Electron Microscopical Comparison of Cotton Fabrics Resin Treated by the Pad-Dry-Cure and Pad-Flame Dry-Cure Techniques

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Received 8 September 1979; accepted 4 March 1980

Cotton fabrics chemically modified by the pad-dry-cure and pad-flame dry-cure processes were examined in the electron microscope. Extensive layer expansion obtained by the polymerization of methacrylate within the fibre and the greater dissolution in 0.5 M cuene exhibited by the pad-flame dry-cure samples in comparison with the pad-dry-cure samples at comparable bound resin levels have been attributed to the retention of the swollen structure at the time of crosslinking as a result of rapid drying.

The textile industry is making rapid strides towards tailor-making fabrics endowed with specific performance characteristics. However, it is known that the migration of resin to the fibre surface in a resin impregnated fabric occurs during drying, resulting in a non-uniform distribution of the resin. As a result of this, the treated fabric will have poor abrasion and tensile properties. To minimize these losses, several new techniques for resin finishing have been tried. These include: (1) limited application technique which enables removal of excess of moisture prior to drying, (2) core crosslinking technique in which the catalyst on the fabric surface is poisoned prior to curing, thereby having a cotton-like surface, and (3) flash curing technique in which drying and curing operations are carried out simultaneously in one step at high temperatures. The pad-flame dry-cure technique also appears to be highly promising. The present investigation is concerned with the changes in the microstructure of fibres from fabrics resin treated by the pad-dry-cure and pad-flame dry-cure techniques as revealed by transmission electron microscopy.

Materials and Methods
Desized, scoured and bleached 100% cotton poplin fabric (39's x 39's; 120 x 62) was used for preparing pad-dry-cure samples, while the pad-flame dry-cure treatments were carried out on desized, scoured and bleached poplin fabric (39's x 39's; 120 x 62) obtained from another source.

Catalyst—Phosphoric acid and a mixed catalyst, consisting of 25% magnesium chloride hexahydrate and 15% catalyst DC (Indian Pat.114033), on the weight of solid resin were used.

Resin—Dimethylol dihydroxyethylene urea (DMDHEU) was used.

Resin finishing—In the pad-dry-cure process, fabric samples were padded twice with liquor containing 2, 4 or 6% DMDHEU and a mixed catalyst, squeezed through rolls to an average wet pick up of 70%, dried at 100°C for 2 min to reduce the moisture content of the treated fabric to about 10% and cured at 150°C for 2 min. In the pad-flame dry-cure process, fabric samples padded with 6% DMDHEU and phosphoric acid (1%) as catalyst were squeezed to a wet pick up of 70%, dried over a controlled flame for 10, 20 and 30 sec and subsequently cured for 2 min at 100°C. From preliminary experiments, it was established that drying over a flame for 10, 20 and 30 sec would reduce the moisture level to 40, 30 and 20% respectively. All the treated fabrics were given the usual process wash.

Test methods—Dry and wet crease recovery data were obtained with the Monsanto wrinkle recovery tester (ASTM D1295-67) and abrasion resistance was determined on a Stoll flex-abrader (ASTM D1175-67). The tear strength was determined on an Elmendorf tear tester (ASTM D1424-56T) and tensile properties were determined on the Instron tensile tester using the ravelled strip method (ASTM D1682-64).

Microscopic studies—Changes in the microstructure of fibres from treated and untreated fabrics were followed from electron micrographs of ultra-thin sections before and after immersion in 0.5 M cupriethylene diamine hydroxide (cuene dissolution technique) as well as by layer expansion technique.

Results
Cuene dissolution—The electron micrographs (Figs.1-4) illustrate the changes in the response of cotton fibres to swelling in 0.5 M cuene after
crosslinking to achieve different crease recovery levels. It is known that the sections of fibres from untreated and resin-treated fabrics do not show structural details, such as evidence of layered or fibrillar structure, which would enable one to distinguish between them. However, their behaviour is markedly different when they are immersed in 0.5 M cuene. Untreated cotton cellulose on immersion in cuene goes into solution rapidly without normally leaving any recognizable residue. On the other hand, crosslinked cotton does not dissolve completely and the 'solidity' of fibre residues gives an indication of the effectiveness of the inter- or intra-lamellar crosslinking.

Fig. 1 shows the electron micrographs of fibres from a pad-dry-cure fabric containing 0.19% nitrogen. Dissolution has been reduced considerably. Considerable variability in the crosslink distribution is also apparent. Photograph 1A reveals that the fibre is crosslinked mainly near the periphery of the fibre. The uncrosslinked central portion has been dissolved. Photograph 1B indicates a fairly uniform distribution of crosslinks throughout the fibre cross-section. There

![Fig. 1](image)

Fig. 1—Electron micrographs of pad-dry-cure samples with 0.19% N after immersion in 0.5 M cuene showing the variation in dissolution [(A) x 4290 and (B) x 5400]

![Fig. 2](image)

Fig. 2—Electron micrographs of fibre cross-sections with 0.56% N (A) and 0.76% N (B) after cuene swelling (x 5400)
is considerable dissolution, because the extent of crosslinking is not sufficiently high. In the case of the fabric treated with 0.56% N, the cuene technique shows that the crosslinking is quite extensive, with the result that the fibre offers considerable resistance to dissolution by cuene (Fig. 2A). The fabric with 0.78% N was found to be completely resistant to cuene dissolution (Fig. 2B).

The electron micrographs of sections from a pad-flame dry-cure sample with 0.56% N after immersion in cuene are shown in Fig. 3A and B. It is seen that the reaction is uniform and there is considerably more dissolution in this sample compared to that in the pad-dry-cure fabric with more or less the same nitrogen content (Fig. 2A). The pad-flame dry-cure sample with 0.7% N exhibits a similar behaviour (Fig. 4A.

![Image](A) ![Image](B)

**Fig. 3**—Cuene dissolution patterns of pad-flame dry-cure samples with 0.56% N showing the variation in dissolution [(A) x 5400 and (B) x 4290]

![Image](A) ![Image](B) ![Image](C)

**Fig. 4**—Partial cuene dissolution patterns of flame-dried samples with 0.71% N (A x 4290 and B x 5400) and 0.78% N (C x 4290)
and B), except that the extent of dissolution is considerably less compared to that with 0.56% N. Apparently there is no dissolution of the fibres from a pad-flame dry-cure sample with 0.78% N (Fig. 4C).

Layer expansion—Rollins et al. observed that if the fibre swollen in water is impregnated with methacrylate, the methacrylate expands when it polymerizes and the expanding polymer pushes the fibrillar elements apart. The untreated cotton with no

![Fig. 5—Typical fibre cross-sections of untreated cotton after methacrylate layer expansion (x 3150)](image)

Fig. 5—Typical fibre cross-sections of untreated cotton after methacrylate layer expansion (x 3150)

hindrance from the crosslinks exhibits almost completely uninhibited separation of cellulosic layers (Fig. 5). On the other hand, the swelling pattern of cotton which has been crosslinked differs from that shown in Fig. 5, depending on the extent of crosslinking, as well as on the conditions prevailing at the time of crosslinking (Figs. 6-9).

In a pad-dry-cure sample with 0.19% N, the microfibrillar separation is not as extensive as that shown by the untreated cotton fibre. As noted from the cuene micrographs, the layer expansion technique also reveals considerable variation in the distribution of crosslinks. Photograph 6A shows considerably less crosslinking, while photograph 6B indicates sufficient crosslinking which results in very little layer separation. Fig. 7A shows the layer expansion pattern of a pad-dry-cure sample with 0.56% N. In this sample, the crosslinking is quite extensive as well as uniform and hence only traces of incipient layering throughout the cell wall are seen. The fibre sections from fabrics containing 0.76% N show practically no response to water- and methacrylate-swelling (Fig. 7B). These observations support the earlier conclusions drawn from the cuene patterns, i.e. solidity of the structure in cuene.

Fig. 8 shows the layer expansion patterns exhibited by fibre sections from a pad-flame dry-cure sample with 0.56% N. These fibre sections exhibit more extensive layering compared to that shown by the pad-dry-cure sample with more or less the same nitrogen content. Even the fibres with 0.71% N show significant layer separation (Fig. 9A and B). Even in

![Fig. 6—Expansion patterns of pad-dry-cure samples with 0.19% N showing variability in layer expansion ([A] x 4290 and [B] x 5400)](image)
**Table 1—Mechanical Properties of Pad-Dry-Cure and Pad-Flame Dry-Cure Fabrics**

<table>
<thead>
<tr>
<th>Resin padded %N</th>
<th>Residual moisture content %</th>
<th>Crease recovery angles (W + F)°</th>
<th>Tensile loss %</th>
<th>Abrasion loss %</th>
<th>Tear loss %</th>
<th>Resin padded %N</th>
<th>Residual moisture content %</th>
<th>Crease recovery angles (W + F)°</th>
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<tr>
<td>6.0</td>
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<td>18-20</td>
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Discussion

A comparison of the crum patterns (Fig. 2A vs Fig. 3 and Fig. 2B vs Fig. 4) or the layer expansion patterns (Fig. 7A vs Fig. 8 and Fig. 7B vs Fig. 9) of pad-dry-cure and pad-flame dry-cure samples at comparable nitrogen levels leads to the conclusion that the pad-flame dry-cure samples exhibit greater dissolution and more extensive layer separation than the pad-dry-cure samples at comparable resin levels. The greater dissolution shown by the flame dried samples cannot be attributed to the non-uniform distribution of crosslinks. As a matter of fact, the pad-dry-cure samples at least at low resin add-on have exhibited predominant crosslinking near the fibre surface. The following explanations can be offered to account for the difference in behaviour of the pad-dry-cure and pad-flame dry-cure samples: (1) the conditions prevailing in the pad-flame dry-cure process are equivalent to those in the mild cure process; (2) the catalyst used in the pad-flame dry-cure process prevents the already swollen fibres from collapsing.
during drying and curing; (3) flash drying employing a flame may initiate crosslinking during drying when the fibres are in the swollen condition; and (4) differences in the fabric preparatory conditions.

Reinhardt et al. have concluded from an electron microscopic study using cuene dissolution and layer expansion techniques that a high degree of crosslinking is uniformly produced by the mild cure process with HCl as catalyst and the crosslinked structure at about the same level of resin is essentially equivalent to that produced by the conventional pad-dry-cure process, though the mild-cure fabrics exhibit higher wet crease recovery angles (by 5-15°) than the dry crease recovery angles. This rules out the first explanation.

Phosphoric acid being a powerful swelling agent can cause some swelling even at low concentrations and retain the fibres in the already swollen state during drying. Because of the excessively high temperature of the flame, some crosslinks might have been formed when the fibres were in the swollen condition. These crosslinks could prevent collapse of the fibres during further drying and curing.

Pierce and colleagues have shown that the fibres crosslinked with formaldehyde in phosphoric acid exhibit high resistance to cuene dissolution. But these
fabrics have been shown to exhibit extensive and uniform layer expansion. However, the treated fabrics show improved wet crease recovery only. Recently, Pierce et al. have shown that certain water soluble, high boiling point additives such as glycol ether, which have little or no reactivity towards cellulose and even certain inorganic salts such as sodium nitrate, when added to the resin bath in small quantities (\% and above), could produce fabrics with improved moisture regain and higher wet crease recovery with a little reduction in dry crease recovery angle. These fabrics have been found to exhibit extensive layer expansion. The fabrics treated by the pad-flame dry-cure process have been found to have improved moisture regain and high wet and dry crease recovery angles.

The only difference in the properties of the pad-dry-cure and pad-flame dry-cure fabrics is in abrasion.

Fig. 9—Electron micrographs of flame dried samples with 0.71\% NaA and Bi and 0.75\% NaC showing typical expansion patterns (× 5400)
resistance. Fabrics widely differing in their abrasion resistance have been DMEU treated by the conventional pad-dry-cure technique and these fabrics have been shown to exhibit more or less the same losses in tensile strength, tear strength and abrasion resistance at comparable crease recovery levels. This suggests that the differences observed in the cuene dissolution and layer expansion patterns are not due to the differences in the fabric preparatory conditions used.

From the above discussion it appears that the superior behaviour of the flame dried samples is due to the retention of the swollen structure at the time of crosslinking as a result of rapid drying. Rapid drying under the conditions of flame drying can be expected to result in migration of resin. However, the initiation of the reaction leading to crosslinking during flame drying and the higher residual moisture on the flame dried samples appear to cause to some extent the back diffusion of migrated crosslinking agents, resulting in better distribution of crosslinks.

Acknowledgement
The authors wish to express their sincere thanks to Dr R.J. Berni and Mrs Jarrel Carra of the Southern Regional Research Center, U.S. Department of Agriculture, New Orleans (USA) for the electron micrographs. They also wish to thank Dr N.E. Dweltz, Assistant Director, ATIRA, for useful discussions and Dr P.C. Mehta, Director, ATIRA, for permission to publish this paper.

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