

## Acetylation of Cotton Treated with Sodium Hydroxide

S. H. ZERONIAN, *Department of Consumer Sciences,  
University of California, Davis, California 95616*

### Synopsis

The reactivity of mercerized, ethanol-washed, never-dried cotton, as indicated by acetylation, is higher than that of mercerized, water-washed, never-dried cotton. Hygroscopicity measurements indicate that the ethanol-washed cotton is not fully amorphous. They also reveal that the accessibility of cotton treated with caustic soda solution of mercerizing strength will be higher than that of cotton treated with ethylamine regardless of whether water or a solvent of lower hydrogen-bonding capacity is used to extract the swelling agent. Based on microscopic examination, acetylation of mercerized, ethanol-washed fibers apparently takes place relatively uniformly. The breaking load of cotton fibers is similar to that of mercerized, ethanol-washed cotton fibers of about 8% acetyl content. However, the crystallinity of these materials, as shown by hygroscopicity studies, is markedly different. This indicates that the fine structure of the cotton fiber can be modified considerably without causing a loss in strength. Yarn tensile tests indicate that mercerized, ethanol-washed cotton yarn with acetyl content between 10% and 30% has a breaking load which is about 12% lower than that of cotton.

### INTRODUCTION

The effect of the supramolecular structure of cellulosic fibers on their reactivity has been the subject of many investigations.<sup>1</sup> Using acetylation as the indicator, comparisons have been made between the reactivity of ethylamine-treated, never-dried cotton and that of mercerized, never-dried cotton.<sup>2,3</sup> It has been shown that if water is used as the solvent for extracting the swelling agent, then the reactivity of the cotton treated with caustic soda is higher than that treated with ethylamine.<sup>3</sup> However, the reactivity of ethylamine-treated, pyridine-extracted, never-dried cotton is higher than that of the mercerized, water-extracted, never-dried material.<sup>2,3</sup> The type of solvent used to remove ethylamine from cotton is known to have a marked effect on the ease of acetylation of the treated material.<sup>3</sup> The present investigation was made to determine the effect of extraction with a solvent of lower hydrogen-bonding capacity than water on the reactivity of mercerized, never-dried cotton and the effect that such treatment would have on the fine structure of the resulting products.

## EXPERIMENTAL

### Materials

"Cut skein" samples<sup>4</sup> of commercially kiered cotton yarn (80/2's filling twist) were used as starting material. All chemicals were of analytical reagent grade.

### Methods of Treatment

**Treatment with Sodium Hydroxide** (*Mercerization*). Cotton was immersed in 20% sodium hydroxide solution (4 g yarn per 200 ml of solution) for 1 hr at 21°C in a stoppered ground-glass bottle. The caustic soda was then filtered off and the cotton was extracted with water or ethanol.

**Extraction with Water.** The sample was washed in several changes of distilled water and then steeped in 10% acetic acid for 15 min. The cotton was rewashed in distilled water, the water being changed periodically until it was free of acid. The product was kept in water for acetylation.

**Extraction with Ethanol.** The treatment was similar to that described for extraction with water, except that absolute ethanol was used as the solvent and the acetic acid was diluted with ethanol also. The product was preserved in ethanol for acetylation.

**Acetylation.** Samples (4 g) of material to be acetylated were washed in 100 ml of pyridine. With air-dry samples, the washing was repeated three times while with samples wet with water or ethyl alcohol, the washing was repeated four times. The final portion of pyridine was adjusted to 100 ml by weighing and 100 ml of acetic anhydride was added. The mixture was shaken well and kept at 25°C for the required length of time. Then the acetylation mixture was decanted and the product was washed with distilled water until free from acid. Part of the sample was dried under vacuum over phosphorus pentoxide and used for the measurement of hygroscopicity. The remainder was dried by exposure to an atmosphere of 65% R.H. and 21°C.

### Characterization of Products

**Acetyl Content.** The method used has been described previously.<sup>3</sup>

**Hygroscopicity.** Moisture regains were measured at 59% R.H. and 21°C, using a previously described method.<sup>5</sup>

**Infrared Spectra.** Spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer using a potassium bromide pellet technique similar to the method of O'Connor et al.<sup>6</sup> Absorptivity of bands at 1429  $\text{cm}^{-1}$  and 893  $\text{cm}^{-1}$  were measured.

**Tensile Tests.** Breaking loads and percentage extensibilities of single fibers were measured with a table model Instron Universal Testing Machine. A mount similar to that described by Meredith,<sup>7</sup> but made of aluminum, was used to clamp the fiber between the jaws of the Instron. A fiber was taken from the yarn and laid along the center of the aluminum

mount and secured at each edge with Duco cement and then further secured by an epoxy glue. The mounted fiber was clamped between the grips of the Instron and the sides of the mount were cut. The test span was 0.5 in. Fifty tests per sample were carried out at a constant rate of elongation of 0.05 in./min at 65% R.H. and 21°C.

Breaking loads of yarns were determined on the Instron also. The samples were preconditioned at a relative humidity of 12% at 21°C before exposure to the test atmosphere of 65% R.H. and 21°C. The tests (40 per sample) were carried out on lengths of 3 in. at a constant rate of elongation of 1 in./min.

**Effect of Cupriethylenediamine Solution on Acetylated Materials.** The technique was similar to that described previously,<sup>5</sup> except that cupriethylenediamine hydroxide reagent (0.5M in copper) was used as the swelling agent.

## RESULTS AND DISCUSSION

### Reactivity of Cotton Swollen with Sodium Hydroxide

When cotton was mercerized, water-washed, and then air-dried, its reactivity as indicated by acetylation was lowered (Table I). This agrees with the results of earlier work.<sup>2</sup> Again, in agreement with previously reported results,<sup>2,3</sup> the reactivity of mercerized, water-washed cotton which had been solvent-exchanged to pyridine was higher than that of cotton. In addition, it can now be seen that the reactivity of the cellulose was further increased if the cotton treated with caustic soda was washed with ethanol instead of water.

The lower reactivity of the water-washed material can be explained on the following basis. Water (unlike ethanol) can form more than one hydrogen bond per molecule. Thus, a water molecule may attach itself to hydroxyl groups in adjacent cellulose chains and consequently draw the chains close enough for them to become linked directly by hydrogen bonds between hydroxyl groups at neighboring sites. With the formation of

TABLE I  
Effects of Acetylation of Cotton for 24 Hours at 25°C after  
Various Swelling and Washing Treatments

Sample	Acetyl content, %
Cotton	7.2
Mercerized, water-washed cotton, air-dried	1.7
Mercerized, water-washed cotton, solvent exchanged to pyridine and never dried	17.7
Mercerized, ethanol-washed cotton, solvent exchanged to pyridine and never dried	29.0

interchain hydrogen bonds, the cellulose becomes less accessible to the acetylating agent and thus less reactive. Ethanol, in contrast, forms hydrogen bonds with the free hydroxyl groups in the amorphous regions, thus preventing the cellulose chains from coming close enough together to be able to form hydrogen-bond crosslinks.

In a study on ethylamine treatment of cotton,<sup>5</sup> acetylation conditions were similar to those used in the present work, but the sample of cotton was different. In that study, the acetyl content of cotton was 7.9% after 24 hr of acetylation and the acetyl content of ethylamine-treated, pyridine-washed cotton was 25.5%. Thus the reactivity of the cotton had been increased by a factor of 3.2 by the swelling treatment. In the present study, the reactivity of cotton was increased by a factor of 4.0 by treatment with caustic soda followed by ethanol washing (Table I). Thus it appears that cotton will have a higher reactivity if treated with sodium hydroxide solution of mercerizing strength and then washed with ethyl alcohol, rather than if treated with ethylamine and then washed with pyridine.

### Hygroscopicity of Acetylated Materials

The relation between moisture regain, at 59% R.H. and 21°C, and acetyl content of samples prepared from mercerized, ethanol-washed cotton that has not been dried is shown in Figure 1. The rate of fall of hygroscopicity with increasing acetyl content was constant in the range of acetyl contents considered here. The slope of the line is similar to that obtained previously with cotton, ethylamine-treated, water-washed, never-dried cotton, and ethylamine-treated, pyridine-washed, never-dried cotton.<sup>5</sup>

The interpretation of the relation between moisture regain and acetyl content has been given previously<sup>3,5</sup> and will not be repeated in full. At the acetyl contents considered here, acetylation proceeds in the amorphous regions. The linearity of the relation indicates that the amount of inter-

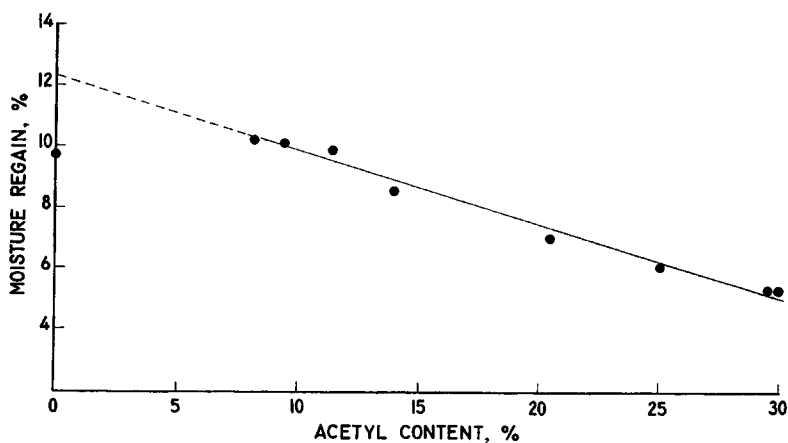


Fig. 1. Relation between hygroscopicity and acetyl content of mercerized, ethanol-washed cotton.

chain hydrogen bonding has not altered during acetylation but is fixed by this process at the preexisting level. Also, acetylation itself does not cause any decrystallization at the levels of acetyl content being considered. Extrapolation of the line in Figure 1 to the ordinate axis yields a value of 12.4% as the moisture regain of mercerized cotton at 59% R.H. and 21°C. A less detailed study of mercerized, water-washed, acetylated samples gives an extrapolated value of roughly 11% as the regain for mercerized cotton.

The regains obtained by extrapolation are the values that would be expected if no loss in accessibility occurs when mercerized cotton is dried. The loss is avoided by preventing the formation of interchain hydrogen bonds in the amorphous regions by the introduction of acetyl groups.<sup>3</sup> The marked loss in accessibility that will occur if interchain hydrogen bonding is not prevented can be seen from the fact that a direct determination of moisture regain for mercerized, water-washed cotton gave a value of 9.70%. The moisture regain for mercerized cotton obtained from the ethanol-washed, acetylated materials is higher than that obtained from the water-washed, acetylated materials because a loss in accessibility had occurred in the latter samples as the sodium hydroxide solution was removed by water. This loss in accessibility may have been due to interchain hydrogen bonding occurring in the presence of water. Such bonding does not occur readily in ethanol (see previous section).

Estimated values of the moisture regain of amorphous cellulose have been discussed previously.<sup>5</sup> Available evidence indicates the regain would not be less than 15.2% at 59% R.H. and 21°C, while that of mercerized, ethanol-washed cotton, as obtained by extrapolation, was 12.4%. Thus it appears that mercerized, ethanol-washed, never-dried cotton is not fully amorphous. Such a conclusion is in agreement with the work of Jeffries.<sup>8</sup>

It is of interest to compare the water vapor sorption of mercerized materials with that of ethylamine-treated samples. The regains used were obtained by extrapolation of curves relating moisture regain and acetyl content. The results were converted to sorption ratios, since the cotton used in the mercerization experiments was not the same as that used in the ethylamine work.<sup>5</sup> Sorption ratio is defined as the ratio of the moisture regain of a cellulose to that of cotton at the same relative humidity and temperature. The sorption ratios for mercerized, ethanol-washed cotton and mercerized, water-washed cotton were 1.97 and 1.76, respectively. Those of ethylamine-treated, pyridine-washed cotton and ethylamine-treated, water-washed cotton were 1.84 and 1.52, respectively.<sup>5</sup> Both ethylamine and caustic soda solution of mercerizing strength are intracrystalline swelling agents. However, the sorption ratios indicate that the accessibility of cotton treated with caustic soda will be higher than that of cotton treated with ethylamine, both when water is used as the solvent to extract the swelling agent and when a solvent of lower hydrogen-bonding capacity is used.

Valentine<sup>9</sup> has related sorption ratio to the fraction of amorphous material in a cellulose. Using his relation, the fraction of amorphous ma-

terial in mercerized, ethanol-washed cotton is 0.76. This is the value for a sample in which no loss of accessibility has occurred during drying. It is the value also for mercerized, ethanol-washed, acetylated cotton in which the acetyl content does not exceed 30% since acetylation up to this level does not affect the crystallinity of the fiber. The fraction of amorphous material in cotton is 0.38.

### Microscopic Evaluation Using Cupriethylenediamine Hydroxide

It has been demonstrated previously<sup>5</sup> that cuprammonium hydroxide solution can be used for locating areas of cotton fiber that have been highly acetylated. In the present work, cupriethylenediamine solution was used for a similar study of mercerized, ethanol-washed, acetylated fibers. Up to an acetyl content of 14%, the fibers behaved similarly to unacetylated mercerized cotton. Namely, they swelled rapidly and dissolved. Apparently esterification of the mercerized, ethanol-washed fibers took place relatively uniformly and no highly acetylated regions were produced. Such regions would have hindered the dissolution of the fibers.

At acetyl contents of 20% to 25%, little or no swelling occurred in some parts of the fibers. In other parts the fibers swelled uniformly and ballooning also occurred. In certain instances, particles of broken fibers were seen and these in turn dissolved. At about 30% acetyl, in many fibers there was no swelling and no dissolution. In a few fibers, some ballooning and swelling occurred and particles of broken fibers were observed. The ballooning and fragmentation presumably occurred in areas of relatively low acetyl content or at weak points in the fibers.

### Tensile Properties

Results of the single-fiber tensile testing are given in Table II. The difference between the breaking load of the mercerized, ethanol-washed, acetylated fiber and that of the mercerized fiber is not statistically significant, but the difference between the extensions at break is significant. The acetyl groups may be the cause of the lower extension at break of the acetylated sample. The breaking load of cotton is little different from that of the mercerized, ethanol-washed, acetylated fiber.

TABLE II  
Tensile Properties of Fibers

Sample	Acetyl content, %	Breaking load <sup>a</sup>			Extension at break		
		g	c.v., %	SD	%	c.v., %	SD
Cotton	0	5.23	33	0.23	6.32	38	0.32
Mercerized cotton	0	5.97	31	0.28	12.5	29	0.54
Mercerized, ethanol-washed, acetylated cotton	8.2	5.45	32	0.25	9.69	36	0.51

<sup>a</sup> c.v. = coefficient of variation; SD = standard deviation.

It is known that mercerization and also ethylamine treatment can increase the strength of cotton fibers<sup>5,10</sup> The increase is thought to be due to a relief of strains in the fiber structure set up during the drying and crystallization of cellulose while the fibers are in the boll.<sup>10</sup> The regions of strain would be relatively weak and fiber rupture would be likely to occur at such locations. A reduction of crystallinity by mercerization will ease movement of cellulose chains and allow them to readjust to relieve strain at weak points. As a consequence, the fibers would acquire a greater breaking load. It should be noted that a reduction in crystallinity, beyond that required to relieve internal strain, could lower the breaking load of the fiber by affecting the interchain hydrogen bonding present. It is widely accepted<sup>11</sup> that the rupture of cellulose molecules is primarily involved in the rupture of native cellulose fibers. However, if the amount of interchain hydrogen bonding is lowered sufficiently by decrystallization, then fiber rupture could occur by the cellulose molecules slipping apart rather than breaking. The breaking loads of cotton and of mercerized, ethanol-washed cotton of 8.2% acetyl content are similar. The number of acetyl groups in the acetylated fiber are probably too few to have an effect on the breaking load of the sample.<sup>5</sup> Thus it appears that increasing the amount of amorphous material in cotton by 100% by mercerizing and then washing with ethanol is not sufficient to affect the strength of the fiber.

Yarn tensile tests were carried out on mercerized, ethanol-washed yarns with acetyl contents up to 30%. The breaking load (357 g) of the cotton yarn was not changed significantly by mercerization (364 g), but mercerized, ethanol-washed acetylated yarns of acetyl content between 10% and 30% had breaking loads about 12% lower.

### Infrared Spectra

Infrared spectra did not yield any significant information on the fine structure or crystallinity of the samples. The spectra of mercerized, ethanol-washed cotton and mercerized, water-washed cotton of similar acetyl content appeared similar. The ratio of the absorptivity of the band at  $1429\text{ cm}^{-1}$  to that at  $893\text{ cm}^{-1}$  was measured. The values for cotton and mercerized cotton were 3.0 and 0.59, respectively. This ratio can be affected both by mercerization and by decrystallization,<sup>12</sup> thus it cannot be used to follow changes in crystallinity of the materials considered here. For mercerized, ethanol-washed cotton acetylated to acetyl contents up to 30%, this ratio remained approximately constant, with values ranging between 0.53 and 0.59.

### References

1. L. Segal, in *Chemical Reactions of Polymers*, E. M. Fettes, Ed., Interscience, New York, 1964.
2. L. Loeb and L. Segal, *Text. Res. J.*, **24**, 654 (1954).
3. T. P. Nevell and S. H. Zeronian, *Polymer*, **3**, 187 (1962).
4. E. Midgley and F. T. Peirce, *J. Text. Inst.*, **17**, T305 (1926).

5. S. H. Zeronian, *J. Appl. Polym. Sci.*, **9**, 313 (1965).
6. R. T. O'Connor, E. F. DuPré, and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).
7. R. Meredith, *J. Text. Inst.*, **36**, T107 (1945).
8. R. Jeffries, *J. Appl. Polym. Sci.*, **12**, 425 (1968).
9. L. Valentine, *Chem. Ind.* (London), 1279 (1956).
10. R. S. Orr, A. W. Burgis, F. R. Andrews, and J. N. Grant, *Text. Res. J.*, **29**, 349 (1959).
11. R. Meredith, in *Recent Advances in the Chemistry of Cellulose and Starch*, J. Honeyman, Ed., Interscience, New York, 1959.
12. M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, **8**, 1311, 1325 (1964).

Received September 29, 1969