

Finishing of Textile Materials

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Received 8 November 2000; accepted 18 November 2000

ABSTRACT: With increasing awareness of environmental concerns, various chemical finishes for processing of textiles have been discussed. In this paper major changes which have occurred to satisfy the consumer's demand in terms of comfort, easy care, health, and hygiene are reviewed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 631–659, 2002

Key words: durable press finishes; formaldehyde; free finishes; softeners; bioprocessing; breathable coatings; antimicrobial finishes; silk-like polyester.

INTRODUCTION

In the past five decades, extensive work has been performed with the aim of developing new textile products using new fibers, fiber blends, as well as treating textiles with chemical finishes to impart specific functional properties in addition to improving their aesthetic values.

Many investigations^{1–4} have been reported which were designed to achieve a better understanding of the mechanisms by which the various finishes act, and to replace the empirical approaches with those developed by systematic studies.

Today, with increasing awareness of environmental concerns, a significant amount of legislation on ecotoxicological considerations has been introduced.^{5–7} It is related to such important issues as health and safety during storage, application and use, and safe disposal of chemicals into landfills, into water, or release in air during chemical processing of textiles. These have imposed changes in chemical finishes and finishing methods. So, integrated pollution control would continue for developing ecofriendly processes as we approach the next millennium.

Holme⁸ has indicated the challenges faced, and accordingly the changes required in functional

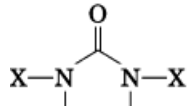
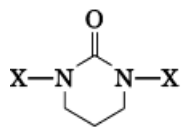
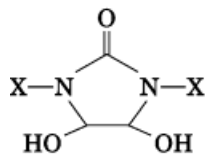
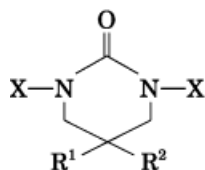
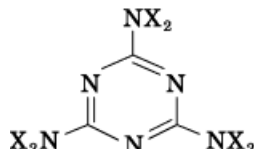
finishes for cotton. The major factors that will act as a driving force for change in the chemical finishing for cotton in the next decade are the following:

- The need for better quality and higher added value chemical finishes for cotton
- More environment-friendly chemical finishes and application methods
- Increased possibility of process integration to minimize the use of water and energy
- Increased levels of process control, monitoring, and automation in textile finishing machinery.

In addition to the ecofriendly finishes, significant changes in the application methods have also been made. The major treatment methods currently practiced for producing durable press cotton and other textiles are: pre-cure, garment dip treatment, vapor phase, low wet pick (kiss roll technique), post-cure, spray application and lamination, coating and lamination technology, foam finishing; and low pressure plasma technology.

In this report, a comprehensive review of various finishing agents leading to wrinkle-free fabrics with good and soft handle, breathable fabrics, antimicrobial textiles, etc., is given. Developments in bioprocessing, silk-like polyester, and various other emerging technologies have also been highlighted.

Table I Structural Formula of Customary Reactants for Dry Cure Process

Reactants	Durability to			Lightfastness of Reactive and Direct Dyestuffs	
	Reactivity	Laundrying	Chlorine		Hydrolysis
X—HN—CO—NH—X		+(+)	-	+	++
		+++	+	+	+
		+++	+++	+	+
ROCONX ₂		+++	++(+)	++(+)	+++
		+++	+	+++	+++
		+++	++(+)	++(+)	+++
		+++	+(+)	++	+(+)

Note: X = CH₂OR; R = H, alkyl; R¹ = alkyl, hydroxyalkyl, alkoxyalkyl; R² = alkyl; +++, very good; ++, good; +, fair; -, bad.

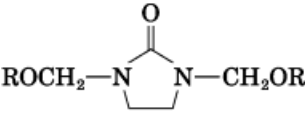
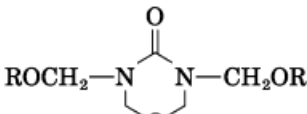
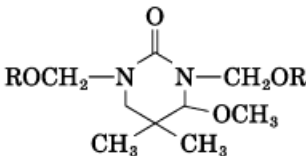
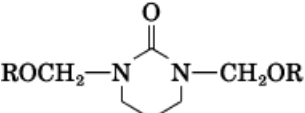
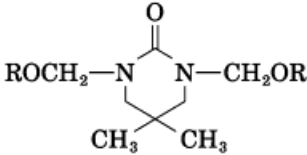
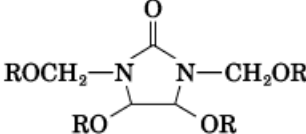
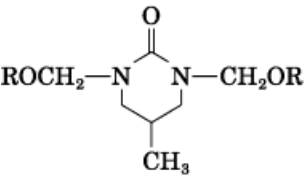
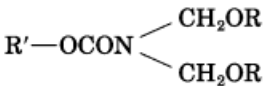
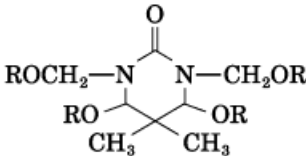
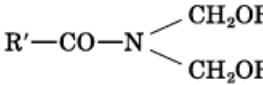
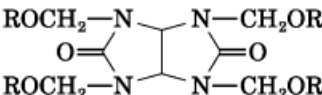
DURABLE PRESS FINISHES FOR COTTON

Wrinkle-free cotton fabrics continue to dominate the market and are gaining universal acceptance. *N,N*-dimethylol 4,5-dihydroxyethylene urea (DMDHEU) has been accepted as an easy-care finishing agent. It exhibits high acid hydrolytic stability and relatively low reactivity, whereas *N,N*-dimethylol ethylene urea (DMEU) possesses high reactivity and only limited hydrolytic stability. The structure and reactivity of various methylol derivatives^{1,9,10} as crosslinking agents is shown in Table I. Bis(hydroxymethyl) or bis(alkoxymethyl) derivatives of carbamates have also been used for easy-care finishing of cotton. Interestingly, there is a direct correlation between the hydrolytic stability of the reactant and its effect

on the lightfastness of cotton dyed with direct and reactive dyes. In DMDHEU, it is assumed that all the four reactive groups combine with cellulosic hydroxyl groups (Fig. 1), but the 4,5-dihydroxy ethylene ureas also undergo a chemical change and convert to hydantoin which are responsible for the increased chlorine retention of the crosslinked cellulose, because the free N—C groups combine readily with chlorine.

Normally, crosslinking of cellulose with these dimethylol compounds takes place in the presence of acid-liberating catalysts, e.g., magnesium chloride, zinc chloride, or nitrate by the pad-dry-cure method. Crosslinking occurs within the accessible regions with hydroxyl groups. Intermolecular crosslinking provides an increase in the fiber resistance to deformation and improved elastic re-

Table II

1 Group	2 Group	3 Group
High Reactivity, Low Hydrolysis Stability	Moderate Reactivity, Medium Hydrolysis Stability	Low Reactivity, Good Resistance to Hydrolysis
		
		
		
$\text{ROCH}_2\text{—HNCONH—CH}_2\text{OR}$		

urea, natural shellac, chitosan, TEA.HCl, and EDTA along with DMDHEU has been studied. Formaldehyde release was minimal in TEA.HCl (Figs. 4 and 5). By these methods, it has been possible to limit the formaldehyde release.^{20,21} However, in the 1990s, the quest has been to search for zero formaldehyde-based reactants for cotton that will provide a low-cost efficient alternative to the products derived from *N*-hydroxymethyl derivatives. One approach has been to use glyoxal urea-based derivatives such as that based

on *N,N*-dimethyl, 4,5 dihydroxyethylene urea (DMeDHEU). This is a zero-formaldehyde-based crosslinking agent for cotton that crosslinks through the ring hydroxyl groups of cellulose. However, such derivatives are more expensive and somewhat less effective than DMDHEU at the same add-on level, possibly through hydant-

Table III Sources of Formaldehyde in the Atmosphere in the United States

Source	Amount (%)
Exhaust gases of vehicles and aircraft	53–63
Photochemical reactions (mainly from the hydrocarbons in exhaust gases)	19–32
Heating systems, combustion of refuse	13–15
Oil refining	1.2
Production and processing of formaldehyde	1

Source: Text Month, May 1997, p 35.

Table IV Thresholds for Formaldehyde in the Workplace (Status 1996)

Country	Thresholds (ppm)
Austria	0.5
Belgium	0.3
Denmark	0.3
Finland	1 (15 min)
France	0.5
Germany	0.5
Greece	2
Italy	0.3
Netherlands	1
Norway	1
Sweden	0.5
Switzerland	0.5
United Kingdom	2

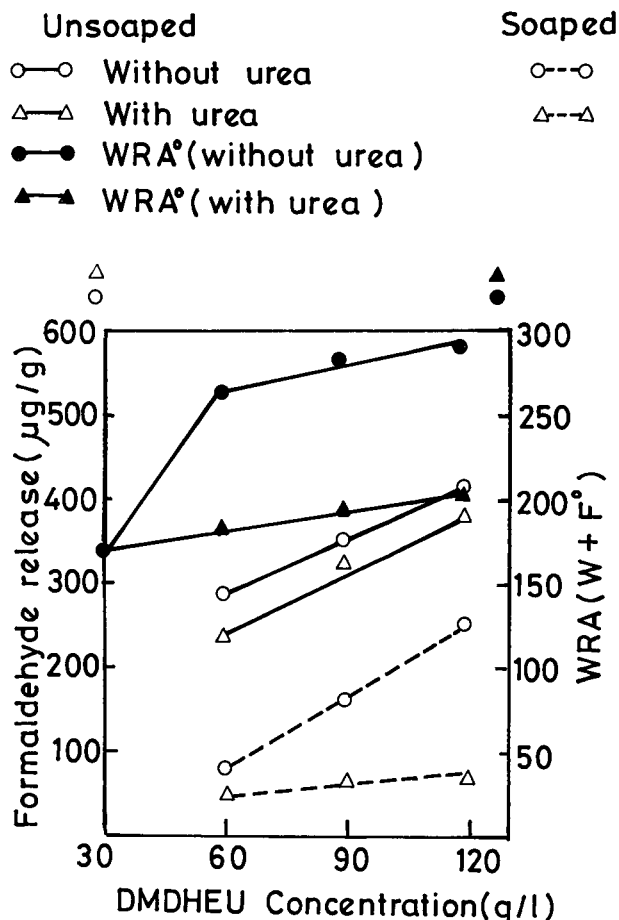


Figure 4 Effect of urea (10 g/L) as scavenger in resin bath on formaldehyde release and WRA before and after soaping.

toin formation.¹⁷ More active curing systems are therefore often required. Polycarboxylic acids forming ester links with cellulose have also been developed as formaldehyde-free finishing agents.

Application of all of these finishes and their mechanism of reactions are discussed below.

FORMALDEHYDE-FREE FINISHES

Glyoxal

Cotton on treatment with glyoxal in the presence of an acid catalyst such as boric acid or ammonium chloride and aluminum sulphate on heating gives monoacetals and diacetals of glyoxal with cellulose (Fig. 6).

Free aldehyde groups present because of single-ended attachment of glyoxal as in (I) were found to be removable by oxidation with chlorous acid or reduction with potassium borohydride. Be-

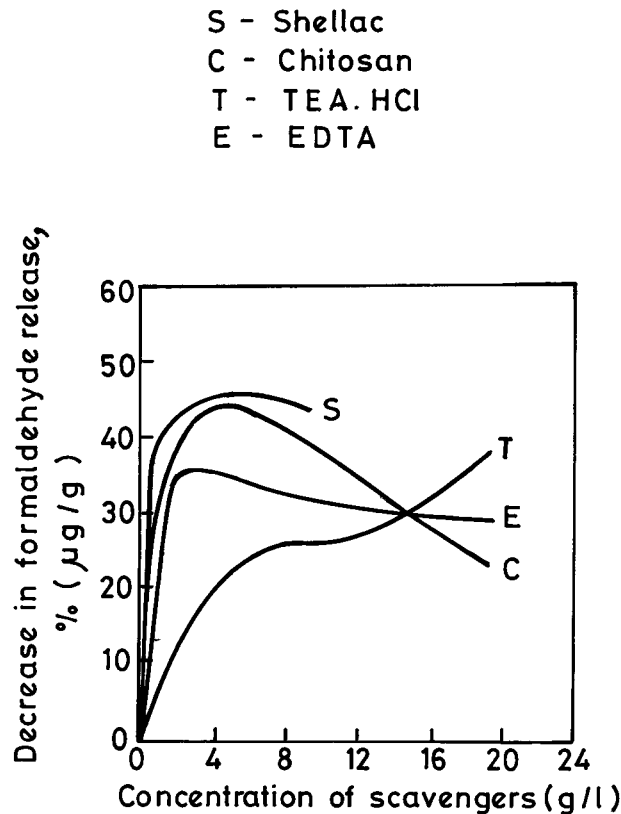


Figure 5 Effect of concentration of scavengers in resin bath on formaldehyde release from cotton fabrics.

cause glyoxal molecules can form four linkages to cellulose, as in product (II), glyoxal may be regarded as tetrafunctional.

Magnesium chloride was used as catalyst in early studies for applying a very high glyoxal concn (10% by wt). In the absence of active hydrogen compounds as coreactive additives, fabric weight gain was only 1.4%.

With active hydrogen compounds such as alcohols, phenols, amides, or thiols, as coreactants, much higher fabric weight gains were observed. But the problem with $MgCl_2$ is that it produces

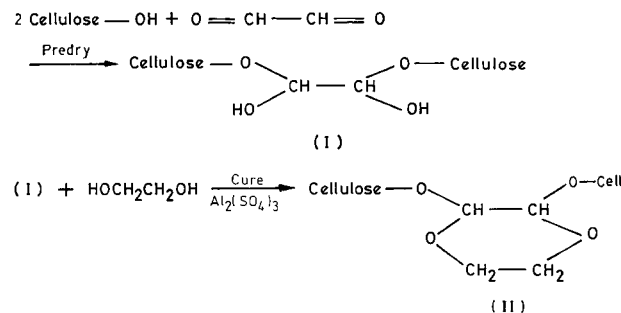


Figure 6 Reaction of Glyoxal with cellulose.

fabric yellowing and severe fabric strength losses. The use of aluminum sulphate as the curing catalyst leads to high levels of wrinkle resistance. An excess of glyoxal appears to serve as a chelating agent and diluent for aluminum ions, thus moderating the tendency of the catalyst to degrade the cellulose.^{19,20}

Glyoxal-Glycol Mild Cure Process

The addition of polyhydric alcohols^{19–21} to the treating formulations results in improved fabric whiteness and increased durable press (DP) ratings. α -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 and the order of effectiveness of various acid catalysts is as follows: succinic < lactic < malic < glycolic < citric < tartaric acid. A silanol-terminated silicone fabric softener appeared to exert a synergistic effect with glyoxal and aluminum sulphate in improving the DP ratings. 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, which alters the spatial configuration, polarity, and flexibility of the three-dimensional crosslink network produced in the cellulose.

High-Temperature Glyoxal-Based Processes

The advantage of high-temperature curing is that 15 to 60 s of residence time of the fabric in the curing oven is sufficient to achieve cellulose crosslinking,²¹ and also to heat-set the polyester to final fabric dimensions. Aluminum chlorohydroxide $\text{Al}_2(\text{OH})_5\text{Cl}\cdot 2.5\text{H}_2\text{O}$ is an effective high-temperature (170°C) catalyst in the presence of α -hydroxy acid for all cotton fabrics.

A mixture of aluminum sulphate and magnesium sulphate has been recommended as a non-yellowing catalyst for the application of glyoxal at temperatures such as 190–205°C in the presence of a reactive silicone, which appears to exert a synergistic effect with the glyoxal.^{22,23} 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 DMDMEU-treated fabric. This comparison was made on 65/35 polyester/cotton. A fur-

ther process improvement consists of adding a buffer such as sodium metaborate to the formulation. This raises the pH of the final finished fabric sufficiently to eliminate the need for an afterwash to remove acidic catalysts.

The glyoxal-glycol process has been conducted at curing temperatures of 145–160°C on all-cotton fabric. The catalyst was aluminum sulphate buffered with aluminum dihydroxyacetate stabilized with boric acid (Fig. 6). Curing times of 15–20 s were sufficient to impart a high level of DP properties when 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.²²

Monomeric Adducts of Glyoxal with Ureas

The cyclic addition product of glyoxal with *N,N'*-dimethylurea is the most important member of this family and is named as 1,3-dimethyl-4,5-dihydroxyethyleneurea (DHDMI).

DHDMI imparts a moderate level of wrinkle resistance to cotton fabric in the presence of MgCl_2 , zinc nitrate, or zinc fluoborate as curing catalyst. Zinc fluoborate was by far the most effective curing catalyst in terms of wrinkle recovery angles observed before and after multiple launderings performed on the DHDMI finished fabric. DHDMI was found to be less effective than DMEU. However, it produced a finish very resistant to chlorine damage even after multiple launderings under severe conditions, and was superior to DMEU in this respect. DHDMI produced a finish that offered greater resistance to acid hydrolysis than that of DMEU, but inferior to that of *N,N*-dimethylolurea. 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. Overall, the SN_1 mechanism is followed by DHDMI with cellulose, whereas the SN_2 mechanism in the case of DMEU-treated cotton.

The stability of DHDMI at room temperature makes it suitable for use in finishes that are to be postcured 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%

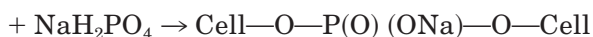
DHDMI formulations produce a marked increase in DP performance.²⁴ DHDMI, glutaraldehyde, and 1,1,4,4-tetramethoxybutane carboxylic acid formaldehyde-free crosslinking agents give less uniform distribution of crosslinks in the cotton fiber than do conventional *N*-methylol agents. DHDMI shows complete lack of interlamellar crosslinking, yet DHDMI-treated fibers were almost completely insoluble in cupriethylenediamine hydroxide, indicating extensive crosslinking, which accordingly must be intralamellar. The moisture regain and affinity for C1 Direct Red 81 shown by DHDMI-crosslinked cotton was the 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.²⁵

It has been shown by reverse gel permeation chromatography²⁶ that fibers of cotton fabric crosslinked with DHDMI retain substantially more accessible internal volume across the entire range of pore sizes than do fibers crosslinked with DMDHEU. Increased add-on of DMDHEU further reduces the accessible internal volume, whereas increased add-on of DHDMI raises the accessible internal volume.

An added dimension to the after drying of DHDMI-finished fabric is the major effect of post-mercerization. Mercerization of DHDMI-crosslinked fabric with 23% sodium hydroxide was followed by dyeing. Direct dyes that normally gave poor results because of their higher molecular size were strongly absorbed. Remarkably, the dyeings were considerably deeper on DHDMI-crosslinked, post-mercerized cotton than on unfinished cotton, regardless of whether the latter was mercerized or not specifically with Direct Red 81.

Inorganic Phosphates as Crosslinking Agents

The phosphorylation of cotton cellulose can be performed by heat curing of fabric impregnated with either a 1 : 1 mixture of mono- and disodium phosphate, or preferably sodium hexametaphosphate. When the phosphorus content of treated fabric exceeds 1.6%, the fibers are found to be insoluble in cupriethylene diamine hydroxide solution, and the cellulose appears to be crosslinked.



Crosslinking of cellulosic fabric can also be achieved by phosphorylation with a mixture of

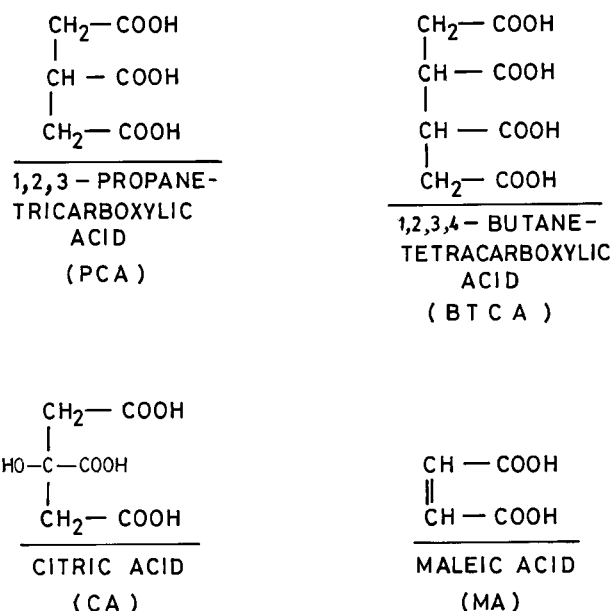


Figure 7 Polycarboxylic acids effective in durable press finishing of cotton.

urea with mono- or diammonium phosphate. A moderate level of DP properties is imparted by these pad-dry-cure methods at sufficiently high degree of phosphorylation. High levels (approximately 12%) of monosodium or monoammonium phosphate, and in some instances very high levels (12–24%) of urea are required.

Polycarboxylic Acids

Citric acid was found to be the most effective polycarboxylic acid,^{27,28} in the absence of added catalyst by pad-dry-cure treatment, although it produced more fabric discoloration than the other agents. The crosslinks were formed in cellulose by acid-catalyzed esterification with citric acid itself furnishing the protons needed for the autocatalysis. Saponification of the ester crosslinks by hot 0.1 mol/L sodium hydroxide eliminated the wrinkle resistance of the cotton fabric but did not restore the tensile strength.

Polycarboxylic acid (Fig. 7) with four to six carboxyl groups per molecule in the presence of alkaline catalysts was found to be more effective than acids having only two or three carboxyl groups. Sodium carbonate or triethyl amine was added as catalyst. These salts act as buffers and greatly diminished acid-induced tendering during high-temperature curing. The wrinkle-resistant finishes obtained were recurable. In the presence of heat, the transesterification of ester crosslinks

Table V Comparison of Some Formaldehyde-Free DP Finishing Agents with DMDHEU

Agent	Catalyst	DP Rating	Wrinkle Recovery Angle	Tear Strength Retained (%)	Breaking Strength Retained (%)
DHDMI	Zn(BF ₄) ₂	3.4	254–271	43–51	59–73
	Zn(NO ₃) ₂	3.2–3.3	249–265	64	82
	MgCl ₂	2.8–3.3	227–247	62–66	80
	MgCl ₂ -CA	2.5–3.0	241–244		45
BTCA	NaH ₂ PO ₂	4.0–4.7	285–300	51–67	49–59
	Na ₂ HPO ₃	4.0–4.2	286	63–66	59–72
	NaH ₂ PO ₄	3.5–4.4	282–304	51–59	50–55
	Na ₂ HPO ₄	4.0	267–285	65–73	55–76
CA	NaH ₂ PO ₂	3.3–4.0	240–268	62	50–61
	Mixed	3.8–4.0	247–264		55–64
DMDHEU	MgCl ₂	4.3–4.8	261–280	49–57	44–60

by neighboring cellulose hydroxyls causes the crosslinks to be mobile.

The newer catalyst which is more effective than sodium carbonate or tertiary amines is alkali metal salts of phosphorous-containing minerals acids. The order of decreasing effectiveness is as follows: NaH₂PO₂ > Na₂HPO₃ = NaH₂PO₃ > NaH₂PO₄ > Na₂H₂P₂O₇ > Na₂P₂O₇ > Na₃P₃O₁₀ = (NaPO₃)₆ > Na₂HPO₄ = Na₃PO₄ > Na₂CO₃.

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

A variety of polycarboxylic acids^{29–32} have been compared 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 295–300°. 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 with 99% respectively for the DHDMEU finish catalyzed by MgCl₂. This is attributed to the buffering action of sodium hypophosphite catalyst and the absence of Lewis acid catalysts.

Thus, 1,2,3,4-butanetetracarboxylic acid (BTCA) is the most effective of the polycarboxylic acids studied with respect to the level of DP performance, speed of curing, laundering durability, re-

tention of fabric whiteness, and free from odor (Table V).

In the presence of weak bases as esterification catalyst, the reactions proceed by intermediate formation of cyclic anhydrides of BTCA as the actual esterifying agents. The catalyst increases the rate of anhydride formation as well as the rate of crosslinking. It was found that loss of weight corresponded to water loss as anhydrides were formed on heating BTCA and CPTA, *cis*-cyclopentane tetracarboxylic acid.³³

The effect of highly polar additives on BTCA reaction with cellulose has been studied. Triethanolamine acted as a crosslink modifier that enhanced DP appearance rating, laundering durability of the finish, and fabric strength retention. *N,N*-Disubstituted amides increased the conditioned and wet wrinkle recovery, as well as DP rating, but had no effect on fabric strength retention. The amides may have altered the hydrogen bonding, the degree of fiber swelling, and the crystallinity of the cotton. Recently, malic acid³¹ activated by BTCA or small amounts of BTCA with high concentrations of citric acid as a DP finishing agent have been found to be very effective.

Finishing of silk fabrics with a mixture of glyoxal and urethane compounds has also been reported by Kawahara and Coworkers^{34–36} 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 agents.

Tsang and Dhingra³⁷ have also given a brief account of various finishes used for silk fabrics.

Durable finishing with butanetetracarboxylic acid gave excellent results.

SOFTENING AGENTS

Softener is defined as “an auxiliary that when applied to textile material improves its handle with more pleasing to touch.” Softening of textile fabrics is generally achieved by reducing the coefficient of friction between the fibers, filaments, and yarn. Because the major function of softener is that of a lubricant rather than a plasticizer, the modulus of the fiber is not affected. Softeners are surface active agents with long chain hydrophobic part and short hydrophilic polar water solubilizing group.

Based on the polarity and the ionic nature, softeners can be classified³⁸⁻⁴² into six categories.

1. Cationic softeners: quaternary ammonium and other cationic products
2. Anionic softeners: sulphated oils, soap, sulphated alcohols and tallows, oil emulsions
3. Nonionic softeners: polyoxyethylene derivatives (ethoxylates), polyethylene emulsion, wax emulsions
4. Amphoteric softeners: imidazoline, carboxylate salts, amine oxides
5. Reactive softeners: softeners similar to reactive dyes having reactive groups attached to a long chain softening group
6. Special softeners: silicones

Anionic Softeners

The anionic softeners are generally sulfated or sulfonated compounds used primarily to lubricate yarns or fibers through processing. Generally, the anionic are good lubricants, provide soft raggy hands, and show good stability to alkaline conditions. Most show good heat stability and some have good yellowing resistance.

Anionics tend to provide inferior softness compared with the cationics and nonionics. Furthermore, they have limited durability to laundering or drycleaning. 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. Because they will not migrate or exhaust readily onto a fabric they must be applied mechanically by padding.

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. This is especially true when a polyethylene polymer is present in the system.

Cationic polyethylenes are effective in processing napped or raised pile fabrics in which fiber-to-metal friction reduction is essential. In napping softeners, 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 two parts polyethylene lubricant to one part amino amide 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. Discoloration on white fabrics may also be a concern. The development of a fishy odor on a fabric can be a problem with certain systems.

Nonionic Softeners

Nonionics are the most widely used type of softeners. This class includes polyethylenes, glycerides such as glycerol monostearate, ethoxylates such as ethoxylated castor wax, coconut oil, and corn oil, and ethoxylated fatty alcohols and acids. The nonionic 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 dyestuffs, and with careful selection, minimal impact on fastness properties. Most are resistant to discoloration and yellowing.

The most serious concern comes with the fastness of certain dyestuffs in some nonionic systems which may impart the wet or dry crock fastness. Also, because nonionics do not have any significant charge, they must, in general, be mechanically applied to a fabric by padding.

Silicone Softeners

Silicones⁴³⁻⁴⁸ have been used to formulate textile softening chemicals since the 1960s. Initially, polydimethyl siloxane (PDMS) were used. But in the late 1970s, the introduction of aminofunctional polydimethyl siloxanes opened a new dimension for textile softening. They confer high lubricity to the fiber owing to their low surface energy, but only small proportions can be used because of their high cost. Care must be taken with emulsification, because spotting can easily occur.

Methyl groups are the most important of the organic substituents used in commercial silicones, the vast majority of which are PDMS. Because of their inorganic/organic structure and the flexibility of the siloxane bonds, silicones have some unique properties including thermal/oxidative stability, low temperature flow ability, low viscosity change versus temperature, high compressibility, low surface tension (spreadability), hydrophobicity, dielectric properties, and low fire hazard. PDMS can be modified to formulate a wide range of products with tailored hydrophobicity and durability to modify the feel and appearance of fabrics or to improve the processing. Silicone softeners currently available can be classified into three groups: 1. nonreactive silicone softeners; 2. conventional reactive softeners; and 3. organofunctional silicone softeners.

Nonreactive Silicone Softeners

Nonreactive silicone softeners are based on polydimethylsiloxanes (Fig. 8). The viscosities useful for textile applications are generally in the range of 10,000 to 12,500 centistoke. Polydimethylsiloxane imparts desirable properties to fabrics because of their flexibility polymer backbone, stable bonds, and low intermolecular forces. However, the softening effect is not very durable to washing because there is no reactive sites in the polydimethyl siloxane polymer.

Conventional Reactive Silicones

These are polydimethylsiloxane polymers modified with silane hydrogen or silanol functional groups. Apart from the above, 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 which are better than PDMS. Silanol functional polymers are also the basis for silicone elastomers textiles finishes. Rooks⁴⁹ disclosed the use of high molecular weight emulsion polymerized dimethyl polysiloxane with terminal silanol reactivity as a textile finish to improve hand and performance of durable press fabrics.

Organofunctional Silicones

Aminofunctional groups which are bound to a polydimethylsiloxane backbone improve the orientation and substantivity of the silicon on the fiber. The improved orientation of aminofunctional silicones leads to an extremely soft hand, which is frequently described as "supersoft." In this class of softener, in place of silanol group in conventional reactive silicone, organoreactive groups such as amines, epoxides, and alcohols are

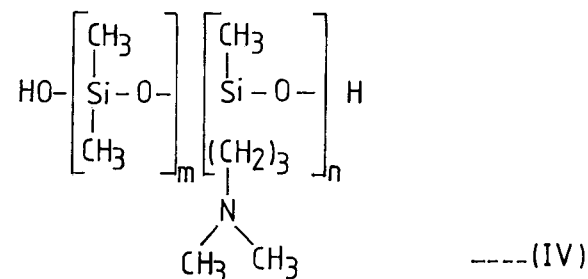
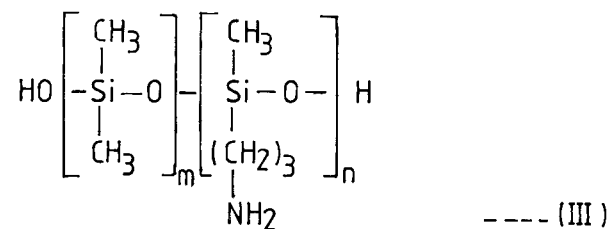
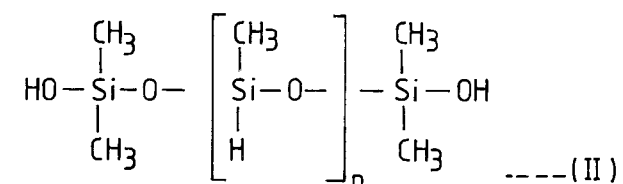
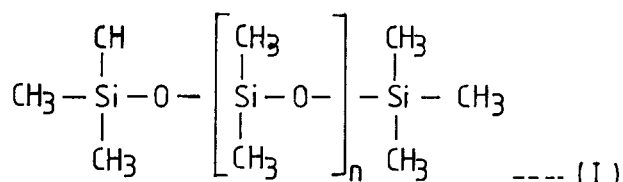


Figure 8 Chemical structure of reactive and nonreactive silicone softeners.

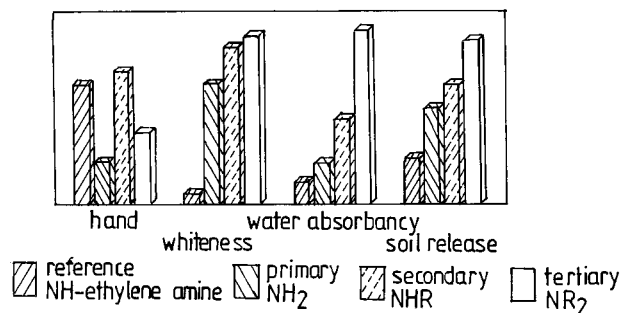


Figure 9 Properties of aminosilicone-treated fabrics.

introduced along the PDMS backbone (Fig. 8, Structure III).

New Amino Functional Silicones

The amino group (primary to tertiary) in polydimethylsiloxanes was substituted. The structure of the amino group was as follows.

R	Abbreviation	Aminostructure
—NH ₂		Primary
—NH—Me	NH-methyl	
—NH—(CH ₂) ₃ Me	NH-butyl	
—NH—(CH ₂) ₁₁ Me	NH-lauryl	
—NH—C ₆ H ₁₁	NH-cyclohexyl	Secondary
—NEt ₂ , —N		Tertiary
—NH—CH ₂ —CH ₂	NH-ethylene	Primary and secondary
—NH ₂	amine	

By comparing the effects due to primary, secondary, and tertiary amines, it is clear that whiteness, water absorbency, and soil release improve with increasing degree of substitution, from primary to secondary to tertiary (Fig. 9).

Improved whiteness arises partly 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. The very strong tendency of the aminoethylamino propyl group toward yellowing indicates a synergistic acceleration of the oxidative degradation. No conclusive structure effect correlation is possible for softness—the most important criterion for evaluation. Only the silicones substituted with secondary amine structure show values as good as the silicones based on the amino

ethyl aminopropyl group, 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 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 and Coworkers^{50,51} demonstrated the effect of “Magnasoft® TA-15” additive (which is based on dialkyl oxalate) on yellowing properties of amino-modified silicone fabric softeners. This chemical modification results in the formation of a stable emulsion of amide-modified silicone with nonyellowing 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, a blend of Magnasoft Plus (aminosilicone) and PDMS-amino polyalkylene oxide block copolymer, called Magnasoft SRS provides good softness along with soil release properties on polyester/cotton blends (Fig. 10).

Shenai⁵² deals with nonionic surfactants with considerable water solubility made from the mixed type of poly(organo-siloxanes). A very useful property of such nonionic condensates is that, unlike other silicones, which require an emulsifying agent before their application to textile materials in the form of an emulsion, they are soluble in water, and hence do not require an emulsifying agent.

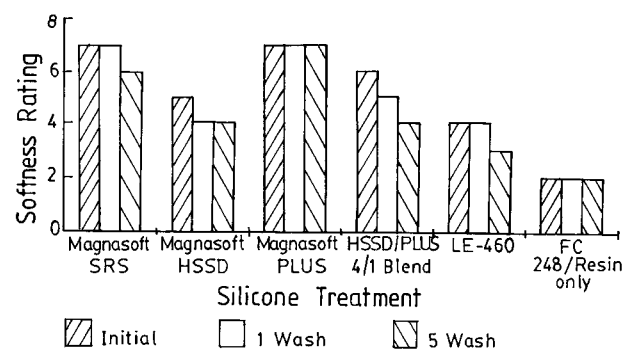


Figure 10 The effect of washing on softener ratings of 65/35 polyester/cotton rated with 1% FC-248 and 0.6% silicone.

Table VI Properties of 65/35 Terry/Cotton Treated with Resin and Softener

Bath Composition (wt %)	PE Softener	Organo-Reactive	Silicon Reactive
DMDHEU resin	18.0	6.0	6.0
Zn (NO ₃) ₂ catalyst	3.6	1.2	1.2
PE softener (50%)	1.0	—	—
Silicon emulsion (40% solid)	—	0.85	0.85
Catalyst	—	—	0.05
Silane crosslinker	—	—	0.04
Wrinkle recovery (warp) ^o	147	153	151
Flat appearance (five washes)	3.5	3.5	3.8
Abrasion cycles	10,800	10,500	10,100
Tensile (lbs.)	153	173	175
Hand	Soft	Very soft	Very soft

Application of Silicone Softeners

Silicone softeners are used by emulsion techniques. The ideal emulsifying agent is the one which is destroyed or rendered inert during the processing of the fabrics. The key factors in emulsion stability are proper choice of emulsifier, size and size distribution of the emulsified particles, and temperature.

A comparison of the properties of 65/35 terry/cotton treated with a resin and a single-component organo-reactive silicone, a three-component silicone-reactive softener, and a polyethylene softener is shown in Table VI. Both hand Panel & Kawabata Evaluation System (KES) are utilized to evaluate the performance of different types of silicone softeners for 65/35 terry/cotton blends (Table VII).

Environmental Considerations for Silicone-Based Softeners

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 wastewater discharged. They are highly resistant to biodegradation by micro-organisms, but they undergo very effective degradation via natural chemical processing. PDMS breaks down into lower molecular weight silanols. No adverse effects were seen for seed germination, survival percentage. 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 based on PDMS technology have many advantages over

initial PDMS, such as low yellowishness, high softness, high smoothness, they require a low concentration, and are environmentally safe. In addition, the ability to blend with other organic softeners while retaining their original performance is exhibited.

BIOPROCESSING OF TEXTILES

Biofinishing

Processing of cellulosic fabrics and garments with cellulase enzymes, generally referred to as biofinishing started in the late 1980s.⁵³⁻⁶¹ Superior hand and novelty finishes on rayon, linen, and

Table VII Performance of Silicone Softeners on 65/35 Polyester/Cotton Fabrics

Qualities	Silicone			
	Amino	Epoxy	Std.	Dimethyl
Softness				
Hand-panel	7.0	7.5	5.0	3.5
Calculated	6.5	6.5	4.3	2.8
Smoothness				
Hand-panel	5.0	6.5	5.0	3.5
Calculated	5.4	5.3	4.6	3.7
Crispness				
Hand-panel	2.5	5.0	5.0	6.0
Calculated	5.2	4.3	6.4	6.9
Fullness				
Hand-panel	4.0	3.0	5.0	5.0
Calculated	3.0	4.4	4.9	5.5

Pad bath: DP resin + 0.6% silicone.

Source: Text Chem Colour 1987, 19, 25.

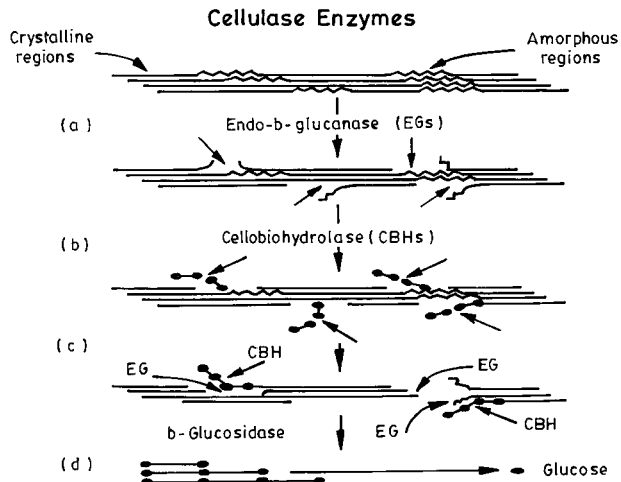


Figure 11 Schematic representation of synergistic action of enzymes on cellulose.⁶⁰

cotton knits can be achieved with cellulases. In addition, the benefits of cellulase enzyme treatment include prevention of fuzz and pills, increased smoothness and softness, increased luster, and superior color brightness.

Cellulases are multicomponent 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. The proposed mechanism of cellulase action onto cellulose is illustrated in Figure 11. Endoglucanases or endocellulases hydrolyze cellulose randomly along the chains, preferentially the amorphous region. Cellobiohydrolases or exo-cellulase attack the chain ends and produce primarily cellobiose coupled with the binding domains associated with the enzyme.

The cellobiose and any small chain oligomers produced by exo-cellulases are then hydrolyzed by the third enzyme β -4-glucosidase into glucose.

Enzymes are active at atmospheric pressure in the temperature range of 30 to 60°C. Based on their sensitivity to pH, they are classified as: acid stable (pH 4.5–5.5), neutral (pH 6.6–7), or alkali stable (pH 9–10).

Biopolishing consists of a cellulase enzyme treatment to give a partial hydrolysis of cotton or other cellulosic fiber, with a weight loss of around 3 to 5% and loss of strength of 2 to 7%. However, Kumar et al.⁶⁰ have reported the strength loss of cotton knit and viscose rayon for high surface polishing under acidic conditions at 60°C between 25 to 30%. With proper control of pH and temper-

ature, standard whole acid cellulases can be used to finish delicate cellulosic fabrics (Fig. 12). Some of the biofinishing processes used are listed in Table VIII. The effect of pre-existing dyes and the crosslinking agent on the reactivity of cellulase has been studied in depth. It seems planar structure of vat dyes with larger molecular sizes than indigo dye seems to play an important role in inhibiting the action of cellulase.^{62,63}

Stoneless Washing of Denim

The disadvantage of the pumice stones method in denim washing created incentives to develop alternate agents. The use of enzymes for denim washing^{64–66} have the following advantages over pumice stone washing: 1. superior garment quality with increased load handling (30–50%); eco-friendly and energy-saving processing (less pollution loads); less damage to seams, edges, and extra softener not necessary; less equipment wear, ease of handling, storage, and disposal.

Suitably desized denim is treated with the cellulase enzyme, after washing with detergents followed by rinsing and drying. The treatment conditions of enzymatic action depends on the garment type, design of the washing-machine, and the type of cellulase used (Table IX). The time of washing could vary between 60–120 min depending on the type of effect required. The pH depends on the type of cellulase enzyme (acid, neutral, or alkaline stable) used. Generally, acid cellulase gives best results in the pH range of 4.5–5.5. Temperature is kept between 30–60°C depending on the time of washing. If short wash cycles are used, then temperature is kept high (30 min, 55–60°C) and low temperature is used for longer wash cycles. The amount of cellulase enzyme required depends on the type of enzyme used and the substrate concentration. Acid cellulase can give the same level of abrasion with a concentration of one-fifth to one-tenth that of the liquid

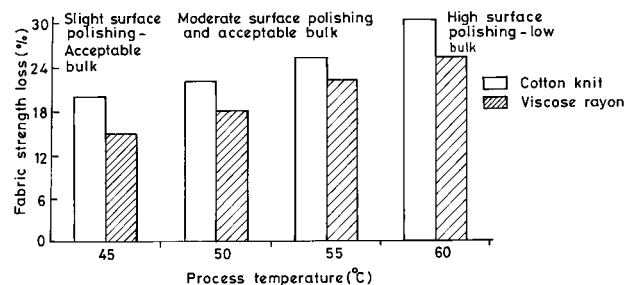


Figure 12 Effect of process temperature on fabric strength loss.⁶⁰

Table VIII The Biopolishing Process

Treatment Conditions	Results
3% Rucolase ZEV, 1 : 10 liquor ratio, pH 4.5–5.5, 55°C, 30–45 min for knitted cellulose fabrics Process designed by TS chemicals for woollen/worsted fabrics Treatment of cotton/wool blend fabric 3 or 5% owf cellulase, pH 4.5, 1 : 10 liquor ratio, 60°C, 1 h (at 60°C, 4.5 pH)	Increase in softness, better handle and washing quality Improved handle, softness, pilling resistance, cleaner surface, and improved drape
3 or 5% owf protease enzyme pH 8.5 (NaOH) 1 : 10 liquor ratio, 60°C 1 h (60°C, 8.5 pH)	Strength loss 12–18%, abrasion resistance loss 40–55%, softness increased 50–55%, pilling resistance improved, dry W.R. improved 5–11°
Silk waste treatment Soaping for 30 min (25% owf 1 : 30 liquor ratio)	Wetting time reduced, removal of impurities, removal of kitties (only 2–3% remain after the treatment)
Cellulase enzyme 30–40 μ per g of fabric, buffer of 5.2 pH, 50°C, 3 h Degummase treatment: degummase 1000 L, 50°C, pH 8.7 (buffer), 3 h Bleaching by H ₂ O ₂	

neutral cellulase, depending on the wash time. But, the use of acid cellulases causes more backstaining than the neutral or alkaline stable cellulase enzymes. The redeposition of indigo removed from the fabric that remains suspended in the liquor is termed backstaining. It is undesirable because it decreases the color contrast of the stone-washed samples.

The pH of the washing liquor exercises great influence on backstaining which is minimum at pH 7. Thus, neutral cellulase could be preferred for denim washing. Typical recipes for denim washing are shown in Table IX. Some researchers have also reported the combined effect of cellulase and pumic stone washing or combined alpha-amylase with cellulase enzyme for single-step procedure. The production of a peach-skin-like surface of cellulosic or its blends has also been disclosed in a patent by Toyo Boseki.⁶⁷ A woven

fabric of polynosic rayon fibers was napped using emery paper, scoured, treated with an aqueous solution of 6 g/L Enzylon® CM (cellulolytic enzyme) at 35°C to give a fabric with peach-skin-like surface without naps. Stone washing using endoglucanases (fungal cellulase) for reduced backstaining on fabrics has also been disclosed.⁶⁸

Pretreatment Processes

Desizing of Cotton Fabrics

Because of the selective action and ecofriendliness, enzymes are commercially used for desizing cotton, i.e., breaking down of starch into water-soluble forms by the amylase enzymes.^{69–71} The amylase enzyme is highly specific and reacts only with starch. Thus, cellulose remains intact and there is no strength loss. Amylase breaks starch into low molecular weight dextrin that could be

Table IX Denim Washing

Treatment Conditions	Property Change
0.5–2.0 gpl cellulase acid enzyme, MLR 1 : 10, pH 4–5.5 (NaOH: acetic acid buffer) 55–60°C Stone-eze® (stoneless finish) Acid cellulase, MLR 1 : 10, 4–5.5 pH (buffer), 55°C	Weight and strength loss are a function of time, temperature, and amount of cellulase Improved handle, less strength loss, less damage to surface Acid cellulase does more backstaining (function of time), reproducibility more, if enzyme concn is less and stability to pH broad

washed off easily. Nowadays, liquid bacterial preparations of higher activity are also available for use.

The desizing process consists of the following steps: 1. impregnation of the enzyme solution into the fabric for thorough wetting of the fabric at 70°C or higher with suitable nonionic wetting agents; 2. incubation, where breakdown of starch into water-soluble dextrans takes place by steaming at 110–115°C for 15–20 s; and 3. after wash to remove the size breakdown products from the fabric.

Removal of Cotton Pectin

Cotton pectin forms 1% and is a major component of the impurities present in the primary wall of fiber as well as deposits in the lumen from dried protoplasm. Pectins are present as water-insoluble calcium, magnesium, or iron salt in cotton. This insoluble form can be converted into soluble form by exchange of polyvalent cations with monovalent cations such as ammonium or sodium. The conventional process of pectin removal involves a severe boil with high concentration of caustic soda for many hours, but with the pectinase process, the pectin could be removed effectively in a short time. Chloroform-extracted cotton is treated with suitable enzyme concentration at 50°C and pH 5. It is observed that enzyme degradation is very rapid and after 1 h, 70–80% of the pectin gets degraded.

Pretreatment of Wool and Silk

In the recent past, there has been an ever-increasing interest for the introduction of enzymes in wool processing.^{72–75} Areas of special interest are increased comfort, increased softness, surface appearance, and reduced pilling performance. The treatment of wool by Bactosol® SI has a significant effect in reducing wool shrinkage and at the same time improving the whiteness as compared with the untreated sample.⁷⁵ In a patent,⁷⁶ antifelting property has been achieved by plasma treatment followed by treatment with a protease, preferably subtilisin.

Application of enzymes in degumming of silk and bast fibers has also been reported. Recent research has shown the effectiveness of enzymatic action on processing of waste-silk fabric. Silk spun from waste silk poses some problems during processing because it contains many impurities in the form of broken chrysalis, straw, lignin, hair, and some cellulosic particles. Conventional processes are not effective in removing

all the impurities but protease enzymes that are capable of hydrolyzing the peptide bonds are for silk degumming^{77,78} and in wool processing/finishing as well. Proteases have been reported to give the fabric a softer handle and reduced lousiness. The procedure recommended for scouring and bleaching of the spun silk is: soaping, treatment with enzyme degum of suitable concentration at 50°C for 3 h, at pH 5.2, and bleaching with hydrogen peroxide. Such a process enhances the surface characteristics, wettability of the fabric, and removes the impurities as well. Some of the enzymes used in processing of natural fiber fabrics are listed in Tables X and XI.

WATERPROOF BREATHABLE FABRICS

Waterproof/moisture permeable fabrics from several synthetic fibers have been designed for skiwear, track suits, rainwear, and mountaineering clothing.⁶⁷ The application of a one-piece overall made from a woven nylon fabric (30-den flat nylon warp yarns; weft of 900-den air jet textured yarns) in the 1986 dogsled race in Alaska has been described by Hunton.⁷⁹ A nylon glove with a Gore-Tex® liner was also designed for this purpose.

Woods⁸⁰ has studied the relation between clothing thickness and cooling during motorcycling in the range from –1 to +24°C. To maintain a normal body temperature in winter on a motorcycle without a protective shield, much thicker clothing (a mean clothing thickness of 20 mm) inside the windproof oversuit is needed at 5°C, but it is only effective if perspiration does not accumulate inside the clothing.

Lightweight 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, condensation can accumulate on their inner surface. This problem arises because of the water-vapor impermeability of the polymer coating. A buildup of moisture vapor inside the clothing may therefore cause discomfort.

To overcome this problem, breathable polymer coatings are now available that have made possible great improvements in the comfort of this type of clothing. Microporous polytetrafluoroethylene (PTFE) Gore-Tex® laminates have been successfully introduced as breathable fabrics.^{81,82} Comparative assessment of Gor-Tex® and Neoprena®

Table X Pretreatment Process

Treatment Conditions	Property Change	Reference
Cotton		30
Boerozym AC, CA3, CB# enzyme 1 : 30 MLR, pH 5 (citric acid: NaOH buffer), 40°C	Wt loss 6%, T.S. loss 5%, 10% after alkaline boil, Boerozym AC shows high swelling, CA3 shows poorest whiteness	
Alkaline peroxide boil Cellulase enzyme, 1 : 10 MLR, pH 5, 30 s, stored at 60°C in a moist cabinet	T.S. loss up to 40% (for 24-h treatment), average DP reduces, whiteness reduces 8–10%, capillary action rise increases, Tegewa drop spread increases	31
Pectinase process to remove pectin, fabric wt 80 g, 3 µg/mL of enzyme concn in 1 L, pH 5, 60°C	70–80% pectin removal after 1 h	21
Silk		32
Silk degumming Biopril 50 (2.5 g/L), 1.0 g/L nonionic wetting agent, pH 9, 50°C for 6 min	Up to 90% degumming achieved	

vapor barriers in firefighter suits has also been made.⁸³

A breathable fabric is waterproof and breathable because of the enormous difference between the size of a water droplet and a water-vapor molecule. The former is 100 µm in diameter whereas the latter is 0.0004 µm, i.e., there is a factor of around 250,000 between the two sizes.⁸⁴

Classification of Breathable Fabrics

The breathable fabrics can be classified into three main categories^{85,86}: 1. coated fabrics^{87–90}; 2. laminated; and 3. high-density woven fabrics.

Microporous Coating and Laminating Films

The microporous barrier layer “breathes” primarily through a permanent air-permeable pore structure. Diverse techniques have been used to manufacture microporous coatings and films. The most important methods are listed below.

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 Gore-Tex®, two-layer and three-layer laminates. The thin microporous membrane is made from solid PTFE sheet by a novel drawing and annealing process. In drawn form, the tensile strength is

increased three-fold. The manufacturers claim that these PTFE membranes contain approximately 9 billion pores per square inch, with a pore volume of up to 80% and a maximum pore size of 0.2 µm.

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 dimethylformamide is being used exclusively as the solvent and the fabric is passed through a 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 nonsolvent. 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 lower boiling solvent (methyl ethyl ketone) evaporates preferentially as the fabric passes through the oven thereby increasing the concentration of the nonsolvent in the coating. When the concentration of the nonsolvent reaches

Table XI Enzymes Used in Textile Processing

Trade Name/Source	Principal and Additional Enzymes	Primary Action on Substrate	Utilization	Recommended Values	
				pH	°C
Animal diastase, dog pancreas glands	α -Amylase, protease, lipase	Liquifies starch	Desizing agent in textile industry sewage disposal	6.8–7.0	38–40
Exsize®	α -Amylase, protease	Hydrolyzes starch	Desizing of textile	6.5–7.0	60
Gumase®	Polysaccharidase gums, mucilages	Hydrolyzes vegetable oil well-drilling fluids	Baking, sizing textiles	4.0–6.0	40–50
HT-44 and HT-440 bacterial	α -Amylase, protease	Liquifies starch	Textiles, adhesives, paper, brewing grain alcohol	5.5–7.5	20–75
NF-VIII papain, papaya plant (potency adjusted to NF VIII)	Protease	Hydrolyzes protein	Softening woollen fabrics, toothpaste	5.0–6.0	—
Pancreatin pancreas glands	α -Amylase protease, lipase	Liquifies starch, protein, fat	Leather, pharmaceuticals, textile desizing	6.0–8.0	20–50
Rapidase®, bacterial	Amylase	Hydrolyzes starch	Desizing	—	—
Rapidase, S-400 bacterial	Protease	Hydrolyzes proteins, gelatin	Desizing, degumming of silk	—	—
Rhozyme® PF	Protease, amylase starch	Hydrolyzes protein products, laundry, brewing, dairy, 6×fish, fresh water	Textile paper, photographic	5.0–8.5	60
Rhozyme H-39 bacterial pentosanase	α -Amylase heat stable substituted starches, pentosans	Liquifies starch, cocoa, and candy; distilling and fermentation; laundry paper; starches and syrups; textiles; miscellaneous	Baking, brewing, cereals	4.0–10.0 (optimal 6.1)	60–80
SL Papain® (standardized with lactose)	Protease	Hydrolyzes proteins	Softening woollen fabrics, toothpaste	5.0–6.0	—
Talase®, formulation	Amylase, protease, and gelatin	Hydrolyzes starch, gum	Textiles	6.0–8.0	20–50
Texzyme® (liquid or L-253 powder)	Protease	Hydrolyzes proteins	Desizing textiles (silk and rayon fabric)	6.5–7.0	33–40
RSR, formulation	Protease	Hydrolyzes proteins	Garment cleaning	—	—

Source: Asian Text J, Feb. 1997, p 48.

a critical level, the polyurethane precipitates out in a highly porous form and the remainder of the solvent and the nonsolvent evaporate from the coating as the fabric passes through the oven.

Solvent Extraction

Finely divided water-soluble salts or other compounds can be formulated into the polymer and

subsequently extracted from the dried film or coating with water to get a microporous structure.

Electron Bombardment

A process has been developed for rendering the solid coated fabrics microporous by bombarding the polymer coating with an electron beam. The technique involves feeding the coated fabric between two electrodes generating high-voltage electrons which can be focused into discreet beams with a drill through the coating without damaging the fabric beneath.

Ultraviolet–Electron Beam Curing

The Sunbeam process is used to manufacture microporous films and coatings *in situ* by crosslinking suitable monomers with electron beam or ultraviolet light. Radiation curing has the following advantages over the conventional methods: 1. low energy consumption; 2. low environmental pollution; 3. fast curing, and thus fast processing; and 4. short start-up times.

Crushed Foam Coating

Mechanically foamed and thickened lattices are coated onto fabric and dried. Large surface pores are formed which are compacted by calendaring through a pressure nip to yield a microporous fabric.

Hydrophilic Coated and Laminated Fabrics

Hydrophilic coated and laminated fabrics transmit water vapor selectively by a molecular process, i.e., by absorption, diffusion, and desorption through the solid polymer layer. Such a polymer film or coating shows no evidence of voids or microporous structure, and thus is not susceptible to surface contamination by dirt, dust, etc.

The sensitivity of solid polymer to liquid water is extremely variable and depends on their physical and chemical composition. The solid polymer may be completely soluble in water, for example poly(vinyl alcohol), polyacrylic acid, etc. They are too sensitive to liquid water and would either dissolve completely or else would not withstand the rigors of normal use. Thus, they are unsuitable for use as permanent, flexible fabric coatings or polymer films.

The efficiency of water-vapor diffusion through intermolecular pores can be increased by creating a succession of chemical groups (i.e., amines, hydroxyl, carboxyl) which are capable of forming

reversible hydrogen bonds with water-vapor molecules. These groups thus act as “links or conduits,” allowing water-vapor molecules to pass through the polymer from an area of high concentration to an area of low concentration. This mechanism is specific for water vapor and does not allow oxygen, nitrogen, and CO₂ molecules, which are incapable of forming hydrogen bonds.

The water-vapor transmission (WVT) rate in hydrophilic polymers under steady state is given by the relationship,

$$\text{WVT} = \frac{DS(P_1 - P_2)}{t}$$

where $P_1 - P_2$ = partial pressure gradient between the two surfaces; t = thickness of the polymer coat; D = diffusion constant governed by the nature of the hydrophilic polymer; and S = solubility coefficient. The solubility coefficient depends largely on the molecular attraction between the polymer chains and the penetrant. For example, hydrophilic polymers have high solubility coefficients.

Sympatex membrane (made of copolyester) has no pores thus making it absolutely tight to water and wind. However, this can allow water vapors to pass through by the use of a special type of polyester whose molecules have water-vapor transporting properties.

Tarka fabrics are also given a water-repellent finish using 3M's Scotchgard™ fabric protector. Penn-Nyla showed that “unlike other transfer coatings which leave a relatively impervious polyurethane film on the fabric, the Tarka process incorporates a microporous layer, allowing a greater degree of breathability.”

The Tarka fabrics have been extensively tested for practical performance in relation to water-proofness, breathability, and durability by the Ken Ledward Equipment Testing Service, a well-known sportswear testing company, in a program giving the equivalent of 8 months of rigorous use on demanding environments such as the UK's Lakeland Fells and the Austrian Tyrol. The British Textile Technology Group has also performed tests based on both existing and proposed new standards for coated fabrics and for waterproof breathables. Penn-Nyla reports that Tarka fabrics passed all these tests by at least twice the required levels.

New Route

A very novel approach to achieve a waterproof and breathable fabric, using nonporous mem-

branes, has been developed by the Shirley Institute in Manchester (now part of the British Textile Technology Group). They developed a hydrophilic polymer, which is now made by the Baxenden Chemical Company named Witcoflex Staycool®. Baxenden has perfected the techniques for coating this novel polymer onto fabrics where it forms a nonporous layer. In the same way as the Sympatex® film, this hydrophilic coating breathes by passing water-vapor molecules along “built-in stepping stones” to the outside of the fabric. Being nonporous, it also prevents liquid water from entering. The properties of the final coated fabric depend on a number of factors but Baxenden says that when the coating is applied correctly it should have the following performance specifications: 2500–8000 g/m² water-vapor transfer per day on nylon and 3500–10,000 g/m² per day on polycotton and textured fabric. The hydrostatic head which the fabric will support should be a minimum of 150 cm.

Witcoflex Staycool can be applied by standard direct or transfer coating machines. A new development from Baxenden is the X-Liner, a water-proof breathable drop liner which is sewn between the outer fabric and the lining. In this case, moisture-vapor permeability of over 12,000 g/m² per day can be achieved.

Uncoated High-Density Fabrics

In open-weave fabrics, water vapors transmit mainly through interyarn spaces and transfer through individual fibers, and fiber bundles are relatively unimportant. Thus, fabrics of similar open construction, weight, and thickness are expected to show similar transmission rates, irrespective of the type of yarn or fibers used. As the size of the interyarn spaces decreases, the secondary transmission mechanisms become more important. Thus, tightly woven fabrics constructed from absorptive or hydrophilic fibers are more transmissive of water vapor than similar construction of nonabsorptive, hydrophobic fibers.

A number of high-density fabrics have been marketed recently. They use yarns produced from microfibers of less than 1 decitex per filament. Example of some microfiber yarns used for high-density fabrics are:

- ICI with Tactel® micro/24 carat (0.4 dpf) polyamide used, by Finlayson in Microspirit®
- DuPont de Nemours fibre: Supplex® (0.9 dpf) polyamide

- Burlington's Versatech® microfiber-based fabric
- Hoechst with its microfiber Trevira-Finesse® (0.65 dpf) polyester, used by Rotofil AG to weave their CLIMAGUARD®
- Formesa Taffela Co. Microfeel® with nylon and polyester microfibers
- Asahi Kasei developed Leofeel® and Super microft® with microfibers
- Toray Ind. with Dyna-bright® to weave their H₂Off®
- Kuraray with WRAMP to weave Arcus®

Combination

Breathable fabrics can also be obtained by the combination of the above-mentioned techniques, such as a hydrophilic finish on a microporous structure to upgrade the water resistance of the microporous coatings. For example, Ucecoat® NPU 2307 finish on top of Ucecoat 2000 (S) microporous coating is used.

Mechanism of Water-Vapor Transmission

Through textiles, water vapors and liquids are transmitted by the following mechanisms: 1. simple diffusion through the interyarn spaces. The resistance to diffusion is governed by the fabric construction, i.e., the size and concentration of the pores and the fabric thickness; 2. capillary transfer through fiber bundle. The liquid water is wicked up through the yarns and desorbed or evaporated at the outer surface. The nature of these interfiber spaces is determined by the choice of yarn and fabric construction; and 3. diffusion through individual fibres. The ability of the fiber to undergo water-vapor diffusion depends on the hydrophilic or hydrophobic nature of the fiber.

A polymer coating consists of a mesh of relatively thin sections, representing the areas of polymer covering the yarn crowns and thicker sections where it has penetrated into the fabric interstices.

In the case of hydrophobic fabrics, the transmission occurs mainly through the interstices of nonabsorptive, hydrophobic fabrics, and hence through the predominately thicker areas of the polymer barrier whereas cotton or polyester/cotton substrates can also utilize the hydrophilic properties of the fiber bundles under the thinner areas of the polymer coating and thus tend to be more water-vapor permeable than coated hydrophilic of similar structure. Table XII shows the water-vapor resistance of clothing.

Table XII Water-Vapor Resistance of Clothing Fabrics for Comparison

Fabrics	Water-Vapor Resistance (mm Still Air)
PVC coated	1000–2000
Waxed cotton	1000+
Leather	7–8
Typical nonwovens	1–3
Woven microfiber (nylon or polyester)	3–5
Closely woven cotton	2–4
Ventile 128	3–5
Two-layer PTFE laminates	2–3
Three-layer laminates (PTFE, PE)	3–6
Microporous PU (various types)	3–14
Open pores	3–5
Sealed pore	6–14
Hydrophilic PU coated	4–16
Witcoflex staycool in nylon, polyester	9–16
On cotton, poly/cotton	5–10

ANTIMICROBIAL FINISHES

Textiles and fibrous materials are subjected to various finishing techniques to afford (a) protection for the user of textile materials against bacteria, yeast, dermatophytic fungi, and other related microorganisms for aesthetic, hygienic, or

medical purposes; (b) protection of the textile itself from biodeterioration caused by mold, mildew, and rot-producing fungi; and (c) protection for textiles from insects and other pests. A representative range of bacteria and microorganisms⁹¹ used in the evaluation of the antimicrobial activity of protective textiles are listed in Table XIII. Of these, *Staphylococcus aureus*, a pathogenic Gram-positive bacterium, is the most frequently evaluated species, for it is the major cause of cross-infection in hospitals as well as in commercial and home laundry practices.

In an extended review, Vigo⁹² has covered various aspects of finishes, their types, modes of application, and efficacies against different microorganisms and insects, and specific requirements related to end-use, such as persistence and resistance to biological attack as a function of fiber type, as well as synergistic, antagonistic, and cumulative effects of such finishes on other textile properties and many other aspects concerning fiber/finish interactions.

Mechanisms for Antimicrobial Action

Basically, there are three mechanisms by which antimicrobial agents provide protection to textiles and the wearer. These are: 1. the controlled-release mechanism; 2. the regeneration principle; and 3. the barrier or blocking action.

The majority of antimicrobial protective finishes function by the controlled-release mecha-

Table XIII Representative Bacteria Used in Evaluation of Antimicrobial Activity of Modified Fabrics

Species	Resulting Disease or Condition	Typical End-Use
Gram-positive bacteria		
<i>Staphylococcus aureus</i>	Pyrogenic infections	Hygienic, medical
<i>Staphylococcus epidermidis</i>	Body odor	Aesthetic
<i>Corynebacterium diphtheroides</i>	Body odor	Aesthetic
Fungi		
<i>Candida albicans</i>	Diaper rash	Hygienic
<i>Epidermophyton floccosum</i>	Infection of skin and nails	Hygienic
<i>Trichophyton interdigitale</i>	Athlete's foot	Hygienic
<i>Trichophyton rubrum</i>	Chronic infections of nails and skin	Hygienic
Viruses		
<i>Poliomyelitis virus</i>	Poliomyelitis	Medical
<i>Vaccinia virus</i>	Localized disease induced by vaccination against smallpox	Medical
Protozoa		
<i>Trichomonas vaginalis</i>	Trichomoniasis vaginitis	Hygienic, medical
<i>Trematode (blood flukes)</i>	Schistosomiasis	Hygienic, medical
<i>Schistosoma japonicum</i>		

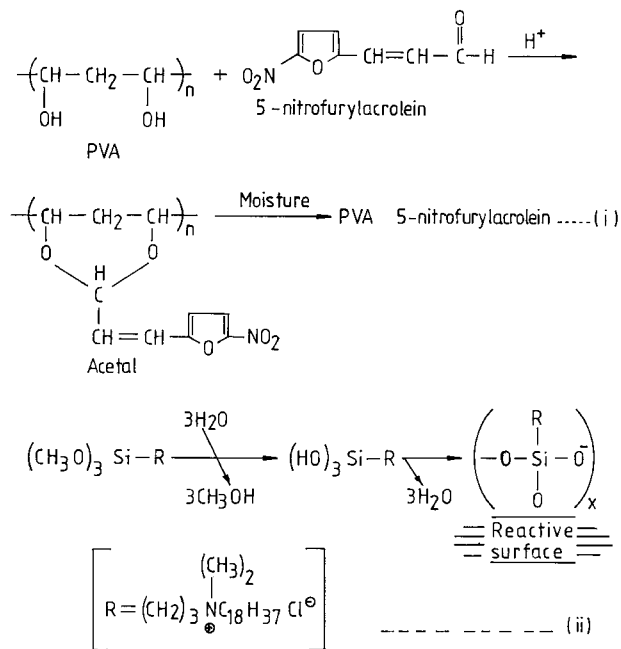


Figure 13 (i) Antimicrobial activity by slow release of the nitrocompound in the presence of moisture; (ii) chemical fixation of alkoxyasilanes.

nism, as do insecticides and insect repellents, even those coapplied to fabrics with film-forming polymers. An excellent example of the controlled-release mechanism is the fiber Letilan®, which is a broad-spectrum antimicrobial fiber. In the preparation of this fiber, poly(vinyl alcohol) fibers are converted to an acetal by their reaction with 5-nitrofurylacrolein in the presence of an acid catalyst. Antimicrobial activity is produced by slow release of the nitrocompound in the presence of moisture (Fig. 13). Another example of the controlled release of an antibacterial substance from fabrics is the Permax process, in which the slow release of zinc and peroxide occurs after repeated laundering. The effectiveness of the controlled-release antimicrobial finish is dependent on properties such as partition coefficient, surface absorption, vapor pressure, and water solubility, which affect the potency of such fungicides and the rate at which they leach off fabrics exposed outdoors. The percentages of peroxide and zinc retained after an initial Permax treatment (5-min cure at 85°C) on cotton are presented in Figure 14. It was noted that the antibacterial activity of the modified cotton fabrics was diminished when zinc and peroxide release subsided.

The regeneration model involves application to a fabric of a finish that would release an active germicidal agent continually regenerated by, for

example, the addition of bleaching agents during the laundering of fabrics or the exposure of a fabric to ultraviolet radiation. The regeneration is achieved by breaking covalent bonds in the chemically modified fiber during laundering or photochemical exposure; thus the model has an unlimited reservoir of a bactericidal agent. The regeneration model still remains a theoretical possibility, although the microencapsulating technique comes very close to it in principle. In this technique, the active agent is sandwiched between two protective plastics layers and migrates to the outer layer as needed when the agent is leached out by water or degraded by ultraviolet radiation. The reservoir of microencapsulated antibacterial agent or insecticide is not unlimited, although the surface remains active for a long time. Thus, microencapsulation is not truly a regeneration system and can be categorized under both the controlled-release and regeneration model classes.

The barrier or blocking mechanisms for protecting fabrics from microbiological attack are effected (a) through either inert physical-barrier films or coatings that are impervious to the transmission of microorganisms through the fabrics, or (b) through the use of films or coatings that have

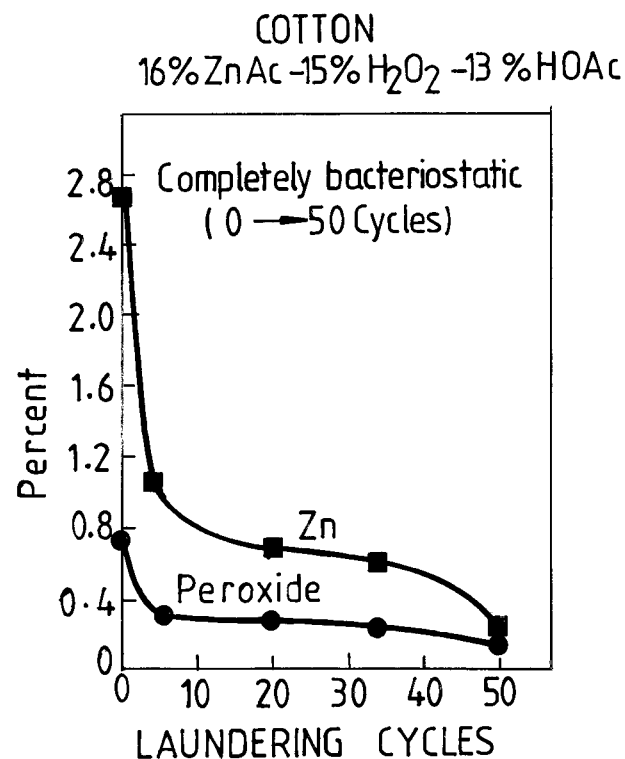


Figure 14 Percentage of peroxide and zinc retained after initial Permax treatment (5-min cure at 85°C).

Table XIV Finishing Techniques for Multipurpose Biological Protection of Textiles

Finishing Technique	Chemical Agents	Organisms Protected Against	Fiber Type
Insolubilization	$(n\text{-Bu}_3\text{SnO})_2$ TIX	Gram-positive bacteria, dermatophytic, and mildew fungi	Polyamide, acrylic, polypropylene fibers
Homo- and copolymerization	Acrylamido-8-hydroxyquinolines and metal salts	Bacteria, mildew fungi	Cellulosic fibers
Resin treatment	Hexachlorophene and DMEU+	Bacteria, mildew fungi	Cellulosic fibers
Covalent bond formation	5-Nitrofurylacrolein	Bacteria, mildew, and yeast fungi	Poly(vinyl alcohol) fiber
Coatings	Hydrolysis product of $(\text{CH}_3\text{O})_3\text{Si-R}$	Bacteria; dermatophytic, yeast, and mildew fungi; algae	All types
Microencapsulation	Any bactericide, pyrethrins, pheromones	Bacteria and insects	Many types

direct surface-contact activity against microbial growth. Achieving protection by the use of an inert physical barrier or coating usually requires much higher add ons than coatings having direct surface contact activity. The only antibacterial finish based on the barrier concept of direct surface contact activity has so far been an organosilicon polymer containing pendant quaternary ammonium groups that form biobarriers on the fabric. The hydrolysis and condensation of a typical 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride with a surface containing a reactive functional group is shown in Figure 13.

The polysiloxane is formed from the application of an alkoxysilane/methanol emulsion, which, upon exposure to air and heat, releases methanol and water to form the polysiloxane. Several problems, however, are associated with this form of topically applied barrier protection. These are that (a) methanol release occurs during the alkoxysilane-bonding processes, which poses toxicity and flammability problems; (b) alkoxysilanes are incompatible with aqueous-emulsion based textile finishes, which leads to undesirable finish application and durability problems; (c) the quaternary-ammonium ion, incorporated into the polysiloxane as a side chain, usually contains a chloride counter ion, which causes severe corrosion problems; and (d) the alkoxysilane, which undergoes a condensation reaction, bonds permanently only to those samples with available hydroxyl groups and thus will adhere permanently to cellulosic fibers but not to acrylic fibers.

To protect against disease-causing bacteria and pathogenic fungi, fibers and fabrics need treatment with antimicrobial agents, because there are no chemically unaltered natural or synthetic fibers that are inherently resistant to these microorganisms. There are, however, differences in the persistence and retention of these microorganisms in various types of fibers. Synthetic fibers retain more odor-causing bacteria than do natural fibers. However, natural fibers such as cellulosic fibers are much more susceptible to attack by mildew and rot-producing fungi and algae than are synthetic fibers. Synthetic fibers, however, are not free from these attacks as evidenced by the reports of mildew growth on nylon, poly(vinyl alcohol), and polyurethane-coated fabrics.⁹¹

Application of Antimicrobial Agents

There is a large variety of antimicrobial agents, whose functional efficiencies depend on the type of biological attack as well as the method of application to the textile substrate. A list of finishing techniques, the types of chemical agents in use, the organisms protected against, and the fiber types on which the finishes are applied, is presented in Table XIV. The application of antimicrobial finishes generally involves the following methodologies: (a) insolubilization of chemical reagents in or on the fiber; (b) graft polymerization, homopolymerization, and/or copolymerization onto the fiber; (c) treatment of the fiber with resins, condensates, or crosslinking agents; (d) chemical

modification of fibers by the formation of covalent bonds; (e) coating of the fiber surface; and (f) microencapsulation of a chemical agent with the fiber in a matrix.

Antibacterial cotton/fabrics containing peroxide complexes of zirconyl acetate have also been reported by Vigo⁹³ and *Santibac*[®] and *Santimit*[®] finishes been developed by SITRA.^{94,95}

SILK-LIKE POLYESTER

Polyester fiber has conquered the leading position among the three major synthetics because of its excellent properties such as high strength, abrasion resistance, wash and wear, and wrinkle-free characteristics. However, polyester does have some deficiencies, i.e., it is hydrophobic and oleophilic. Because of this, it is easily soiled and accumulates static charge. Oily stains are also difficult to remove. Polyester fabrics are, therefore, not as comfortable as natural-fiber fabrics.

To overcome some of these problems, blending with natural fibers, particularly cotton, gained a big market. An extensive work related primarily to polyester fabric comfort has been published in excellent reviews in the recent past. From the wearer trials using knit fabrics, it was reported that the comfort of polyester was substantially improved by cross-section variations, pressure jet treatments, and certain engineering modifications of the polyester.

Then, the Japanese industry has also made great strides in improving the comfort and aesthetic properties of polyester. Silk-like polyester Shingosen[®] has been developed by different technologies. Various approaches have been tried to develop silky polyester⁹⁶ by simulating the characteristic features of silk fiber: 1. the design of cross-sectional shape; 2. enhancement of drape characteristics through weight reduction of conventional polyester fibers or by the development of fine denier fibers; and 3. creation of moderate bulk and soft handle.

Cross-Sectional Shape

The shape of a silk fiber after removing sericine during scouring is triangular. For initiating the triangular shape of silk fibers, polyester fibers have been developed with triangular or trilobal cross-sections. This resulted in lustrous polyester fibers. The appearance also changed from that of plastic to a silk equivalent.

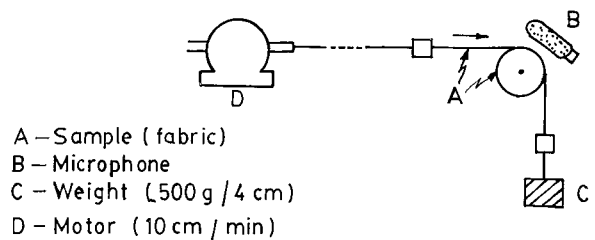
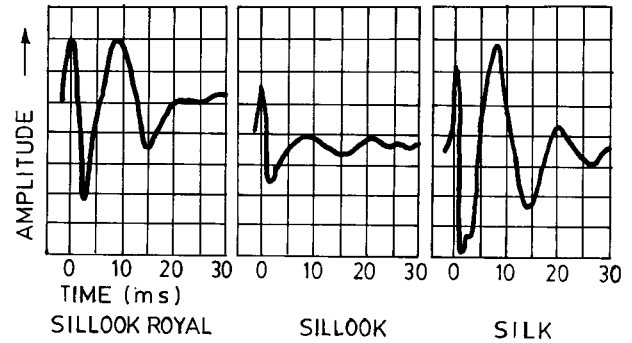


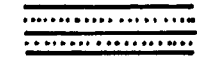
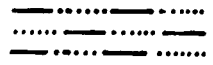


Figure 15 Wave of rustling sound of three typical fabrics.

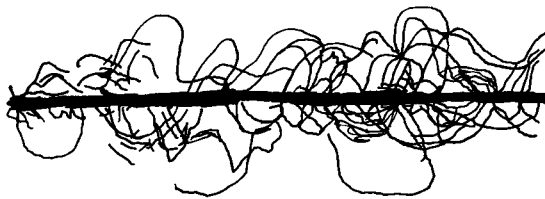
Polyethylene terephthalate (PET) fibers with a tripetal cross-section have also been developed to provide a silky look. There is a groove at the tip of each lobe of trilobal cross-section. This unique cross-section is believed to bring the rustling sound to polyester fabrics when friction occurs among them. The wave of rustling sound of three typical fabrics has been compared (Fig. 15). Sillook royal also has a rustling sound similar to that of natural silk.

Polyester fibers with petal-like cross-sections have been produced by conjugate spinning technology. In this process, small amounts of easily hydrolyzable components are located at the tips of each lobe. During saponification or caustic treatment, this component gets dissolved and grooves are formed. The width and depth of each groove can be controlled at the submicron level.

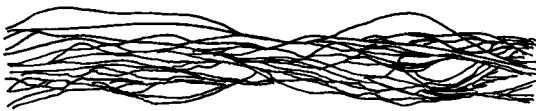
Differential Shrinkage Polyester Yarn

One of the technologies that brings out silk-like bulk and handle in PET is the use of differential shrinkage polyester component yarn. Two methods have been tried to produce different shrinkage levels in mixed yarns. One is a parallel sort of

TYPE	PARALLEL	SERIAL
Method	Mixed yarn of different shrinkage level	Random heat-set among individual fibre
Yarn		
		



Parallel yarn structure



Serial yarn structure

Figure 16 Shrinkage mechanism: parallel and serial yarn structures.

mixture, just like Quiana (nylon yarn produced by DuPont) and the other is a serial kind.

The parallel structure is made by mixing fibers of different shrinkage levels either by using different polymer fibers or by mixing fibers of polyester drawn at different temperatures. The serial type is produced by random heat setting along individual fibers during fiber processing.⁹⁷ The fibers shrink randomly with the heat treatment. In the parallel structure, higher shrinkage components form a core, and lower shrinkage components form waves or loops around the core. However, in the serial type structure, higher and lower shrinkage parts are distributed randomly in the yarn and there is no core. The resulting fabric from serial type arrangement of different shrinkage level fibers showed a more natural silk look than the parallel type (Fig. 16).

Uchida⁹⁸ has also demonstrated the role of shrinkage in producing Shingosen. Fukuhara from Toray Industries has shown that, for the production of Shingosen, initially the dry-heat shrink process was tried and later the wet-heat shrink process. But, a double-shrunk fabric ap-

pears to be closest to silky textiles. It has comparatively higher bulkiness and is more airy and soft. Silook Sildew, produced recently, is a double-shrunk fabric with large waves or loops on the surface of the fabric (Fig. 17).

For making double-shrinkage fibers, the researchers have to first design the polymers by selecting a suitable comonomer and its content for accomplishing the desired shrinkage level. The degree of polymerization (dp) should also be controlled because a polymer with a higher dp is likely to provide higher shrinkage.

After screening the polymer with a desired composition and dp, the fibers can be made from two or more polymer components by the same spinneret from different nozzles. This kind of conjugate spinning provides fibers with *in situ* differential shrinkage. So, additional step for mixing fibers as discussed above is not required and the resulting mixture directly produced from spinning line is uniform.

Topical Finishes

The enhancement of polyester properties by treatment with aqueous sodium hydroxide was recognized soon after the invention of polyester.⁹⁹ Treatment of untextured yarn fabric with alkali produces softer tactility with a less synthetic hand. A calendar heat-set and caustic soda saponified fabric was patented a few years later as the treatment was said to produce high fabric lustre without paper-like handle.

Polyester undergoes nucleophilic substitution and is hydrolyzed by aqueous sodium hydroxide. The hydroxyl ions attack the electron-deficient

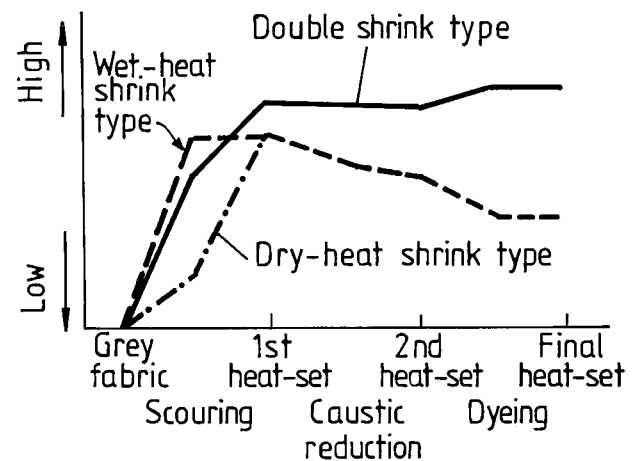


Figure 17 Shrinkage diagram of polyester fabric after caustic treatment.

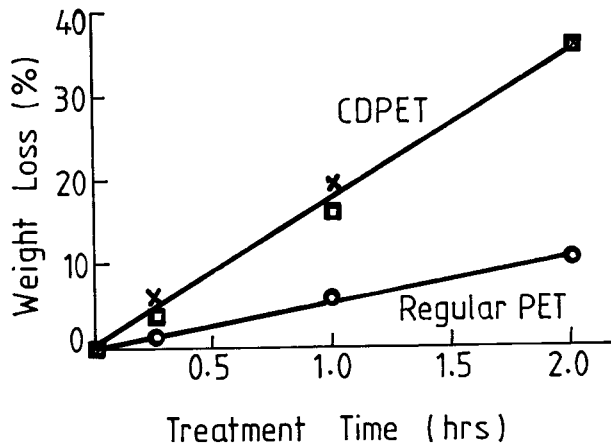


Figure 18 Polyester fabric treated with aqueous caustic soda. (○), Regular polyester; (×), regular polyester having CTAM; (□), AMPET.

carbonyl carbons of the polyester to form an intermediate anion. Chain scission follows and results in the production of hydroxyl and carboxylate end-groups.

The effect of caustic solution on a PET fabric depends on the following parameters^{100–105}: concentration of alkali; time and temperature of alkali treatment; use of surfactants; fiber type (composition and cross-section); and head setting.

The fiber loses weight as the reaction occurs. Over a wide range of temperature, the relation between weight loss and time or square root of residual weight and time has been found to be linear provided that a large excess of alkali is used so that the reagent is not largely consumed during the treatment time. If an excess of alkali is not used and its concentration decreases as the reaction continues, then the weight loss/time relation becomes exponential. It has been concluded that the influence of temperature on the rate of the reaction is greater than that of concentration of alkali, which, in turn, is greater than that of time. Use of quaternary ammonium salts as accelerators for saponification has also been recommended.

Samples hydrolyzed using 10% aqueous sodium hydroxide at 60°C showed a linear relationship between the weight loss and the alkali treatment time (Fig. 18). Further, the addition of a cationic surfactant, namely certrimonium bromide (cetyl ammonium bromide), CTAM, or the replacement of PET with an anionically modified polyester (AMPET) increases the rate of saponification considerably. Gawish and coworkers have shown that the rate of hydrolysis of polyester crepe fabric in 10% NaOH (owf) at 130°C was very

slow and it required 6 h to the theoretical weight loss of 24%. However, with the addition of different quaternary ammonium surfactants as accelerators, the rate of hydrolysis could be enhanced significantly. The activity of the quaternary ammonium surfactants was in the following order: cetyl ethyl methacrylate dimethyl ammonium bromide (CEMDA) > cetyl trimethyl ammonium bromide (CTAM) > oleyl bis-(2-hydroxyethyl)-cetyl ammonium bromide.

In the presence of CEMDA and CTAM, weight loss of 24% could be achieved only in 40 min at 130°C. Correlation between weight loss, strength loss, and flexural rigidity points out that the silk-like soft handle of polyester can be realized when the fabric loses about 16% weight and the flexural rigidity reduces to about 9 mg cm by treating with 15% NaOH at 130°C.

End group analysis of saponified polyester indicates that with increasing weight loss of saponified polyester, the number of end groups of [COOH] increased and a value of 47.10 equivalents/10⁶g was achieved at 21% weight loss. The number for control was 32.8 equivalents/10⁶g. The increased number of [COOH] end groups after the saponification suggests that the reaction of alkali with polyester is of hydrolysis with scission of polyester chain molecules, resulting in more [COOH] end groups, and confirms the mechanism of hydrolysis as shown earlier.

The data on saponified polyester indicates that both the accumulated charge (acceptance potential) and $t_{1/2}$ (the time for half the accumulated charge to decay) reduce with increasing weight loss. The value of acceptance potential reduced from 200 V for the control sample to 90 V for the saponified sample (25% weight loss) and the dissipation time $t_{1/2}$ reduced from 240 to 10 s. The data also show that, up to about 13% weight loss, the acceptance potential decreased rapidly to 115 V and with further increase in weight loss to 25%,

Table XV Effect of Surface Saponification on Electric Conductivity of Polyester Samples

Sample No.	Weight Loss (%)	Acceptance Potential (V)	$t_{1/2}$ (s)
1	—	200	240
2	1.61	190	90
3	5.24	160	30
4	13.51	115	20
5	25.14	90	10

Table XVI Finishing Stages of Polyester Fiber Fabrics

Sample A	Sample B
Loom state	Loom state
Relaxation in washer (110°C, 20 min)	Relaxation in jet dyeing (110°C, 20 min)
Heat-setting in heat-setting unit (190°C, 20 s)	Heat-setting (190°C, 20 s)
Weight reduction (16% in 40 g/L NaOH)	Weight reduction (25% in 40 g/L NaOH)
Dyeing in jet dyeing machine (130°C, 30 min)	Dyeing in jet dyeing machine (130°C, 30 min)
Raising	Raising

it dropped slowly to 90 V (Table XV). The reduction in static charge accumulation of the alkali-treated polyester may be attributed to the surface saponification of polyester as indicated by the increased number of hydrophilic [COOH] and OH end groups, wicking, and, to a limited extent, the moisture regain.

The effect of the caustic solution on a polyester fabric depends also on the fiber type, fabric construction, and heat-setting conditions. Bright fibers with a round cross-section lose weight more slowly than delustrated fibers with a multilobal cross-section. Reasons for this difference in the rate of weight loss could be attributed to the following:

- For a given linear density, a multilobal fiber would have a larger surface area than a round fiber.
- The presence of delustrant may accelerate the weight loss of the fiber.
- For a peach-like effect, high-solubility polymers or inorganic particles are incorporated in PET melt, which essentially solubilize or leach out to give a pit effect on the surface, thereby affecting the feel and handle of the fabric. This radical alteration in the surface has been ensued by the Japanese to prepare dry touch yarn. Microcraters result in low convex-concave configuration.
- Samples appear to lose weight faster after texturing. For example, the losses in weight of nontextured yarn and textured yarn when treated with 5% caustic soda at 104°C for 1 h were 35 and 41%, respectively.

Matsudaira and Matsui¹⁰² have also studied the effect of various finishing stages after the loom state on the fabric handle. The difference between samples A and B is in the stage of relaxing and weight reduction (Table XVI). The effect of relaxing in a washer is expected to be greater than that in a jet dyeing machine. Overall, the

polyester fiber fabric is remarkably softened by relaxation. The improved fabric handle results from desizing, shrinking of fibers, and relaxing of internal residual stress. Subsequent weight reduction caused by alkali treatment produces an “effective gap” between the starting fibers or yarns and the resultant fibers. The minimum amount of weight reduction necessary to split fibers is expected to be approximately 10%. By using discriminant analysis with the primary hand values as variables, a distinctive zone for silk-like and peach-skin-type polyester fabric can be found.

Sodium hydroxide treatment reduces electrostatic charge generation from 280 to 100 V and the half-life from 5 to 2.5 s. Solbrig and Obendorf¹⁰¹ have reported the considerable weight loss after saponifying polyester fiber containing 2% TiO₂ (Fig. 19) and the pitting on the surface, observed through scanning electron microscopy, mainly axially oriented along the fiber surface. Treating polyester fiber with 10% aqueous NaOH at 100°C (by steaming) for 45 min produced hygroscopic polyester fiber.

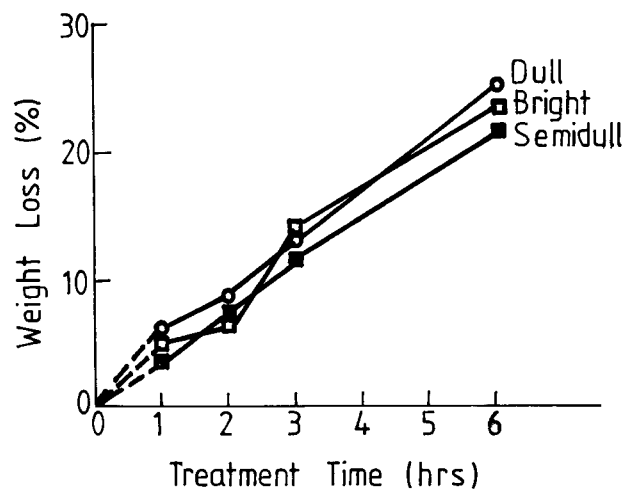


Figure 19 Change in weight of bright, semidull, and dull PET yarns over 6 h of treatment with 10% NaOH solution.

In another study, a wide range of particles have been used for creating microvoids on the fiber surface. A common method is to remove microparticles blended in the polyester polymer by alkali treatment. By applying this method to various polyester fibers containing different types of particles, fibers with various patterns of voids on the surface are obtained. Originally, this modification was performed to give depth of color.

A method of forming a controlled microcrater on the fiber surface is proposed. The fiber pre-treated by a specific resist is exposed to a laser beam and then treated again with chemicals. This process can control the dimensions of voids such as depth, length and height, and their density.

A blend containing PET and 4% BaSO₄ (>2% average diameter <9 μm) was melt spun at 1800 m/min to give 290% elongation at Kuraray Co. The fiber was used as sheath and later on textured by the Taslan process and causticized to give 30% weight loss.

For improved lustre, polyester fibers containing <0.04% inorganic oxide particles and having a birefringence of 0.03–0.08 were draw twisted for >0.15 s at 130–170° and then untwisted to give textured yarn with very good lustre.

The effect of BaSO₄ on the extent of saponification has also been studied in our laboratories. As the treatment time and concentration of NaOH progressively increased from 1 to 2 h and from 5 to 10%, respectively, the loss in weight of the polyester fiber increased from 3.03% (*P*, 5% NaOH, 1 h) to 15.2% (*P*_o, 10% NaOH, 2 h) at 90°C bath temperature.

The effect of silica particles on the lustre and handle of polyester fibers after saponification has also been studied by Yamaguchi. The fine concave and convex structure is formed by a difference in solubility in alkali between the polyester and the particles uniformly dispersed in polyester. For making a fine concave and convex structure of a specific size, first, ultrafine particles, which have a similar refraction rate to fibers and an average diameter below 100 nm, are uniformly dispersed in polyester fiber without cohesion. Silica has a tendency to cohesion by hydrogen bond of silica surface. So, silica in water is stabilized by Na⁺ cation as silica solution. To prevent silica particle cohesion or agglomeration, silica sol is mixed with ethylene glycol and particles are stabilized and PET is made by the direct esterification method.

The fibers containing silica are treated with an etching method using alkali. Their surfaces are peeled off. Silica's solubility ratio against alkali is

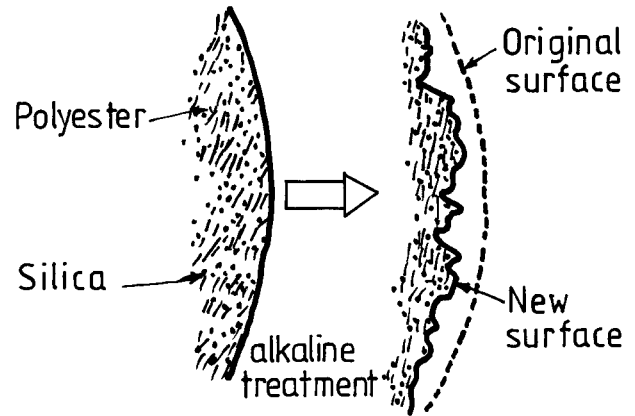


Figure 20 Effect of silica filler: fine concave and convex mechanism after alkaline treatment.

so rapid that a fine concave and convex structure is formed (Fig. 20).

SUMMARY/EMERGING TECHNOLOGIES

The challenges facing the chemical processing industry have intensified within the last decade and are now imposing a remarkable change for the finishers to survive in the global market with ecofriendly finishes. Over the last decade, the following major changes have occurred to meet the consumer's demand in terms of comfort, easy care, health, and hygiene with the commitment to keep the atmosphere free from pollutants:

- All BASF resin finishing agents have been claimed to be free from organically bound halogens, heavy metals, surfactants that contain alkylphenol ethylene oxide (APEO) and belong to water-hazard class 1.
- The major treatment methods currently used are: 1. pre-cure, 2. post-cure, 3. garment dip treatment, 4. spray technique, 5. vapor phase, 6. coating methods, and 7. tailoring of surface properties to extraordinary precision through plasma treatment.

The pre-cure and post-cure treatments are well established. In the United States, the pre-cure process is generally not accepted in the menswear market because of crease requirements; however, in ladies-wear, it finds application for some skirts and casual wear. The garment dip or spray method is also being used in the United States for both menswear and ladies-wear.

So, the emerging technologies that will dominate the research-and-development strategies of chemical manufacturers and textile finishers into the next decade are: ecofriendly formaldehyde-free finishes; bioprocessing of textiles; silicones softeners; waterproof breathable fabrics; and plasma treatment.

REFERENCES

- Sello, S. B. *J Appl Polym Sci Appl Polym Symp* 1977, 31, 229–247.
- Petersen, H. in *Handbook of Fiber Science and Technology*; Lewin, M.; Sello, S. B., Eds., Marcel Dekker: New York, 1983, vol. II, p 47.
- Petersen, H. *Rev Prog Coloration* 1987, 17, 7.
- Holme, I. *Rev Prog Coloration* 1992, 22, 1.
- Products for Textile Finishing: Ecological Evaluation of BASF Textile Chemicals, August 1994, Section 6.
- Holme, I. *Text Month*, May 1997, p 35.
- Miles, L. W. C. in *Textiles: The Technology for a Better Future*; Proceedings of the Textile Finishing Group Conference, Textile Institute, Manchester, Nov. 1995.
- Holme, I. *Text Horizons* 1996, p 17.
- Holme, I. *J Text Inst* 1993, 84(4), 520.
- Cooke, T. F.; Weighmann, H. D. *Text Chem Color* 1982, 14(5), 100/25.
- Petersen, H. *Text Res J* 1971, 41(3), 239.
- Petersen, H.; Pai, P. S. *Text Res J* 1981, 51(4), 282.
- Sello, S. B. *J Soc Dyers Color* 1985, 101, 99.
- Galek, J. *Text Horizons* 1990, 10(7), 18.
- Petersen, H. *Melliand Textil* 1986, 67, 656.
- Kottes Andrews, B. A. *Colourage Ann* 1995, p 87.
- Hurwitz, M. D. *Text Chem Color* 1987, 19(2), 13.
- Bhattacharya, N.; Doshi, B. A.; Sahasrabudhe, A. S.; Mistry, R. P. *Am Dyest Rep* Mar. 1993, p 96.
- Yamamoto, K. *Text Res J* 1982, 52, 357.
- Welch, C. M. *Text Res J* 1983, 53, 181.
- Welch, C. M. *Text Chem Color* 1984, 16, 265.
- Welch, C. M.; Peters, J. G. *Text Res J* 1987, 57, 351.
- Worth, D. L. U. S. Pat. 4,269,603 (to Reigel Textile Corp.), 1981.
- Harper, R. J., Jr.; Frick, J. G., Jr. *Am Dyest Rep* 1981, 70(9), 46.
- Blanchard, E. J.; Reinhardt, R. M. *Am Dyest Rep* 1989, 78(2), 30.
- Bertoniere, N. R.; King, W. D. *Text Res J* 1989, 59, 608.
- Kottes Andrews, B. A.; Welch, C. M.; Trask-Morrell, B. J. *Am Dyest Rep* 1989, 78, 15.
- Trask-Morrell, B. J.; Kottes Andrews, B. A. *Text Res J* 1992, 62(3), 144.
- Blanchard, E. J.; Reinhardt, R. M.; Graves, E. E. *J Soc Dyers Color* 1996, 112, 108.
- Welch, C. M. *Text Chem Color* 1997, 29(2), 21.
- Welch, C. M.; Peters, J. G. *Text Chem Color* 1997, 29(10), 33.
- Welch, C. M.; Peters, J. G. *Text Chem Color* 1997, 29(3), 22.
- Yang, C. Q. 211th American Chemical Society National Meeting Cellulose, Paper and Textile Division, New Orleans, Mar. 24, 1996; Yang, C. Q. *Text Res J* 1991, 61, 298.
- Kawahara, Y.; Shioya, M.; Takaku, A. *Am Dyest Rep* 1995, 84, 36.
- Kawahara, Y.; Shioya, M.; Kikutani, T.; Takkaku, A. *Am Dyest Rep* 1994, 83(10), 28.
- Kawahara, Y.; Shioya, M.; Kikutani, T.; Takkaku, A. *Am Dyest Rep* 1995, 84, 20.
- Tsang, B.; Dhingra, R. C. *Text Asia*, May 1996, p 56.
- Salvi, A. S. *Colourage*, Sep. 1980, p 27.
- Carr, C. M. in *Chemistry of the Textiles Industry*; Blackie Academic & Professional: New York, 1995.
- Datye, K. V.; Vaidya, A. A. *Chemical Processing of Synthetic Fibres and Blends*; John Wiley & Sons: New York, 1984.
- David, J. E. *Text Res J* 1995, 65(2), 118.
- Blanch, R. M. *Melliand Int* 1997, (2), 94.
- Bajaj, P. *Colourage* Mar. 22, 1973, p 29.
- Harper, R. J. *Am Dyest Rep* 1975, 63, 23.
- McGregor, R. R. *Silicones and Their Uses*; McGraw Hill: New York, 1954.
- Patati, S. *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: New York, 1989.
- Shenai, V. A. *Text Dyer Printer*, Dec. 17, 1986, p 21.
- Boddeker, B.; Peeters, A. *Int Text Bull* 1997, p 13.
- Rooks, R. J. *Text Chem Color* 1972, 4(1), 47.
- Czech, A. M.; et al. *Am Dyest Rep* Sep. 1993, p 58.
- Czech, A. M.; Paulenyi, J.; Sabia, A. J. *Text Chem Color* 1987, 29(9), 26.
- Shenai, V. A. *Int Dyer Printer* 1977, 21, 72.
- Rowland, S. P.; Wade, C. P.; Roberts, E. J. *Text Res J* 1973, 43, 351.
- Tyndall, R. M. *Text Chem Color* 1992, 24(6), 23.
- Mehra, R. H.; Mehra, A. R.; Mehra, A. R.; Mehra, S. R. *Text Trends*, Jul. 1993, p 31.
- Sharma, M. *Colourage*, Jan. 1993, p 13.
- Sharma, M. *Indian Text J*, May 1997, p 38.
- Memmpel, W. H. *Int Text Bull*, Mar. 1991, p 5.
- Cavaco-Paulo, A.; Cortez, J.; Almeida, L. *J Soc Dyers Color* 1997, 113, 218.
- Kumar, A.; Yoon, M.-Y.; Purtell, C. *Text Chem Color* 1997, 29(4), 37.
- Morgan, N. *Tech Text Int* 1997, 6/5, 12.
- Choe, E. K.; Park, S. Y.; Cha, H. C.; Jeon, B. D. *Text Res J* 1997, 67(3), 155.
- Beravas, F. *Tekstilec* 1997, 40(5-6), 102.
- Olson, L. *Am Dyest Rep*, May 1958, p 19.
- Paul, R.; Naik, S. K. *Text Dyer Printer*, May 1997, p 13.
- Kumar, A.; McEwan, D.; Purtell, C. *The 78th World Conference of the Textile Institute, Greece, May 1997, vol. 2.*

67. Mamoru, K. (Toyo Boseki, Japan), JP 08,127,974, 1996.
68. Clarkson, A. K.; Larenas, E.; Weiss, G.; Bower, B. S. (Genencor) U. S. Pat. 5,650,322, 1997.
69. Naik, S. R.; Paul, R. *Asian Text J*, Feb. 1997, p 48.
70. Nilsson, T. E.; Lopez Ainaga, J. L. *Rev Quim Text* 1996, 128, 79; Nilsson, T. E.; Lopez Ainaga, J. L. *World Text Abstr* 1997, no. 1532.
71. Završnik, T. *Tekstilec* 1996, 39(12), 277; Završnik, T. *World Text Abstr* 1997, 3774.
72. Chikkodi, S. V.; Khan, S.; Mehta, R. D. *Text Res J* 1995, 65(10), 564.
73. Riva, A.; Cegarra, J.; Prieto, R. *J Soc Dyers Color* 1993, 109, 210.
74. Anon, T. S. Chemicals (UK) Ltd. *High Perform Text*, Oct. 1995.
75. Jovakcic, P. *Tekstil Ind* 1996, 44/7-9, 9; Jovakcic, P. *World Text Abstr* 1997, no. 1534.
76. Lone, D.; Elisabeth, H.; Hartwig, H. (Novo Nordisk A/S, Den), PCT Int. Appl. WO 96,19,611, 1996; *Chem Abstr* 1996, 125(12), 145015t.
77. Sonwalkar, T. N.; Prabhu, J. *Colourage*, Jul. 1992, p 37.
78. Gulrajani, M. L.; Arora, S.; Aggarwal, S. *Indian J Fibre Text Res* 1997, 22(2), 119.
79. Hunton, R. H. *Am Text Int* 1986, 15(6), 71.
80. Woods, R. I. *Ergonomics* 1986, 29, 455.
81. Lomax, G. R. *J Coated Fabrics* 1985, 15, 115.
82. Krishnan, K. *J Coated Fabrics* 1995, 25, 103.
83. Reischl, U.; Stransky, A. *Text Res J* 1980, 51, 643.
84. Davies, S.; Owen, P. *Text Month* Aug. 1989, pp 37-40.
85. Roey, M. V. *J Coated Fabrics* 1991, 21, 20-29.
86. Gottvald, L. *J Coated Fabrics* 1996, 26, 168-175.
87. Beke, R. V.; Dekoninck, L. *Melliand Textil* 1986, 67, 824/E337.
88. Brocks, J. *Melliand Textil* 1988, 69, 66/E33.
89. Mansfield, R. G. *Text World*, May 1985, p 58.
90. Leipnik, P. *J Coated Fabrics* 1995, 25, 137.
91. Bajaj, P.; Sengupta, A. K. *Text Prog* 1992, 22(2/3/4), 68.
92. Vigo, T. L. in *Handbook of Fibre Science and Technology*; Lewin, M.; Sello, S. B., Eds., Marcel Dekker: New York, 1984, vol. II, p 367.
93. Vigo, T. L.; Danna, G. F.; Welch, C. M. *Text Chem Color* 1977, 9, 28/27.
94. Sivakumaran, S.; Rajendran, S. *Proceedings of the 31st Joint Technical Conference of ATIRA/BTRA/SITRA/NITRA*, Feb. 16-17, 1990.
95. Sivakumaran, S.; Rajendran, S. *Colourage*, Oct. 1-15, 1989, p 13.
96. Bajaj, P. *Indian J Fibre Text Res* 1996, 21(3), 79.
97. *Jpn. Pat.* 51-30620, 1976.
98. Uchida, A. *Kokogijutsu* 1990, 25(4), 226.
99. Hall, J. D. H.; Ridge, B. P.; DeMartino, R. N. U. S. Pat. 2,590,402, 1952.
100. Zeronian, S. H.; Collins, M. J. *Text Prog* 1989, 20(2), 70.
101. Solbrig, C. M.; Obendorf, S. K. *Text Tes J* 1991, 61, 177.
102. Matsudaira, M.; Matsui, M. *J Text Inst* 1992, 83, 144.
103. Teijin Ltd. *Jpn. Pat.* 06,263,971; *Chem Abstr* 1995, 122, 190257x.
104. Nippon Ester Co. Ltd. *Jpn. Pat.* 06,313,214; *Chem Abstr* 1995, 122, 190260t.
105. Matsukama, S.; Masai, M.; Mizuta, Y. *Sen-I-Gakkaishi* 1995, 51(1), 17.