<td>285</td>
</tr>
<tr>
<td>60 s</td>
<td>173</td>
</tr>
<tr>
<td>180 s</td>
<td>24</td>
</tr>
<tr>
<td>Helium/argon plasma</td>
<td></td>
</tr>
<tr>
<td>10 s</td>
<td>240</td>
</tr>
<tr>
<td>30 s</td>
<td>94</td>
</tr>
<tr>
<td>60 s</td>
<td>60</td>
</tr>
<tr>
<td>0 s</td>
<td>20</td>
</tr>
<tr>
<td>Wool</td>
<td></td>
</tr>
<tr>
<td>Untreated</td>
<td>&gt;3600</td>
</tr>
<tr>
<td>Acetone/argon plasma</td>
<td></td>
</tr>
<tr>
<td>10 s</td>
<td>&gt;2400</td>
</tr>
<tr>
<td>30 s</td>
<td>2000</td>
</tr>
<tr>
<td>60 s</td>
<td>900</td>
</tr>
<tr>
<td>180 s</td>
<td>60</td>
</tr>
<tr>
<td>Helium/argon plasma</td>
<td></td>
</tr>
<tr>
<td>10 s</td>
<td>&gt;1800</td>
</tr>
<tr>
<td>30 s</td>
<td>150</td>
</tr>
<tr>
<td>60 s</td>
<td>10</td>
</tr>
<tr>
<td>180 s</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

The density (D) of the felting balls reveal that the D

became wet very quickly. It is, therefore, assumed that the surface structures of wool treated with both plasmas are somewhat different. Probably, the helium/argon plasma etches the fibre surface, whereas the acetone/argon plasma causes polymerization of acetone and produces hydrophilic polymer deposits on the fibre surface. Kan et al. have also demonstrated the application of three non-polymerizing gases—oxygen, nitrogen and a mixture of 25% hydrogen/75% nitrogen gas—through low-temperature plasma treatment. The results of \( \mu_0 \), \( \mu_w \), and DFE are shown in Table 7. The \( \mu_0 \) and \( \mu_w \) values of the low-temperature plasma (LTP) treated wool fabrics increased, but the DFE values decreased. The increased \( \mu_0 \) and \( \mu_w \) values are probably due to the LTP etching on the fibre surface, resulting in surface roughness and hence altering the coefficient of friction of the fibre. The reduction in DFE is regarded as a factor in lowering the felting tendency of wool.
values of the LTP-treated samples are much lower. The PN and PM treatments show the same decrease in D values, which is better than the PO treatment. These changes are the same as observed in DFE results, which confirm that the DFE and the ball felting are related to each other. Based on the results of \( \mu \) values and DFE, it may be concluded that the nitrogen plasma and gas mixture plasma impart similar anti-felting effects to wool fibres and that their effects are slightly better than the influence of oxygen.

Ryu et al.\textsuperscript{73} used corona discharge for surface modification of wool fibres and fabrics. An electron spectroscopy for chemical analysis (ESCA) was done to elucidate the changes in chemical composition on the fibre surface. The corona discharge incorporates oxygen atoms into the fibre and increases wettability and laundry-shrink resistance of wool fabrics, but the effects are smaller than those from low-temperature oxygen plasma. It may thus be concluded that the plasma treatment is a good alternative to chlorination pretreatment in Hercosett process of shrinkproofing of wool.

The effect of glow-discharge polymer treatments on the shrinkage behaviour and physical properties of wool fabric has been studied by Zuchairah et al.\textsuperscript{74} In this work, four different polymer systems, viz. Basolan SW (cationic polyether in isopropanol solution, BASF), Basolan MW (weakly cationic aminofunctional polysiloxane microemulsion, BASF), Polymer G (cationic amide-type resin in aqueous solution plus polyethylene wax emulsion as softener), and Polymer PL (cationic acrylic copolymer in aqueous solution, ICI Steleco), are applied onto plasma-treated wool fabric to enhance the degree of shrink resistance. The level of shrink resistance varies significantly with plasma polymer treatments, depending on the kind of polymer systems applied, with Polymers PL and G conferring excellent shrink resistance even for very short plasma pretreatment times of 2 min. The extent of weight loss during washing is also minimized for all plasma-polymer applications relative to polymer-only or chlorinated-polymer treated wool.

5.2 Surface Modification of PET and Polypropylene Fibres

Tsai et al.\textsuperscript{75} have reported some encouraging results from the plasma surface treatment of polypropylene meltblown nonwovens in the UTK one-atmosphere glow discharge plasma reactor. This reactor generates a large volume (up to 2.4 litres), low power (less than 150 watts), and uniform glow discharge plasma in a parallel plate configuration with oval electrodes of 231 cm\(^2\) face area, the lower electrode being covered with a 3.2 mm thick insulating Pyrex surface. The plates are set up in an enclosed box that makes it possible to control the working gas used, and the spacing between the plates can be varied. This reactor is energized by a custom-made high impedance kilohertz power supply capable of supplying up to 5 kilowatts of kilohertz power at RMS voltages up to 10 kV, and over a frequency range of 1-200 kHz.

Tsai et al.\textsuperscript{75} used two groups of working gases, CO\(_2\) and CO\(_2\)+O\(_2\), to treat the webs of PP at different electrical and temperature conditions. Using CO\(_2\) alone at a driving frequency less than 2 kHz would not make the webs wettable, while using the mixture of CO\(_2\)+O\(_2\) as working gas could make the webs wettable if treated at low temperature for 1 min (Table 8).

Shishoo\textsuperscript{76} and Sarmadi et al.\textsuperscript{77} also reported the increase in surface energy for PP and PET samples after plasma treatment, confirming the presence of polar groups on the polymer surface and thereby decreasing the contact angle. Such low-temperature, low-pressure plasma treatment is effective in inducing polarity at the surface vis-à-vis hydrophilic surface layer. Thus, it can reduce the high consumption of chemical wetting agents normally required in chemical processing of textiles.

Grafting of PP fabrics under AN-RF plasma was carried out using ground pressure of 0.05 mm Hg, 0.3 mm Hg pressure in the reactor and 60W and 100W RF power. Reaction time was varied between 30 s and 5 min.\textsuperscript{77} In polypropylene, the plasma is generated by inductive coupling in a tubular shaped argon container and needle valve system permitted acrylonitrile (AN)
to flow into the reaction vessel. The vapour pressure of the AN is above the operational reactor pressure and consequently the monomer is easily fed in gas form to the reaction chamber under vacuum.

PAN surface grafted PP fabrics exhibited improved water absorption and dyeing properties due to the presence of nitrogen and carbon based unsaturated linkages and formation of second generation -C=O groups. Efficient grafting takes place even in short treatment times.

Reactive amine group implantation on polymer surface by cold plasma reactions also represents one of the possibilities for surface functionalization. One approach for attaching reactive amine groups is to use ammonia plasma. Carbaugh et al. have studied the plasma decomposition of ammonia and have proposed the following mechanism:

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH} + \text{H} & \ldots (1) \\
\text{H} + \text{NH}_3 & \rightarrow \text{NH}_2 + \text{H}_2 & \ldots (2) \\
\text{H}_2 & \rightarrow 2\text{H} & \ldots (3) \\
2 \text{NH}_2 & \rightarrow \text{NH} + \text{NH}_3 & \ldots (4) \\
2 \text{NH}_2 & \rightarrow \text{N}_2\text{H}_4 & \ldots (5) \\
2 : \text{NH} & \rightarrow \text{N}_2 + \text{H}_2 & \ldots (6)
\end{align*}
\]

It is suggested that the primary amine radicals are most likely the entities to dominate the reaction mechanisms and combine with surface radicals. However, because of the coexistence of a significant number of mono- and multi-radical species and various reaction possibilities in the plasma state, the molecular fragments other than NH\textsubscript{2} can also predominate under certain experimental conditions. Others have also reported that ammonia plasmas do not produce primary amine efficiently, and consequently saturated and unsaturated amines have been proposed in order to create reactive surface amine groups.

5.3 Water Repellency and Surface Dyeing of Polyester Fabrics

Polyester fabrics\(^1\) have also been successfully treated with \(\text{O}_2\) or \(\text{CF}_4\) plasma under different power, pressure and time conditions. Electron spectroscopy for chemical analysis (ESCA) clearly indicated the surface oxidation and fluoridation. Oxygen plasma treatment improved both water uptake and surface dyeability, while \(\text{CF}_4\) plasma treatment improved water repellency along with improved surface dyeability with C.I. Basic Blue 3.

Unexpected surface dyeability with a basic dye and water repellency effects onto \(\text{CF}_4\) plasma treated PET fabrics have been related to intense fluoridation leading to teflon-like surface and simultaneous unsaturated bonds and trapped free radicals. The mechanism of the reactions for two types of gases, \(\text{O}_2\) and \(\text{CF}_4\), in the discharge system is as follows:

In \(\text{O}_2\), a mixture of active oxygen species is produced in the discharge chamber. Some of the reactions which are believed to occur are:

\[
\begin{align*}
\text{O}_2 & \rightarrow \text{O} + \text{O} & \ldots (7) \\
\text{O} + \text{O} & \rightarrow \text{O}_2 & \ldots (8) \\
\text{O}_2, & \rightarrow \text{O}_2 + \text{hv} & \ldots (9)
\end{align*}
\]
CF₄ dissociates in the first step according to the following equation:

\[
\text{CF}_4 \rightarrow \text{CF}_3 + F
\]  

(10)

In the presence of an organic polymer surface, these radicals will result in surface fluorination:

\[
\text{RH} + F \rightarrow -\text{RF} + H
\]  

(11)

\[
\text{R} + \text{CF}_3 \rightarrow -\text{RCF}_3 + H
\]  

(12)

\[
\text{R} + \text{CF}_3 \rightarrow -\text{RCF}_3 + F
\]  

(13)

\[
\text{R}_n + R_m \rightarrow \text{R}_n \text{R}_m
\]  

(14)

Surface fluorination as shown in Eq.12 or fluorocarbon grafting can occur by mechanism of chain transfer from a radical of CF₄ to the activated fibre. Plasma-induced surface structure modifications were monitored by photoelectron spectroscopy and electron spectroscopy for chemical analysis (ESCA). A high oxygen to carbon (O/C) indicate hydrophilicity, and higher fluorine to carbon (F/C) atomic ratio values of plasma-treated fabrics indicate hydrophobicity.

In another study, Oktem et al. reported the modification of polyester fibres by in-situ plasma or post-plasma polymerization of acrylic acid. Fabrics were directly treated in acrylic acid plasma in one set of experiments, while in the other set of experiments, they were first treated in argon plasma and then immersed in an aqueous acrylic acid bath. The second method resulted in better dyeability and soil repellency in contrast to lower surface wettability.

Anti-soiling of polyester was also achieved by direct current and radio frequency plasma treatment of different durations. The soil repellency increased with the increasing duration of treatment.

Cold plasma treatment of polyester fabric in presence of several volatile monomers containing flame retardant was studied. It is interesting to note that oxygen index values for all plasma-treated samples was found to be somewhat less than that of virgin material (Table 9). However, the burning rates were found to decrease considerably, specifically in hexamethyldisiloxane (HMDS) plasma-treated fabrics (Fig. 8).

5.4 Effect of Plasma Treatment on Dyeability of Wool, Nylon and Cotton

Wakida et al. also demonstrated the effect of oxygen low-temperature plasma treatment of wool and nylon fibres on the dyeing rate and saturation dye exhaustion of acid dyes despite increased electronegativity of the fibre surface with the treatment. The dyeing rate of the plasma-treated wool also increased considerably with natural dyes such as cochineal, Chinese cork tree and madder, but not with gromwell.

In another study, wool, silk, nylon 6 and chinon (promix) fabric dyed with C.I. acid Black 155 were subjected to sputter etching and also exposed to a low-temperature argon plasma. A large number of small microcraters (smaller than the wave length of visible light) were formed which considerably reduced the reflection of incident light, and hence increased the depth of the shade. On the other hand, low-temperature argon plasma treatment did incorporate oxygen atoms onto the surface but the physical changes were negligible.

Yoon et al. also reported the mechanical and dyeing properties of wool and cotton fabrics treated with low-temperature plasma and enzymes. Plasma-treated cotton shows reduced strength, but the rate of weight loss in subsequent cellulase treatment decreased. The rate of dyeing with a direct dye also increased in the following order:

Plasma-treated cotton < untreated cotton < cellulase treatment = plasma/cellulase combination.

| Table 9—Oil values of several plasma/monomer-treated polyester samples and conditions of treatment 
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Power (W)</th>
<th>Plasma duration (min)</th>
<th>Oil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Untreated polyester)</td>
<td>20</td>
<td>60</td>
<td>22.2</td>
</tr>
<tr>
<td>Plasma in vacuum only</td>
<td>20</td>
<td>60</td>
<td>20.0</td>
</tr>
<tr>
<td>HMDS</td>
<td>20</td>
<td>60</td>
<td>19.5</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>20</td>
<td>60</td>
<td>21.8</td>
</tr>
<tr>
<td>Plasma in vacuum only</td>
<td>30</td>
<td>10</td>
<td>21.1</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>30</td>
<td>10</td>
<td>21.4</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>30</td>
<td>10</td>
<td>21.1</td>
</tr>
<tr>
<td>Allylamine</td>
<td>30</td>
<td>10</td>
<td>21.1</td>
</tr>
<tr>
<td>Plasma in vacuum only</td>
<td>40</td>
<td>5</td>
<td>22.2</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>40</td>
<td>5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Fig. 8—Rate of burning as a function of environmental oxygen concentration for untreated polyester fabric and plasma treated fabric at 20W, 60 min (ref. 82)
However, the oxygen plasma treatment onto wool improved its strength and resulted in higher rate of weight loss in the subsequent protease treatment and increase in dyeing rate.

Vohrer has also indicated the importance of glow-discharge treatments for surface modification of technical textiles.

### 6 Antimicrobial Finishes

Antibacterial finishes are germicides applied to fabrics to prevent odours produced by bacterial decomposition, such as perspiration odours, and also to reduce the possibility of infection by contact with contaminated textiles. Fabrics may also be treated with germicides to prevent mildew, a parasitic fungus that may grow on fabrics that are not thoroughly dried. Both mildew and rot may be controlled by treatment with resins.

Natural fibres in particular are prone to attack as they are readily digestible by bacteria and fungi, but synthetic fibres are not completely immune either, especially with the growth of specialty finishes, many of which can provide an important growth medium for the denizens of the microscopic world, enabling them to gain a foot hold to break down the manufactured fibres. Representative bacteria used in evaluation of antimicrobial activity are listed in Table 10.

The protection of cellulosics and manufactured fibres or fabrics to control the growth of bacteria can be accomplished by:

- a finishing process in which an antibacterial additive is fixed on the surface of the material by a resin,
- grafting of antibacterial agents on the cellulosic chain, and
- incorporating agents into the spinning solution of manufactured fibres.

The finishing process is the technique most frequently employed to impart antibacterial activity to cellulosic textiles. However, the durability to laundering achieved by this technique is usually not as good as that obtained by grafting or incorporation during spinning. The damage caused by microorganisms to 100% cotton under different conditions has been studied in-depth, when different finishing materials were used. The damage caused by Aspergillus niger, used as the experimental organism for 100% cotton material, was seen as a decrease in the tensile strength with time, temperature and pH.

<table>
<thead>
<tr>
<th>Table 10 — Representative bacteria used in evaluation of antimicrobial activity of modified fabrics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Species</strong></td>
</tr>
<tr>
<td>---------------------------</td>
</tr>
<tr>
<td><strong>Gram-positive bacteria</strong></td>
</tr>
<tr>
<td>Staphylococcus aureus</td>
</tr>
<tr>
<td>Staphylococcus epidermidis</td>
</tr>
<tr>
<td>Corynebacterium diphtheroides</td>
</tr>
<tr>
<td><strong>Fungi</strong></td>
</tr>
<tr>
<td>Candida albicans</td>
</tr>
<tr>
<td>Epidermophyton floccosum</td>
</tr>
<tr>
<td>Trichophyton interdigitale</td>
</tr>
<tr>
<td>Trichophyton rubrum</td>
</tr>
<tr>
<td><strong>Viruses</strong></td>
</tr>
<tr>
<td>Poliomyelitis virus</td>
</tr>
<tr>
<td>Vaccinia virus</td>
</tr>
<tr>
<td><strong>Protozoa</strong></td>
</tr>
<tr>
<td>Trichomonas vaginalis</td>
</tr>
<tr>
<td>Trematode (blood flukes)</td>
</tr>
<tr>
<td>Schistosoma japonicum</td>
</tr>
</tbody>
</table>

and the change in conditions of the medium are shown to affect the decrease in the tensile strength.

As shown in Table 11, the microbial growths were differently inhibited by several finishing chemicals, but most of them were removed by washing.

Cotton fabric and partially carboxymethylated or cyanoethylated fabrics were treated with glyoxal using ZnCl₂·6H₂O and Al₂(SO₄)₃·18H₂O as catalysts in the presence and absence of a silicon elastomer. The fabrics so treated were monitored for dry crease recovery and retained strength properties after soil burial for two and four weeks. Results obtained indicated that while the cotton fabric undergoes complete decay after two weeks, the cyanoethylated cotton samples having 2.01 %N retained 24.45% and 37.33% of their tensile strengths after two and four weeks of soil burial respectively. This was against the retained strength of 98.27% and 74.73% after the cyanoethylated cotton was given glyoxal treatment in presence of aluminium sulfate and silicon elastomer.
**Table 11 — Antibacterial chemicals**

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical nature</th>
<th>Composition g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Afrotin LC</td>
<td>Na salt of a heterocyclic compound</td>
<td>20</td>
</tr>
<tr>
<td>Mystox ELN</td>
<td>Pentachlorophenyl laurate and non-ionic emulsifying agents</td>
<td>2.5</td>
</tr>
<tr>
<td>Mystox WFE</td>
<td>Aqueous solution of sodium-o-phenylphenate</td>
<td>1</td>
</tr>
<tr>
<td>Antibac MF</td>
<td>An organic compound containing nitrogen with no halogen or heavy metal salts</td>
<td>40</td>
</tr>
<tr>
<td>Antibac MFB</td>
<td>Combination of heterocyclic organic compounds</td>
<td>80</td>
</tr>
<tr>
<td>Fungitex OP</td>
<td>Derivatives of benzimidazole</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 12 — Odour and bacterial counts of towelling**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Odour</th>
<th>Bacterial count CFU/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Very strong, pungent odour</td>
<td>$&gt;10^{10}$</td>
</tr>
<tr>
<td>Softener only</td>
<td>Very strong, pungent odour</td>
<td>$2.6 \times 10^9$</td>
</tr>
<tr>
<td>0.2% PHMB</td>
<td>No odour</td>
<td>$6 \times 10^5$</td>
</tr>
<tr>
<td>Softener and 0.2% PHMB</td>
<td>No odour</td>
<td>$4 \times 10^4$</td>
</tr>
</tbody>
</table>

![Structure of PHMB](image)

Fig. 9 — Structure of PHMB, the active agent in the antibacterial treatment (ref. 91)

Graft or *in-situ* polymerization of acrylates onto cotton and rayon in conjunction with zinc or copper salts produced fabrics with durable antibacterial activity. Cotton fabrics resistant to *Staphylococcus epidermidis* for 50 launderings and to *Staphylococcus aureus* for 25 launderings were produced by *in-situ* polymerization of zinc acrylate, zinc methacrylate and zinc itaconate. Grafting of acrylic acid onto mercerized cotton and rayon followed by immersion in copper sulphate imparted durable antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*.

SITRA has also developed a chemical finish for yarn, fabrics and garments named as **SANTIMIT** (SITRA Antimicrobial Textiles) which possesses almost complete antibacterial potentiality against all major diseases and perspiration odour. These beneficial effects are highly durable even after 50 use-wash-use cycles. The antibacterial effect, both in formulation and on treated materials, has been affirmed by extensive hospital field trials.

Magnesium peroxide-based new antibacterial agents (derived from 28:1 mole ratio of $H_2O_2$: $Mg(OAc)_2\cdot 4H_2O$ with a peroxide content of 24%) and their applications on cellulosics have been described by Vigo et al. They reported several advantages over previous antibacterial agents derived from the *in-situ* application of zinc or zirconyl acetate/hydrogen peroxide systems applied to textiles. Cotton fabrics had much better affinity and durability of the affixed agents than cotton/polyester blends or all synthetic fabrics such as polyester, polyamide and polypropylene.

A new antimicrobial treatment, called Reputex, has been found to be a durable finish for cotton and cotton blends, based on active agent poly(hexamethylene-biguanide hydrochloride) PHMB (Fig. 9). It is readily applied by padding or exhaustion. The antibacterial efficacy of this treatment on fabric has been assessed using qualitative agar plate and quantitative bacterial counting methods (Table 12). Treated cotton is bactericidal for approximately 25-50 wash cycles, depending on the wash conditions.

Bacteria-contaminated fabrics in hospitals are known to be a major source of cross infection. Post-operative infections are the most common hospital acquired infections since bacteria can, by a variety of routes, find their way into an open wound and cause sepsis. Post-operative wound infections develop in 2-5% of patients undergoing surgical procedures. Surgeons gowns and drapes used to surround the operative field should be effective aseptic barriers between the underclothes of the surgeon and the aseptic field and between the patient’s body other than the prepared area and the sterile field. In the operating room, however, liquids such as blood, sweat and saline solutions can carry bacteria with them, and if a liquid is wicked from a surgical gown to a non-sterile surface, one or both sides will become contaminated. In an operating room, a patient’s blood can penetrate surgical gown material and probably contaminate the surgeon’s skin if not well protected.

Several researchers have used antimicrobial finishes to provide fabrics with barriers against microorganisms. Morris *et al.* used an antibiotic as an antimicrobial agent to impart antimicrobial properties...
to cotton. They found that fabrics treated with antibiotics retain excellent bacteriostatic activity. Points and Wadsworth\textsuperscript{40} used a fluorochemical as a repellent finishing agent on spun laced nonwoven fabrics. The surface tension of blood and body fluids ranges between 42 and 60 dyne/cm; to maintain blood repellency, the surface tension of fabrics has to be much lower than that of blood. In order to provide 100\% cotton fabric and 55/45 wood pulp/polyester spun laced nonwoven fabric with barriers against micro-organisms and blood, the samples were treated with gentamicin, a broad-spectrum antibiotic, and a fluorochemical compound using pad-cure method. The antimicrobial activity of the samples was analyzed quantitatively by measuring the number of colonies of \textit{Klebsiella pneumonia} and qualitatively using the parallel streak method with \textit{Staphylococcus aureus}. Blood repellency is assessed with spray and impact penetration tests using both synthetic and human blood. Samples treated with both the antibiotic and the fluorochemical (dual finish) show a high reduction rate in the number of colonies grown and clear zones of inhibition.

Dual finished specimens treated with 1.1\% chitosan concentration also maintain over 90\% reduction in the number of colonies. The blood repellency of dual finished nonwoven fabrics is superior to that of dual finished cotton. As regards the mechanical properties, the bending rigidity and shear rigidity increase when cotton and nonwoven fabrics are treated only with chitosan, but these properties decrease after the fluoropolymer treatment. Air permeability of the specimens decreases slightly after the dual finish.

In another study, chitosan\textsuperscript{96} of specific molecular weight has been used for its antimicrobial activity. Pronated amine groups in chitosan inhibit the growth of micro-organisms by holding negatively charged micro-organism ions. However, the insolubility of chitosan in neutral or alkaline conditions limited its application.

Many antimicrobial finishing agents contain quaternary ammonium groups and attaching such a group to chitosan could improve its antimicrobial activity. Possibly, the aqueous solubility of a quaternary ammonium derivative of chitosan, for example Glycidyltrimethylammonium chloride (GTMAC) as shown in Fig.10, would further increase and improve its use as an antimicrobial finishing agent.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig10.png}
\caption{Reaction scheme for synthesis of HTCC (ref. 96)}
\end{figure}

Preferential reaction of GTMAC with amine groups in chitosan under neutral or alkaline conditions produces N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC) (Fig.10). At very low concentration\textsuperscript{96} of 0.025\% owb, HTCC shows superior antimicrobial activity indicated by an almost 100\% bacterial reduction, whereas 1\% owb chitosan shows only 30\% bacterial reduction. Since HTCC is soluble in water, the application of a non-ionic binder considerably improves the laundering durability of HTCC-treated cotton.

Citric acid (CA) and chitosan\textsuperscript{97} are used as durable press and antimicrobial finishing agents for cotton and are applied by means of the conventional pad-dry-cure process. CA is expected to react with hydroxyl groups in cellulose and chitosan or with amino groups in chitosan to form ester crosslinking or an inter-ionic attraction. Durable press ratings of 3.5-4 are obtained with CA and chitosan treatments. The durable press performance is retained through twenty washings and tumble drying cycles. Strength retention improves more with CA and chitosan than with CA alone.

Durable and regenerable antimicrobial cellulose-containing fabrics have been developed recently based on a theoretical regeneration model proposed by Gagliardi in 1962. In this new technology, the precursors of biocidal compounds, instead of the biocides themselves, have been used in the chemical treatment of cellulosic materials, which successfully demonstrated an innovative approach in preparing regenerable functional materials\textsuperscript{98}. The functional agent used in the chemical treatment is a hydantoin derivative, monomethylol-5,5-dimethylhydantoin (MDMH or Anti-1), a bifunctional compound possessing one side reactive to cellulose and another to active chlorine to form a halamine bond (Fig. 11). The durable and regenerable antimicrobial function of
the treated fabric is attributed to the reversible oxidative properties of cyclic halamine structures. The effectiveness of the antimicrobial fabrics is related to the amount of active halamine agents incorporated onto the fabrics.

The biocidal functions on the fabrics are achieved by two steps of chemical processing including finishing under acidic conditions and rinsing with chlorine bleach. Each of the processes may have its own impact on physical properties of the fabrics. Chemical finishing of the hydantoin compound onto cellulose was performed under acidic conditions that are quite harmful to the chemical structure of cotton cellulose. Active chlorine in bleaching solutions usually damages the tensile strength of fabrics due to its oxidative properties. These factors, affecting the mechanical properties of the treated fabrics, should be investigated to ensure the appropriate properties of the antimicrobial fabrics. Biocidal properties of cotton fabrics processed under different pH are given in Table 13.

Biosil" finish employs an agent which joins quaternary ammonium salt with organosilicone. By graft-polymerizing with fibre, this organosilicone is affixed to fibre firmly. For this reason, the agent does not leach out even by washing. The quaternary ammonium salt destroys cell membranes of bacteria. Biosil is also characterized by the fact that there is no harmful influence resulting from the oozing of the agent. In principle, "Episcall" also employs quaternary ammonium salt as a base. Toyobo has developed "Episcall" as a general-purpose type of "Biosil". "Episcall" can be treated to any fibre, as is the case with "Biosil". Toyobo has adopted "Biosil", however, mainly for cotton textiles, while "Episcall" is for all textiles. The employed agent, namely "Dow Corning 5700" (silicone quaternary ammonium salt), satisfies strict criteria issued by the U.S. Environment Protection Agency (EPA) and a guarantee is given to its safety as well.

"Biosil" and "Episcall" finishes have received acceptance not only for underwear and foundations worn in direct contact with the skin, but also frequently in the sector of work wear and sportswear with their high occurrence of sweating. Bacteria-resistant/deodorizing finishes such as "Biosil" and "Episcall" have become indispensable for socks and panty hose as well.

In addition to after-finishing, there are other products with knead-in bacteria-resistant agents for synthetic fibre, which can bring about similar effects. Toyobo has developed and commercialized "Feelfresh" (acrylic fibre) and "Bioguard-N" (nylon filament).

Kanebo launched an antibacterial nylon fire "Livefresh-N". This fibre is the first one made with an inorganic antibacterial additive Ag-zeolite kneaded in. "Livefresh-N" is used in the field of innerwear including lingerie and hosiery. But there were problems such as yarn breaks in different processes and yellowing when exposed to heat and light. Especially, nylon polymer has a remarkable yellowing compared with other polymers. Instead of Ag-zeolite, it has slow release glass phosphate with silver ions as an antimicrobial additive kneaded into fibres. This enabled to maintain antibacterial effect with less amount of additive. At the same time, yellowing defect was improved by far.

6.1 Bacteria-Resistant Finishes: Escola and Epicomodo

In contrast to bacteria-resistant/deodorizing finishes, which reduce the growth of bacteria to prevent the generation of odors, bacteria-resistant finish gives more priority to the effect of preventing growth of germs.

For some time, the attention has been focussed on "Methicillin-resistant Staphylococcus aureus" (MRSA). Abuses of antibiotics have produced a miserable situation in which antibiotic-resistant microbes have grown conversely and there is no way for medical treatment. Many devices have been
employed in the forefront of medical treatment and responsive actions have been progressing against MRSA. Moreover, actions were requested even for clothing such as uniforms and interior goods such as curtains to prevent the transmission of germs, along with the sterilization of everything which is used at hospitals, in order to prevent hospital infection.

"Epicomodo" is a fabric which Toyobo\(^9\) has developed to cope with MRSA, since it has become a serious task to keep a clean in-hospital environment. Toyobo has proposed 100% polyester, polyester/cotton blends and other fibres in a number of combinations for curtains, white coats and bedding used in hospitals. The mechanism of bacterial-resistant finish used for Epicomodo is as under:

The agents with positive ions attract germs to their environment by acting upon their cell membranes with negative ions to control the activity of the germs by destroying cell membranes as shown in Fig. 12.

One bath process for dyeing and simultaneous antimicrobial finish by methanolic extract (1-5%) of Tulsi leaves (Ocimum sanctum) on cotton\(^10\) has been investigated. It is believed that urosolic acid (C\(_{30}\)H\(_{48}\)O\(_3\)) is the active ingredient which inhibits the growth of several strains of Staphylococci.

7 Waterproof Breathable Fabrics\(^10\)\(^4\)\(^-\)\(^11\)

Waterproof/moisture permeable fabrics from several synthetic fibres have been designed for skwear, track suits, rainwear, and mountaineering clothing.

Light weight fabrics coated with poly(vinyl chloride), polyurethane and other synthetic rubbers have become increasingly popular for foul-weather clothing. Although garments manufactured from these fabrics provide exceptional protection against rain and, to a less extent, wind penetration, but considerable build-up of moisture vapour inside the clothing may cause discomfort. This problem arises because of the water-vapour impermeability of the polymer coating.

To overcome this problem, breathable polymer coatings are now available that have made possible great improvements in the comfort of this type of clothing.

7.1 What is a Breathable Fabric?

A breathable fabric is waterproof and breathable because of the enormous size difference between a water droplet and a water vapour molecule\(^10\)\(^1.\) The former is 100 \(\mu\)m in diameter whereas the latter is 0.0004 \(\mu\)m, i.e. there is a factor of around 2,50,000 between the two sizes. Microporous polytetrafluoroethylene (PTFE) Gore-tex laminates have been successfully introduced as breathable fabrics. Comparative assessment of Gore-tex and Neoprene vapour barriers in fire fighter suits has also been made.

7.2 Classification of Breathable Fabrics

The breathable fabrics can be classified into three main categories:

7.2.1 High-density Woven Fabrics

High-density wovens owe their breathability to the densely woven, thin and smooth yarns that are usually made from microfibres. This type of weaving results in a windproof fabric with an excellent water vapor permeability compared with laminates and coatings. Its water impermeability is, however, not very high, even though a water-repellent finish is usually applied. The major advantage of these fabrics is their good grip. For those applications where grip, water vapour permeability and windproofing are more important than water impermeability, marvellous and fashionable clothing can be made from these fabrics; they can be found in ski clothing.

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![Fig. 12 — Bacterial-resistant mechanism of Epicomodo (ref. 99)](image-url)
7.2.2 Laminated Fabrics

The fabric can be of almost any desired construction. Lamination of the film on a fabric uses special adhesives, sometimes even breathable ones. If non-breathable adhesives are used, care has to be taken not to cover the whole surface in the coating process. This process can be done in rotary-screen-printing, spraying or web-lamination.

The barrier film can be microporous, e.g. Gore-Tex and Microtex. Breathable films are made through biaxial stretching process of Teflon film by mechanical fibrillation.

For certain polymers, biaxial stretching produces microscopic tears throughout the membrane, which imparts a suitable microporous structure. For example, PTFE membranes are used in the Goretex two-layer and three-layer laminates. The thin microporous membrane is made from solid PTFE sheet by novel drawing and annealing process. In drawn form, the tensile strength is increased three folds. The manufacturers claim that these PTFE membranes contain approximately nine billion pores per square inch, with pore volume of up to 80% and a maximum pore size of 0.2 μm.

Hydrophilic polymer film can be extruded or cast from such polymers having polar groups which can absorb, diffuse and desorb water as vapour, e.g. Sympatex film (polyester) developed by Akzo.

Bion II film (polyurethane), a product of Toyo Cloth, and Excepor-U (polyaminoacid/PU), a product of Mitsubishi-Kasei, have also been used as moisture vapour breathable films.

Thintech is a film of 3M in which a polyolefin (microporous matrix) is impregnated with hydrophilic polyurethane.

Thermoplastic elastomers such as copolyetheresters (PEE), having alternating hard polyester segments and soft polyester segments, and polyether-polyester block amides (PEBA) have also been used as breathable films for protective clothing.

7.2.3 Coated Fabrics

7.2.3.1 Microporous Coatings

The microporous barrier layers breathe primarily through a permanent air permeable pore structure. Diverse techniques have been used to manufacture microporous coatings. The most important among them are solvent exchange, phase separation and phase inversion.

**Solvent Exchange:** In this process, a polymer dissolved in a water miscible solvent is coated thinly onto the fabric. The porous structure is developed by passing through a coagulation bath where water displaces the solvent. For example, the textile substrate is coated with polyurethane solution where DMF is being used exclusively as the solvent and the fabric is passed through coagulation bath containing water, where water displaces the solvent to give a porous structure.

**Phase Separation:** The coating polymer is applied from a mixture of a relatively volatile solvent with a proportion of higher boiling non-solvent. Precipitation of the polymer as a microporous layer occurs as the true solvent evaporates faster during the subsequent drying process. For example, Ucecoat 2000, a polyurethane based coating, operates on this principle. Here, a low-temperature boiling solvent (methyl ethyl ketone) evaporates preferentially as the fabric passes through the oven, thereby increasing the concentration of the non-solvent in the coating. When the concentration of the non-solvent reaches a critical level, the polyurethane precipitates out in a highly porous form and the remainder of the solvent and the non-solvent evaporate from the coating as the fabric passes through the oven.

**Phase Inversion:** A solution of polyurethane containing a non-solvent is coated on a fabric. In a selective evaporation step, the solvent is eliminated first. The polyurethane then precipitates in a microporous way. An example is Ucecoat 2000 (S) of UCB Speciality Chemicals.

7.2.3.2 Hydrophilic Coatings

The polyurethane in solution contains hydrophilic groups. After coating, the solvent is evaporated leaving a monolithic (non-porous) layer on the fabric. Examples are Ucecoat NPU series of UCB Speciality Chemicals, Witclex/staycool of Baxenden and Improperm of Bayer.

7.2.3.3 Microporous and Hydrophilic Coatings

A hydrophilic finish on a microporous structure is used to upgrade the water-resistance of microporous coatings. Care has to be taken to select a hydrophilic finish that does not impart an unacceptable loss in breathability. Ucecoat NPU2307 finish on top of Ucecoat 2000 (S) microporous coating is an example.

A microporous coating can be obtained by coating the fabric with a foam. This gives a rather cell
structure which has to be crushed. Breathability is
good but water-proofness has to be improved. An
example is Dicrylan system of Persree/Ciba Geigy.
Performance of various breathable fabrics is shown in
Table 14.

7.3 Evaluation of Breathable Materials

The two most important characteristics of
breathable fabrics are water vapor and heat transport.
In order to gain an insight into the transient states of
such transport across a set of layers of fabrics, an MU
water vapor transport simulator (MU-WVT simulator)
has been developed.

It has been demonstrated that the water transport is not
influenced significantly by surface characteristics—
the hydrophilic or hydrophobic nature of fabrics. On
the other hand, when liquid water contacts a fabric,
such as in the case of sweating, the surface wettability
of fabric plays a dominant role in determining the
water vapor transport rate through layered fabrics. In
such a case, the wicking characteristics, which
determine how quickly and how widely liquid water
spreads out laterally on the surface of/within the
matrix of the fabric, determine the overall water
vapor transport rate through the layered fabrics.

The overall water vapor and heat transport
characteristics of a fabric should depend on other
factors such as the water vapor absorbability of the
fibres and the porosity, density and thickness of the
fabric. The overall dissipation rate of water vapour
depends on both the vapour transport rate and the
vapour absorption by fibres, which are mutually inter-
related. Water vapour transport is governed by the
vapour pressure gradient that develops across a fabric
layer. When a fabric is subjected to given
environmental conditions, the actual water vapour
transport rate greatly differs depending on the nature
of the fibres, even when other parameters such as
density, porosity and thickness are nearly identical.

To understand this process more clearly, Robin
Howie from the Institute of Occupational Medicine in
Edinburgh has developed a method for calculating the
requirements that a breathable clothing should have
under specific conditions, by taking the following
parameters into account:

<table>
<thead>
<tr>
<th>Colour</th>
<th>Fabric sample coating</th>
<th>Total weight g/m²</th>
<th>Water vapor permeability (20°C, 95% RH)</th>
<th>Waterproofness (Hydrostatic Head)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>UCB method 1</td>
<td>UCB method 2</td>
</tr>
<tr>
<td>Green</td>
<td>Standard non-breathable polyurethane</td>
<td>87</td>
<td>286</td>
<td>281</td>
</tr>
<tr>
<td>Grey</td>
<td>Hydrophilic PU</td>
<td>81</td>
<td>1120</td>
<td>2900</td>
</tr>
<tr>
<td>Black</td>
<td>Ucecoat TD 9627/NPU 2307</td>
<td>98</td>
<td>1290</td>
<td>4180</td>
</tr>
<tr>
<td></td>
<td>Hydrophilic PU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td>Laminate; hydrophilic polyester film</td>
<td>145</td>
<td>1290</td>
<td>3470</td>
</tr>
<tr>
<td>Red</td>
<td>Ucecoat 2000 S</td>
<td>95</td>
<td>2190</td>
<td>4240</td>
</tr>
<tr>
<td></td>
<td>Microporous PU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purple</td>
<td>Ucecoat 2000 S/NPU 2307</td>
<td>88</td>
<td>2230</td>
<td>4660</td>
</tr>
<tr>
<td></td>
<td>Microporous and hydrophilic PU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow</td>
<td>PTFE laminate microporous</td>
<td>78</td>
<td>2140</td>
<td>5870</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Work rate</th>
<th>Air flow rate (l/m²/min) at</th>
<th>WVTR³ (g/m²/24hr) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10°C</td>
<td>20°C</td>
</tr>
<tr>
<td>Low</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Moderate</td>
<td>—</td>
<td>80</td>
</tr>
<tr>
<td>High</td>
<td>—</td>
<td>320</td>
</tr>
<tr>
<td>Very high</td>
<td>120</td>
<td>560</td>
</tr>
</tbody>
</table>

³Water vapour transmission rate
Assumptions: Internal RH: 100% External air speed: up to 4m/s
External RH: 50% Garment thermal resistance: 1.4 clo
Internal temp: 33°C Wearer: 70 kg man
External temp: 20-30°C Garment is oil impermeable
Internal air exchange: 50%
Fig. 13 — Temperature-dependence of water vapour diffusion resistance for four membrane type materials (two hygroscopic, two non-hygroscopic) (ref. 112)

- The heat to be carried off by clothing (as a function of physical exertion).
- The estimated thermal resistance of clothing (thermal conductivity).
- The relative ambient humidity.
- The ambient air velocity.

On the basis of this model, the required values for air and water vapour permeability are calculated for various degrees of physical exertion under different ambient temperatures.

For a surgeon in an operating room, the values are given in Table 15. It is interesting to note that the surgeon who is working at 20°C at a moderate work pace, would feel comfortable, provided the air permeability is 100 l/m²/min and the water vapour permeability 400 g/m²/24h. His clothing may then be called breathable.

Gibson112 has described the various test methods for studying the water vapour transport and gas flow properties of textiles, polymer membranes and fabric laminates. In this context, Dynamic Moisture Permeation Cell (DMPC) method satisfies the need for quick automated method for the mass transport properties. DMPC method is ideally suited for temperature-dependent diffusion and concentration-dependent diffusion in membrane laminates. An example of the temperature-dependent water vapour diffusion behaviour of four membrane based materials is shown in Fig. 13. Results are shown for the mean relative humidity condition of 0.40 (40%) (average of 0.80 on one side and 0.0 on the other). Results for other mean relative humidity conditions showed that the temperature effects on the measured diffusion resistance are much greater when the hydrophilic polymer contained less sorbed water. The concentration-dependent behaviour has also been studied. Two semi-impermeable membrane laminates (Gore-tex and Sympatex) exhibit concentration-dependent transport behaviour as compared to microporous PTFE membrane.

References