

## Fine Structure and Tensile Properties of Decrystallized Products Prepared from Cotton

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### Synopsis

A highly decrystallized product was prepared from cotton by treating it with ethylamine, extracting the ethylamine with pyridine, and then partially acetylating the sample in this solvent. The properties of this material were compared with those of cotton, partially acetylated cotton, cotton partially acetylated after treatment with ethylamine and water, and mercerized cotton. It was confirmed that the reactivity toward acetylation of ethylamine-treated, pyridine-extracted cotton (in the never-dried state) was higher than that of the ethylamine-treated, water-extracted sample. However, the acetylation of both these materials and also of cotton can be represented by an equation developed for diffusion-controlled reactions. Acetylation was necessary to retain the highly decrystallized state of never-dried ethylamine-treated cotton that had been pyridine-extracted. It was deduced from hygroscopicity measurements that the fraction of amorphous cellulose in this never-dried material was 0.71. The values for dried ethylamine-treated cotton and mercerized cotton were 0.51 and 0.57, respectively. Comparison of the x-ray diffractograms of cotton and of acetylated ethylamine-treated, pyridine-washed cottons (acetyl contents 8.5–10.6%) showed that the base of the (002) plane diffraction peak of the treated materials was broader and that maxima corresponding to the (101), (10 $\bar{1}$ ) crystalline reflections were no longer present. A comparison of electron micrographs of these materials indicated that the microfibrils in the secondary wall of the decrystallized fibers remained closely parallel though slightly crimped. In mercerized cotton, on the other hand, the microfibrils were swollen and crimped and there was considerable disorientation. Mercerization treatment and ethylamine treatment which was followed by pyridine extraction and partial acetylation increased the strength of cotton by similar amounts. The former treatment also produced a marked increase in the elongation at break of the fibers while the latter did not produce a significant increase.

In a previous investigation<sup>1</sup> of the effect on cotton of treatment with ethylamine, it was shown that the solvent used subsequently to remove the ethylamine had a marked influence on the ease of acetylation of the never-dried treated material. Of the solvents tried, pyridine gave the most reactive product. At an acetyl content in the region of 25% the x-ray photographs of acetylated products obtained from cotton, cotton treated with ethylamine and then water, and cotton treated with ethylamine and then pyridine showed progressively increasing proportions of crystalline

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cellulose acetate.\* Their hygroscopicities increased in the same order also. The hygroscopicity of the ethylamine-treated, pyridine-washed cotton that had been acetylated was higher than that of the cotton from which it had been derived and was double that of the product that had been acetylated without the pretreatment with ethylamine.

It has been established that there is a correlation between the degree of crystallinity of cellulose and its moisture regain (see, for example, Valentine<sup>2</sup>). Thus, it can be concluded that ethylamine treatment of cotton followed by pyridine washing and acetylation produces a highly decrystallized material. A more detailed study has now been made of such products. Special attention has been paid to those materials having a low degree of acetylation since there is then little possibility of crystalline cellulose acetate being formed. Hygroscopicities and tensile properties have been measured and x-ray diffractograms and electron micrographs examined. As controls, similar studies have been carried out on cotton, mercerized cotton, partially acetylated cotton, and ethylamine-treated, water-washed cotton that has been acetylated.

## EXPERIMENTAL PROCEDURE

### Materials

Mechanically cleaned Deltapine cotton (supplied by the Southern Regional Research Laboratory of the United States Department of Agriculture) was used. It was chemically purified by boiling under pressure (35 lb./in.<sup>2</sup>) for 3 hr. with 2% sodium hydroxide. The product was washed with distilled water, the water being changed several times, and it was then steeped in a 0.5% acetic acid solution for one hour. Finally, the cotton was washed with distilled water again, the water being changed periodically until a neutral extract was obtained. The material was dried by exposure to the laboratory atmosphere.

Ethylamine was supplied in a cylinder. When required, it was condensed into a glass vessel cooled by a mixture of acetone and Dry Ice. The transfer of the ethylamine was facilitated by applying a vacuum to the system. The temperature of the ethylamine was raised to 0°C. before it was used.

Pyridine used for the extraction of the ethylamine from the treated cotton was analytical reagent grade.

The acetylating reagent, as before,<sup>1</sup> consisted of a mixture of equal volumes of acetic anhydride and pyridine. Both were analytical reagent grade.

\* It should be noted that the ethylamine-treated materials were preserved in the extraction solvent until acetylation with an acetic anhydride-pyridine mixture. In the case of water-washed samples the water was replaced by pyridine by solvent exchange before acetylation.

### Methods of Treatment

**Treatment with Ethylamine and the Subsequent Extraction of the Ethylamine with Water or Pyridine.** The methods were essentially similar to those described previously.<sup>1</sup>

**Acetylation.** The method described previously<sup>1</sup> was used to obtain the results for the rate of reaction studies. These results are shown in Figures 1 and 2. In some other acetylations the ratio of cotton to acetic anhydride was kept at 2 g. to 50 ml., but the portion of pyridine present was not adjusted by weighing. Also, in these acetylations the reaction was carried out at room temperature. The change in acetylation conditions did not affect the fine structure or tensile properties of the treated materials.

**Removal of Pyridine from Ethylamine-Treated, Pyridine-Washed Cotton by Water.** The treated sample, which had been preserved in pyridine, was washed with numerous changes of distilled water at room temperature for a period of 24 hr. All experiments performed on dried ethylamine-treated, pyridine-washed cotton were carried out on material washed with water, in this way, before drying for the following reasons. Water washing makes the treatment given to the sample comparable to that given to other modified celluloses which were all dried after being washed in water. Also, dried pyridine-washed samples will retain some pyridine. Staudinger and Döhle<sup>3</sup> have shown that both polar and nonpolar organic liquids can be included in cellulose.

**Treatment with Sodium Hydroxide (Mercerization).** Cotton was immersed in 20% sodium hydroxide solution for 30 min. at room temperature (24°C.). The product was washed with distilled water, the water being changed several times, and then it was steeped in 10% acetic acid for 15 min. Finally, the cotton was washed in distilled water again, the water being changed periodically until a neutral extract was obtained.

**Drying of Prepared Materials.** The portion of the sample to be used for the determination of acetyl contents and fluidities was dried by exposure to the laboratory atmosphere. The remaining portion was dried in a vacuum desiccator over phosphorus pentoxide. Depending on the subsequent use, the dried sample was then exposed either to the laboratory atmosphere or to an atmosphere of constant humidity.

### Characterization of Products

**Acetyl Content.** The method described previously<sup>1</sup> was used.

**Hygroscopicity.** Moisture regains were determined by drying duplicate samples (0.5–1.5 g.) of material in a vacuum desiccator over phosphorus pentoxide and exposing them to an atmosphere of 59% R.H. at 21°C. (obtained by means of a saturated solution of sodium bromide<sup>4</sup>) until they reached a constant weight.

**X-Ray Diffractograms and Measurements.** X-ray diffraction measurements were made on airdry disks pressed from fibers that had been ground

in a Wiley mill to pass through a 20-mesh screen. Moisture contents of the ground materials were calculated by determining the loss in weight of samples that had been dried in an oven at 110°C. for 3 hr. Making allowance for the moisture present, and for acetyl content, 0.500 g. portions (based on dry weight of cellulose) of the ground materials were placed in a 1-in. diameter pellet mold and pressed at 20,000 lb. pressure for 15 sec. The method of holding the disks and the x-ray equipment used have been described by Parker.<sup>5</sup> The diffraction pattern was measured from an angle of 4° to 30°  $2\theta$  using  $K\alpha$  radiation obtained from a copper target and nickel filter at 35 kv. and 20 ma.

From the diffractograms, the crystallinity indices of native cellulose samples were calculated. The crystallinity index has been defined<sup>6</sup> as  $I_{002}I_{am}/I_{002} \times 100$ , where  $I_{002}$  is the intensity of the (002) reflection of cellulose I at  $2\theta = 22.8^\circ$  and  $I_{am}$  is the intensity of the scattered radiation measured at  $2\theta = 18^\circ$ . This index gives an empirical measure of the degree of crystallinity of native cellulose samples. Determinations from duplicate samples agreed to within 3%.

The same formula was used also to give a measure of the degree of crystallinity in acetylated materials. The index calculated from this formula for such samples will be called molecular order index.<sup>7</sup> Determinations from duplicate samples agreed to within 3% except for some samples of molecular order index less than 46% when agreement between duplicates was within 7%.

The half widths of the (002) reflections were also determined. A base line for the (002) diffraction peak was drawn between 18 and 26°  $2\theta$  and the half-width measured in the manner described by Gjønnes and Norman.<sup>8</sup> Determinations from duplicate samples agreed to within 8%.

**Electron Micrographs.** The secondary wall of the fibers was examined. Fragments sufficiently thin for direct observation were obtained by beating the fibers in water in a Waring Blender.<sup>9</sup> The air-dry sample (0.5 g.) was cut into 1-cm. lengths and soaked in distilled water (200 ml.) for 15 min. It was then transferred with the water to the Waring Blender and beaten for 20 min. From the slurry, a drop of the suspension was placed on a collodion-film grid and allowed to dry at room atmosphere. The specimen was shadowed with palladium at a 30° angle and then examined in an RCA EMU-3-F electron microscope.

**Tensile Tests.** Breaking loads and percentage extensibilities of single fibers were measured with a table model Instron Universal Testing Machine using a technique developed by Wink and Van Eperen. The tests (50 per sample) were carried out at a constant rate of elongation of 0.508 cm./min. at 50% R.H. and 23°C. The dry samples were conditioned at this humidity for a minimum of 18 hr. before testing. The fibers were gripped by the jaws of the zero-span instrument<sup>10</sup> suitably adjusted to permit a test span of 1 cm. The clamping pressure on the jaws was 775 kg./cm.<sup>2</sup>. In order to cushion the fibers, the jaw surfaces were covered with cellulosic film.

**Fluidity Determinations.** The fluidities in cuprammonium hydroxide (0.5% solution at 20°C.) were determined by the method of Clibbens and Geake.<sup>11</sup> The composition of the cuprammonium solvent was 15 g. of copper/l. and 200 g. of ammonia/l.<sup>12</sup>

**Effect of Cuprammonium Hydroxide Solution on Acetylated Materials.** A technique similar to that of Tripp and co-workers was used.<sup>13</sup> Observations were made with a light microscope at a magnification of 100. A small number of fibers were mounted in air between a slide and a coverglass. After the fibers had been brought into focus, cuprammonium hydroxide solution, of the strength used for fluidity determinations, was introduced under the coverglass.

## RESULTS AND DISCUSSION

### Rates of Acetylation

Figure 1 shows the rate of acetylation of cotton (curve 1) and of never-dried ethylamine-treated cottons (curves 2 and 3). It can be seen, by a comparison of curves 2 and 3, that never-dried ethylamine-treated cotton, that has been extracted with pyridine has a higher reactivity than the water-extracted material. This confirms previous observations.<sup>1</sup>

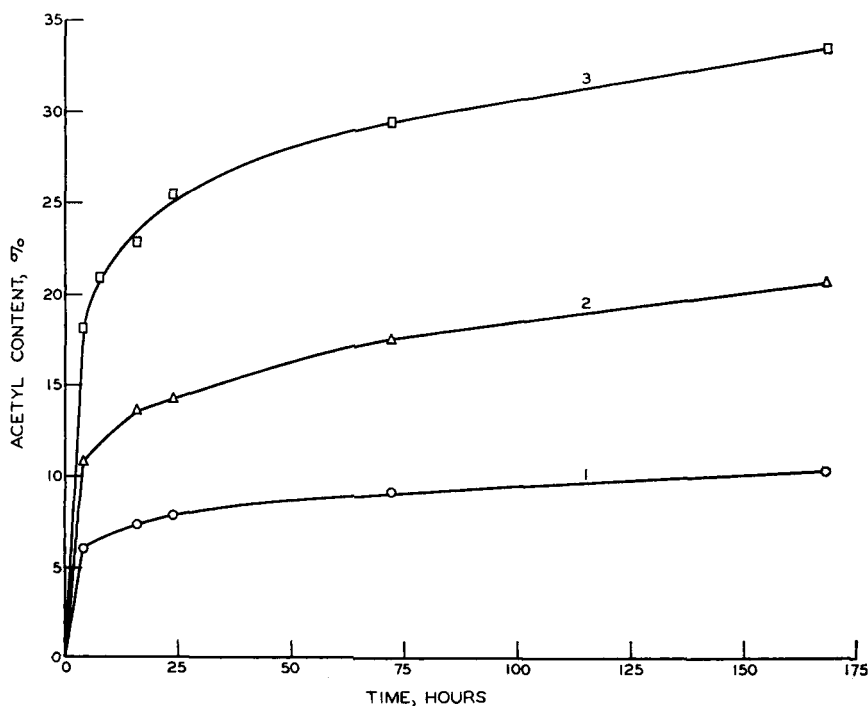


Fig. 1. Rate of acetylation of cellulose: (1) cotton; (2) ethylamine-treated, water-washed cotton; (3) ethylamine-treated, pyridine-washed cotton.

If the conditions of acetylation are such that fiber swelling is limited, Tripp and co-workers<sup>13</sup> have observed that, initially, some portions of cotton fibers will be highly acetylated while others remain virtually unacetylated. Highly acetylated cellulose will not dissolve in cuprammonium hydroxide solution until deacetylation, by alkaline hydrolysis, has taken place. Thus, by observing the effect of this solution on acetylated cotton of low degree of substitution it is possible to differentiate between regions of high and low acetyl content. In the present study, observations were made on fibers with acetyl contents between 9.2 and 10.8%. It was found that both cotton and acetylated cotton pretreated with ethylamine and pyridine dissolved rapidly. No swelling of the fibers was observed. In the case of acetylated cotton pretreated with ethylamine and water the fibers swelled uniformly before dissolving. A marked difference was noted with cotton

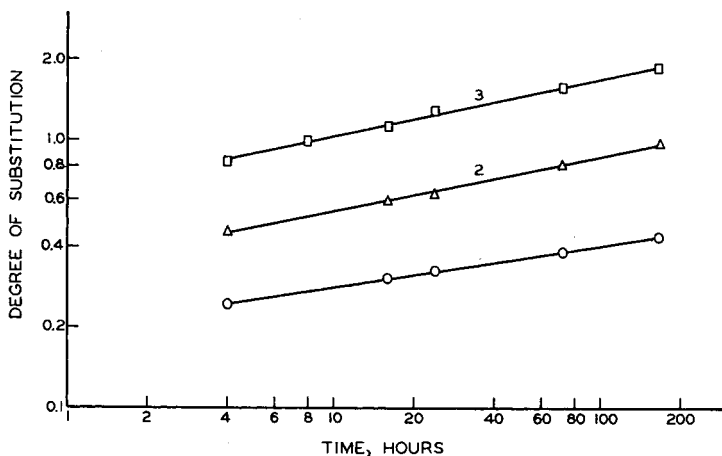


Fig. 2. Degree of substitution as a function of time for acetylated cellulose: (1) cotton; (2) ethylamine-treated, water-washed cotton; (3) ethylamine-treated, pyridine-washed cotton.

acetylated without ethylamine pretreatment. The fibers exhibited extremely uneven swelling and dissolved at a significantly slower rate. They resembled swollen cotton fibers in which the winding layer had restricted lateral expansion (for an illustration of such a fiber see Hock<sup>14a</sup>).

The following conclusions can be drawn from these observations. First, there is a skin of highly acetylated cellulose on cotton fibers acetylated without pretreatment. This indicates that the esterification has taken place mainly on and near the surface of the fibers. Secondly, acetylated fibers pretreated with ethylamine and pyridine do not have any highly acetylated regions to hinder the rapid dissolution of the material. Thus, the esterification must have taken place more uniformly. Thirdly, since acetylated cotton that has been pretreated with ethylamine and water swells homogeneously before its dissolution, the uniformity of the acetylation is intermediate between the first two cases. It can be seen, therefore, that the

treatment of cotton with ethylamine before acetylation has a marked effect on the location of the acetyl groups within fibers of low acetyl content.

It has been found, however, that the acetylation of cotton and of never-dried ethylamine-treated cotton obey the conditions for a diffusion-controlled reaction. Sakurada<sup>16</sup> has suggested that in heterogeneous reactions of cellulose, the kinetics of the reaction are controlled by the velocity of diffusion of the reagent into the cellulose. Sakurada has proposed that diffusion-controlled reactions can be represented by the equation  $x = kz^m$ , where  $x$  is the amount of cellulose reacted,  $z$  is the time of reaction, and  $k$  and  $m$  are constants. The results shown in Figure 1, when replotted as the logarithm of degree of substitution against logarithm of time, give straight lines (Fig. 2). Thus, irrespective of the reactivity of the cellulose, acetylation proceeds in the same manner. It should be noted that, although the reactions may be diffusion-controlled, they may still be taking place primarily in the amorphous regions of the cellulose at the acetyl contents being considered here. Also, the fact that highly acetylated areas were detected in partially acetylated cottons of low degrees of substitution does not necessarily imply that acetylation of the crystalline regions is taking place.

### Hygroscopicity of Acetylated Materials

Figure 3 shows the relation between moisture regain and degree of acetylation of samples prepared from cotton, never-dried ethylamine-treated, water-washed cotton, and never-dried ethylamine-treated, pyridine-washed cotton. It can be seen, in agreement with previous observations,<sup>1</sup> that the

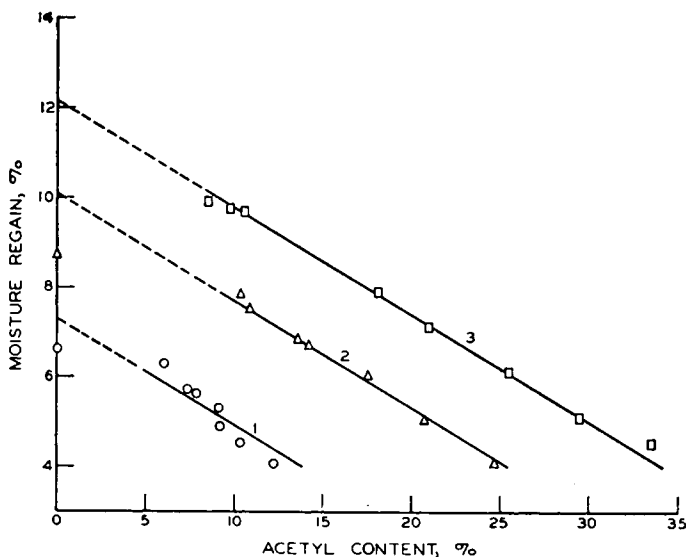


Fig. 3. Relation between hygroscopicity and acetyl content of acetylated cellulose: (1) cotton; (2) ethylamine-treated, water-washed cotton; (3) ethylamine-treated, pyridine-washed cotton.

rate of fall of hygroscopicity with increasing acetyl content is the same, over the ranges considered, for both cotton and ethylamine-treated water-washed cotton. An identical fall in hygroscopicity with increasing degree of acetylation occurs also for ethylamine-treated, pyridine-washed cotton. Figure 3 shows that the hygroscopicity of equally acetylated products prepared from cotton, cotton treated with ethylamine and water, and cotton treated with ethylamine and pyridine progressively increases in this order.

The relation between moisture regain and acetyl content for samples prepared from cotton and ethylamine-treated, water-washed cotton was discussed in detail previously.<sup>1</sup> It was found for cotton that the moisture regain-acetyl content curve fell into two parts: an initial linear portion followed by a second portion of markedly lower slope. It was stated that the first portion corresponded to the acetylation of the amorphous regions of the cellulose and that the slope changed (at 14% acetyl content) when the acetylation extended to the crystalline regions (cf. Bailey, Honold, and Skau<sup>16</sup>). For ethylamine-treated, water-washed cotton only the initial linear portion was considered. The slope of this curve and of the initial portion of the curve for cotton were identical. It was stated that in the range of acetyl contents considered (up to 27.5%) acetylation of the ethylamine-treated, water-washed cotton had occurred in the amorphous regions. The following conclusions were drawn. First, the linearity of the relation between moisture regain and acetyl content showed that the amount of interchain hydrogen-bonding was not altered during acetylation but was fixed by the process at whatever level it may have been when acetylation began. Secondly, acetylation of ethylamine-treated, water-washed cotton did not cause any additional decrystallization until substitution in the amorphous regions was complete. These conclusions can now be seen to apply to ethylamine-treated, pyridine-washed cotton. In this case, also, only the initial linear portion of the curve is being considered.

The moisture regains of cotton, ethylamine-treated, water-washed cotton, and ethylamine-treated, pyridine-washed cotton obtained by extrapolating the curves in Figure 3 back to the ordinate axis are 7.28, 10.06, and 12.17%, respectively. These values are higher than the corresponding directly determined values which are 6.61, 8.73, and 8.71%, respectively. Thus, the importance of adding acetyl groups in order to prevent a loss in accessibility when ethylamine-treated, water-washed cotton is dried is confirmed. It can be seen that the effect of acetyl groups in preventing a decrease in accessibility has been even more marked in the case of the ethylamine-treated, pyridine-washed samples. As stated earlier, the moisture regain determinations on ethylamine-treated, pyridine-washed materials were made after the samples had been washed with water to remove the pyridine. It is interesting to note that the hygroscopicity of ethylamine-treated, water-washed cotton is not altered, within experimental error, if the ethylamine is extracted by pyridine before the material is washed with water. It has been shown that the hygroscopicity of an acetylated product prepared from ethylamine-treated, pyridine-washed cotton is markedly



higher than that of a sample of equal acetyl content prepared from ethylamine-treated, water-washed cotton. It can be deduced, therefore, that when ethylamine-treated, pyridine-washed cotton is washed with water, the water will induce the formation of interchain hydrogen bonds in some parts of the decrystallized regions. Water can act in this manner due to its ability to form more than one hydrogen bond per molecule. A water molecule may, therefore, act as a crosslink by being attached to hydroxyl groups in adjacent chains. When this occurs, the chains will be sufficiently close for them to be directly linked by hydrogen bonds between hydroxyl groups at neighboring sites.

From the sorption isotherm for amorphous cellulose obtained by Beaver and Valentine,<sup>17</sup> it can be deduced that the moisture regain of completely decrystallized cellulose is 15.2% at 59% R.H. and 22°C. Another value is obtained by using Valentine's relation,<sup>2</sup>  $SR = F_{am} 2.60$ , where  $F_{am}$  is the fraction of amorphous material in a cellulose and  $SR$  is its sorption ratio (that is, the ratio of the moisture regain of the cellulose to that of cotton at the same relative humidity and temperature). Taking the value of 6.61% as the moisture regain of cotton at 59% R.H. and 21°C. it can be calculated that the moisture regain of completely decrystallized cellulose is 17.2% at this relative humidity. The moisture regain of ethylamine-treated, pyridine-washed cotton at 59% R.H. and 21°C. obtained by extrapolation of curve 3 is 12.17%. Irrespective of which value is taken as the moisture regain of completely amorphous cellulose, it is clear that the never-dried ethylamine-treated, pyridine-washed cotton is not completely decrystallized.

By using Valentine's relation, the fractions of amorphous material in never-dried ethylamine-treated, pyridine-washed cellulose and in never-dried ethylamine-treated, water-washed cellulose can be determined from the moisture regains obtained by extrapolation of curves 2 and 3 in Figure 3. They are 0.71 and 0.58, respectively. It may be calculated from the equation that the value for cotton itself is 0.38. The mean moisture regain for dried ethylamine-treated materials is 8.72% and thus the fraction of amorphous material is 0.51. To retain the higher accessibilities, the ethylamine-treated material has to be acetylated before it is dried. It is interesting to note that the fraction of amorphous material in the sample of mercerized cellulose is 0.57 (moisture regain = 9.74%). Thus, the accessibility of the mercerized cotton is higher than that of ethylamine-treated cotton but is far lower than ethylamine-treated, pyridine-washed cotton that has been acetylated.

### X-Ray Diffractograms of Prepared Samples

All x-ray diffractograms were obtained on airdry materials. The diffractograms in Figure 4 show the effects of the different treatments on the crystalline regions of the cotton cellulose. It can be seen that extraction of the ethylamine from the cotton by either water or pyridine (followed by water washing) will cause reversion of the crystal lattice to the Cellulose I

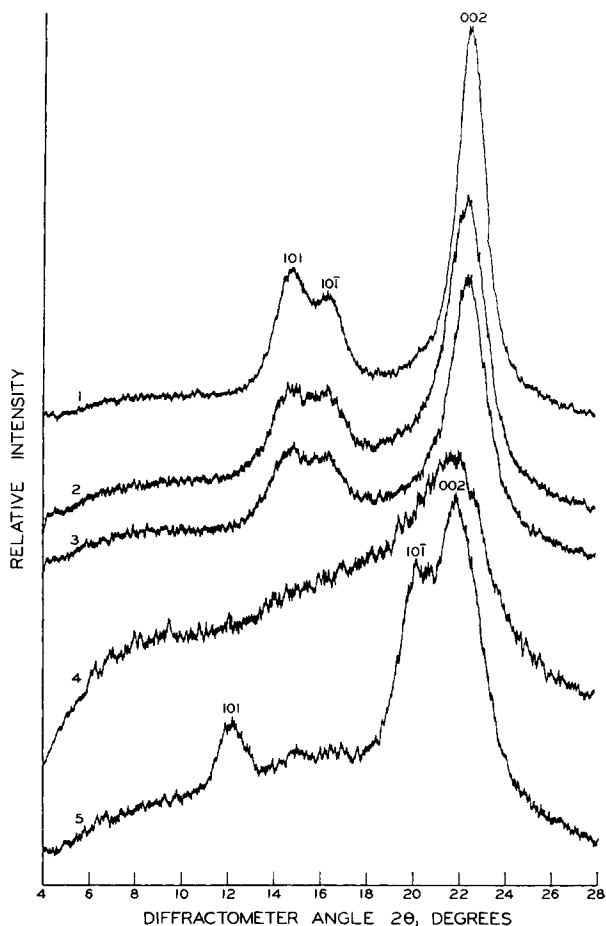


Fig. 4. X-ray diffractograms of (1) cotton, (2) ethylamine-treated water-washed cotton, (3) ethylamine-treated, pyridine-washed cotton, (4) ethylamine-treated, pyridine-washed cotton acetylated to an acetyl content of 9.8%, and (5) mercerized cotton.

form. Crystallinity index measurements (Table I) show that both methods of extraction cause equal amounts of decrystallization. This agrees with the moisture regain results. The marked reduction in crystallinity achieved by acetylating never-dried ethylamine-treated, pyridine-washed cotton can be seen by comparing diffractograms 3 and 4. There has been a broadening of the base of the (002) plane diffraction peak, and there are no signs of maxima corresponding to (101), (10 $\bar{1}$ ) crystalline reflections. At the acetyl contents being considered, the acetyl groups themselves would not have any marked effect on the x-ray diffractogram. A comparison of the x-ray diagrams in Figure 5 makes this clear. All the acetylated materials have roughly the same acetyl content (9.8–10.5%). However, only in the case of the material prepared from ethylamine-treated, pyridine-washed cellulose are the (101), (10 $\bar{1}$ ) diffraction peaks no longer present.

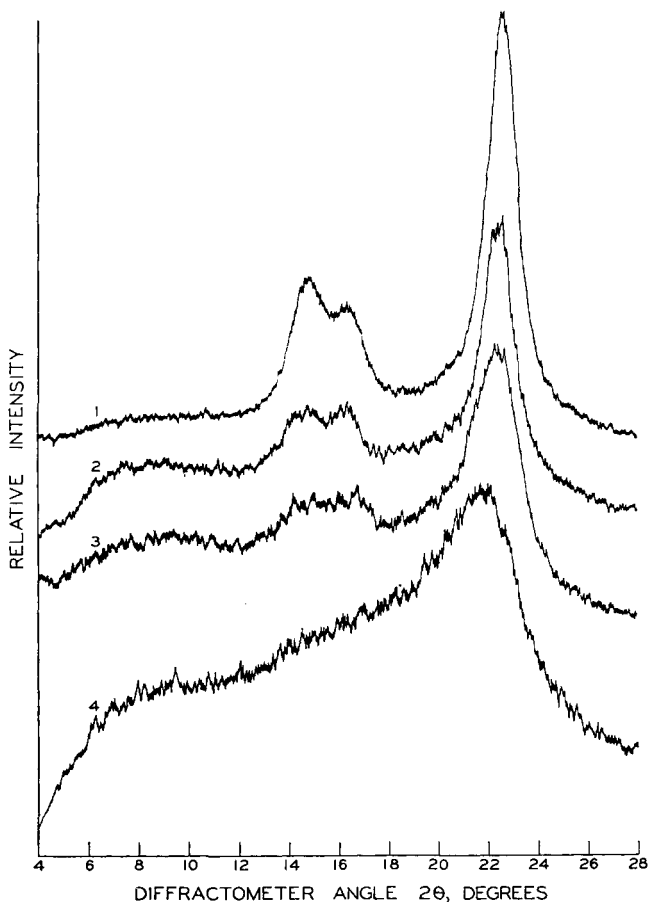


Fig. 5. X-ray diffractograms of acetylated cellulose: (1) cotton, 0% acetyl; (2) cotton, 10.4% acetyl; (3) ethylamine-treated, water-washed cotton, 10.5% acetyl; (4) ethylamine-treated, pyridine-washed cotton, 9.8% acetyl.

The molecular order indices of acetylated samples of cotton, ethylamine-treated, water-washed cotton and ethylamine-treated, pyridine-washed cotton were measured (see Table I). The range of acetyl contents covered were 9.2–12.3%, 10.5–13.6%, and 8.5–10.6%, respectively, and the molecular order indices varied for each set in the following ranges: 69.9–75.0%, 53.9–57.1%, and 32.2–42.7%, respectively. It is clear that a considerable amount of disorder has been achieved by ethylamine treatment followed by pyridine washing and acetylation.

It is not possible to make a meaningful comparison between crystallinity indices and molecular order indices although both have been calculated from the same formula. For example, the crystallinity indices of cotton and of ethylamine-treated pyridine-washed cotton are 82.8% and 70.4%, respectively. The molecular order indices of acetylated cotton of acetyl

TABLE I  
Some Properties of Prepared Materials

Sample	Acetyl content, %	Moisture regain, %	Crystallinity index, %	Molecular order index, %	Half-width of (002) reflection, $2\theta$
Cotton	0.0	6.61	82.8	—	1.36°
Acetylated cotton	9.2	5.36	—	75.0	1.38°
	10.4	4.58	—	69.9	1.45°
	12.3	4.06	—	74.9	1.30°
Ethylamine-treated, water-washed cotton	0.0	8.73	68.9	—	1.77°
Acetylated ethylamine-treated, water-washed cotton	10.5	7.83	—	55.7	1.90°
	10.8	7.58	—	53.9	2.07°
	13.6	6.83	—	57.1	1.90°
Ethylamine-treated, pyridine-washed cotton	0.0	8.71	70.4	—	1.76°
Acetylated ethylamine-treated, pyridine-washed cotton	8.5	9.87	—	42.7	—
	9.8	9.73	—	32.2	—
	10.6	9.68	—	36.4	—
Mercerized cotton	0.0	9.74	—	—	—

content between 9.2–12.3% fall in the range 69.9–75.0%. If a direct comparison is made between the two indices it would appear that acetylation of the cotton has produced approximately the same amount of decrystallization as ethylamine treatment. This would be contrary to the deductions made from the hygroscopicity measurements that at such levels of acetylation, the acetylation occurs primarily in the amorphous regions. It is suggested that the presence of acetyl groups in the amorphous regions of the cellulose will increase the intensity of scattered radiation and that the intensity of the (002) reflection will not be affected. Thus, the formula  $I_{002} - I_{am}/I_{002} \times 100$  will record a decrease, although the crystallinity of the material has not been lowered. There is some evidence supporting this interpretation of the results. Decrystallization of the cellulose would be expected to cause a broadening of the base of the (002) reflection. Gjønnnes and Norman<sup>8</sup> have shown that the degree of amorphousness of cellulosic materials, as measured by the method of Ellefsen et al.<sup>18</sup> increases monotonically with the half width of the (002) reflection. In the present case, the half-widths of the (002) reflections of cotton and of the ethylamine-treated cotton are, in the units of degrees  $2\theta$ , 1.36 and 1.76, respectively. On the other hand, the values for the acetylated cottons lie in the range 1.30–1.45. Thus, within experimental error, it is clear that the acetylation has not caused a decrease in the crystallinity of the cellulose but that the ethylamine treatment has.

It would appear that the best empirical measure of the relative crystallinities of partially acetylated and unacetylated materials would be the half widths of the (002) reflections. However, it is difficult to draw a base-

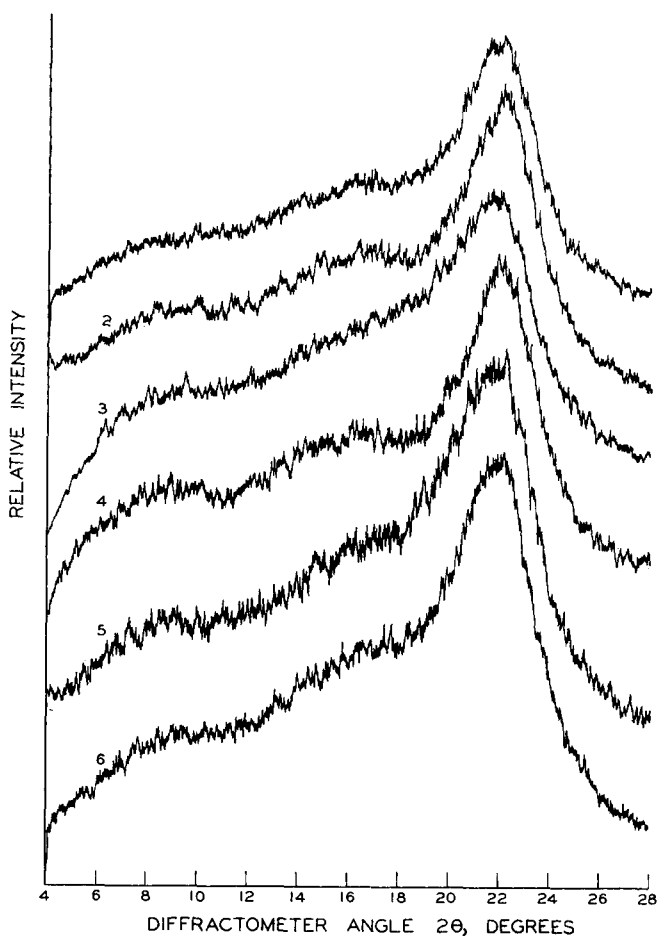


Fig. 6. Effect of boiling in water for 3 hr. on the x-ray diffractograms of acetylated materials prepared from ethylamine-treated, pyridine-washed cotton: (1) Sample of 8.5% acetyl content; (2) preceding sample boiled in water; (3) sample of 9.8% acetyl content; (4) preceding sample boiled in water; (5) sample of 10.6% acetyl content; (6) preceding sample boiled in water.

line, with any degree of accuracy, to the (002) reflection of ethylamine-treated, pyridine-washed samples that have been acetylated.

In order to determine whether recrystallization would be induced, three samples of ethylamine-treated, pyridine-washed cotton that had been acetylated and then dried were boiled in water for three hours. The acetyl contents of the samples ranged between 8.5 and 10.6%. X-ray diffractograms of the samples before and after the treatment are shown in Figure 6. Only in one sample (acetyl content 9.8%) are there any signs of some recrystallization. In this material there is an indication of the reappearance of the (101), (10 $\bar{1}$ ) diffraction peaks. The molecular order indices (see Table II) calculated from the diffractograms agree with these conclusions. They

also show that it is the sample with the lowest molecular order index that has recrystallized. The indices indicate that the fine structure of all three samples remains highly disordered after boiling in water.

TABLE II  
Effect of Boiling in Water for 3 Hr. on the Molecular Order Index of Acetylated Ethylamine-Treated Pyridine-Washed Cotton

Acetyl content, %	Molecular order index, %	
	Before boiling	After boiling
8.5	42.7	44.8
9.8	32.2	44.3
10.6	36.4	37.2

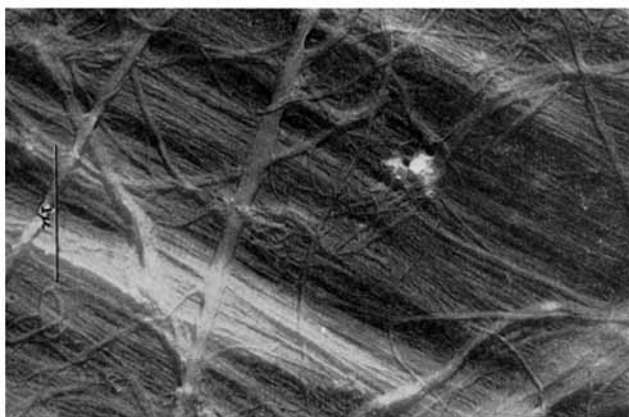
### Fibrillar Structure of Prepared Samples

The effect of the ethylamine treatment on the fibrillar structure of cotton has been examined. Observations were made on fragments of the secondary walls of samples that had been acetylated after pretreatment with ethylamine and pyridine and compared with those of cotton and of cotton treated (without restraint) with 20% sodium hydroxide. Sodium hydroxide solutions of this strength produce marked changes in the fibrillar structure of cotton. In cotton the microfibrils can be clearly distinguished and are arranged in a parallel formation (Fig. 7a). In the mercerized cotton the microfibrils are not so clearly defined. They are swollen and crimped, and there is considerable disorientation (Fig. 7c). These observations are in agreement with those of Rollins and co-workers.<sup>19</sup> The fibrillar structure of ethylamine-treated, pyridine-washed cotton that has been acetylated to a small degree is much closer to that of cotton than of the mercerized cellulose. The microfibrils remain closely parallel though slightly crimped (Fig. 7b). They are clearly distinguishable and do not appear swollen. It is surprising that, although highly decrystallized, the fibrillar structure of this type of material has altered only a slight amount. However, there is evidence<sup>20</sup> that sodium hydroxide solutions cause more swelling than ethylamine in the amorphous regions of cotton. This would help to explain why the microfibrillar structure of the mercerized cotton shows the greater change.

Figure 8 illustrates that the microfibrillar structure of ethylamine-treated, pyridine-washed cotton and ethylamine-treated, water-washed cotton are similar. The size of the microfibrils appears to be little different from those of untreated cotton. Hock<sup>14b</sup> has stated that the (micro)fibrils of cotton are swollen to several times their original diameter by ethylamine treatment. The experimental procedure he used to obtain the micrograph that he shows to support this statement is not given in detail. It is difficult, therefore, to comment on the reason for the difference in results. However, in the present study, it was found that if the fragments examined by trans-



(a)



(b)

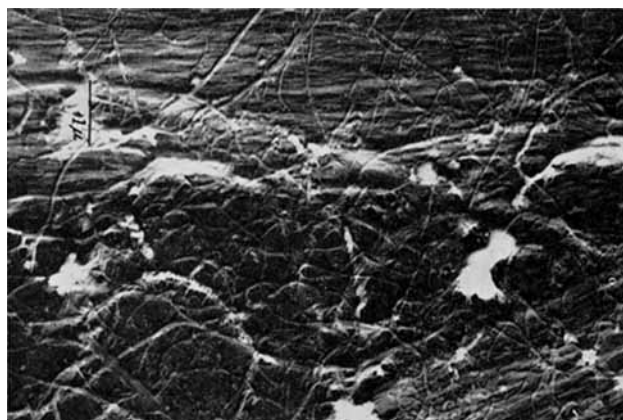


(c)

Fig. 7. Electron micrographs of fragments of secondary wall of (a) cotton, (b) ethylamine-treated, pyridine-washed cotton that has been acetylated (acetyl content 8.5%), and (c) mercerized cotton (17,500 $\times$ ).



(a)



(b)

Fig. 8. Electron micrographs of fragments of secondary wall of (a) ethylamine-treated, water-washed cotton (17,000 $\times$ ) and (b) ethylamine-treated, pyridine-washed cotton (8,500 $\times$ ).

mission electron microscopy are too thick, the fibrillar structure will not be well defined. The appearance of such fragments is almost identical with those in the micrograph shown by Hock.

### Tensile Properties

The single fiber breaking loads and extensibilities of the tested materials are given in Table III, together with their coefficients of variation (CV). In the case of the unacetylated materials it will be seen that two sets of results are given for each treatment. Each set has been obtained on a separate sample and the samples have been given the treatment at different times. It is generally accepted (see, for example, Meredith<sup>21</sup>) that the rupture of native cellulose fibers is determined primarily by the breakage of their chain molecules. Thus, a comparison of breaking loads will give a valid indication of the effect of the treatments on the fine structure of the



cotton. The comparison will be affected if the treatments degrade the fibers. Fluidity measurements showed that in the preparation of the modified celluloses there was a small increase in fluidity. The value for cotton was 3.3 and the maximum increase recorded was 0.6. It is unlikely that the amount of degradation that this represents will have a significant effect on the tensile properties of the fibers.

TABLE III  
Tensile Properties of Prepared Materials

Sample	Acetyl content, %	Breaking load		Extension at break	
		g.	CV, %	%	CV, %
Cotton	0.0	3.7	36	8.5	32
	0.0	3.9	41	9.1	35
Acetylated cotton	9.2	4.0	44	8.1	37
Ethylamine-treated, water-washed cotton	0.0	4.3	51	9.8	44
	0.0	5.1	33	8.4	38
Ethylamine-treated, pyridine-washed cotton	0.0	5.3	40	9.9	37
	0.0	4.6	43	8.6	36
Acetylated ethyl- amine-treated, pyridine-washed cotton	8.5	6.4	32	9.4	30
	9.8	6.2	34	10.0	28
	10.6	5.9	37	8.1	33
Mercerized cotton	0.0	6.3	27	11.7	37
	0.0	5.9	36	10.8	40

The following conclusions can be drawn from the breaking load results. First, the strength of cotton is increased by ethylamine treatment. The increment does not appear to be affected by the solvent (pyridine or water) used for the extraction of the ethylamine and is less than that produced by treatment of the material with 20% sodium hydroxide solution. Orr and co-workers<sup>20</sup> have also observed that the effect of mercerization treatments on the strength of cotton is greater than that of ethylamine. Secondly, a further increase in strength is produced if the ethylamine-treated, pyridine-washed cotton is acetylated. The breaking loads of the acetylated materials (acetyl contents 8.5–10.6%) and of the mercerized cotton are about the same. The results given by Grant<sup>22</sup> show that the breaking loads of cotton acetylated without ethylamine pretreatment to acetyl contents between 13.8 and 15.3% are 7–9% lower than that of the unacetylated samples. In the present series of experiments the breaking load of a cotton acetylated without ethylamine pretreatment to an acetyl content of 9.2% is not significantly different from that of the unacetylated sample. This evidence indicates that the acetyl groups do not contribute directly to the increase in strength of the ethylamine-treated, pyridine-washed materials that have been acetylated up to an acetyl content of 10.6%. It is not conclusive by itself since the location of the acetyl groups in the ethylamine-

treated sample is different from that in samples that have not had ethylamine treatment. This may have an effect on tensile properties. It is suggested that the most probable explanation for the increase in strength is that the acetyl groups prevent crystallization of the ethylamine-treated sample.

Orr and co-workers<sup>20</sup> have explained the strength changes resulting from mercerization and ethylamine treatments as a relief of strains in the fiber structure set up during the drying and crystallization of cellulose while the fibers are in the bolls. Regions that are strained would be weak points in the fiber and rupture of the fiber would be likely to occur at such locations. A reduction in crystallinity will permit greater freedom of movement in the cellulose chains and enable them to readjust to relieve strain at weak points. The fibers will then be able to withstand greater loads before rupture. From the present results it can be seen that mercerized cotton and acetylated ethylamine-treated, pyridine-washed materials have approximately the same breaking load although the latter samples are more highly decrystallized. Thus, it appears that the decrystallization produced by mercerization is sufficient to eliminate all areas of strain in the fibers tested.

There is considerable scatter in the breaking extension results (see Table III). The only treatment to produce a significant increase in breaking extension was mercerization. Ethylamine-treated, pyridine-washed cotton that has been acetylated to an acetyl content in the range 8.5–10.6% does not give such an increase although it is the more highly decrystallized product. There is insufficient evidence to explain why the mercerized samples have the higher elongations at break. It has been shown that mercerization will cause a greater contraction in fiber length than ethylamine treatment.<sup>20</sup> It may be deduced then that mercerization should give the higher breaking extension. However, acetylation of the ethylamine-treated cotton could cause a further contraction in its fiber length. Grant<sup>22</sup> gives results which show that cotton fibers acetylated without ethylamine pretreatment to an acetyl content between 13.8 and 15.3% will have decreased in length by 4–12%. Other results given by Grant<sup>22</sup> show that the breaking extensions of these materials will have decreased by 16–22%. Grant suggests that the decrease is due to the acetyl groups producing a more rigid structure. In the present series of experiments one sample was tested that had been acetylated without an ethylamine pretreatment to an acetyl content of 9.2%. It had a lower breaking extension than cotton, but the decrease was not significant. Even if a marked decrease in breaking extension had been found it would not be possible to draw any conclusions about the ethylamine-treated samples. It has been shown that in samples of equal acetyl content, the location of acetyl groups in the material prepared from cotton is different from that in materials prepared from ethylamine-treated cotton. The location of the acetyl groups could play a significant part in determining the breaking extension of the acetylated products. Thus, further evidence is required to clarify the effect of decrystallization on the elongation at break of cotton.

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### Résumé

Un produit fortement décristallisé a été préparé à partir du coton en le traitant avec l'éthylamine, en extrayant l'éthylamine avec de la pyridine et ensuite en acétylant partiellement l'échantillon dans ce solvant. Les propriétés de ce produit sont comparées à celles du coton, du coton partiellement acétylé, et du coton partiellement acétylé après traitement à l'éthylamine et à l'eau et du coton mercerisé. On a pu confirmer que la réactivité envers l'acétylation du coton traité à l'éthylamine et extrait à la pyridine (sous une forme hydratée) était plus grande que celle de l'échantillon traité à l'éthylamine et extrait à l'eau. Cependant, l'acétylation de ces substances et aussi du coton peut être représentée par une équation exprimée au moyen de réactions contrôlées par diffusion. L'acétylation est nécessaire pour conserver l'état de décristallisation élevé du coton traité à l'éthylamine "non séchée" qui a été extrait à la pyridine. On a déduit à partir de mesures hygroscopiques que la fraction de cellulose amorphe dans cette substance jamais séchée était de 0.71. Les valeurs obtenues pour le coton traité à l'éthylamine séchée et pour le coton mercerisé sont de 0.51 et 0.57 respectivement. La comparaison des diagrammes des rayons X du coton et du coton acétylé traité à l'éthylamine, des cotons lavés à la pyridine (contenu en groupes acétyles de 8.5 à 10.6%) montre que la base du plan (002) du pic de diffraction des substances traitées était plus grande et que les maxima correspondant aux réflexions cristallines (101), (10 $\bar{1}$ ) ne sont pas prés-

entes. Une comparaison des micrographies électroniques de ces substances montre que les microfibrilles dans la paroi secondaire des fibres dé cristallisées demeurent étroitement parallèles bien qu'ils soient légèrement en boucles. Dans le coton mercerisé, d'autre part, les microfibrilles sont gonflés et sous forme de boucles et il existe une désorientation considérable. La mercerisation et le traitement à l'éthylamine suivi d'une extraction à la pyridine et l'acétylation partielle augmentent la force du coton dans des proportions semblables. Le premier traitement produit aussi une augmentation importante de la résistance à la traction des fibres tandis que le dernier traitement ne produit pas d'augmentation marquée de ces propriétés.

### Zusammenfassung

Durch Behandlung von Baumwolle mit Äthylamin und Extraktion des Äthylamins mit Pyridin und darauffolgender teilweiser Acetylierung der Probe in diesem Lösungsmittel wurde ein hochgradig dekristallisiertes Produkt hergestellt. Die Eigenschaften dieses Materials wurden mit denen von Baumwolle, teilweise acetylierter Baumwolle, nach Behandlung mit Äthylamin und Wasser teilweise acetylierter Baumwolle und mercerisierter Baumwolle verglichen. Es wurde bestätigt, dass die Reaktivität in bezug auf Acetylierung von mit Äthylamin behandelte, mit Pyridin extrahierter Baumwolle (in nie getrocknetem Zustand) grösser war als die einer mit Äthylamin behandelten und mit Wasser extrahierten Probe. Immerhin kann die Acetylierung beider Materialien und auch von Baumwolle durch eine für diffusionskontrollierte Reaktionen entwickelte Gleichung ausgedrückt werden. Die Acetylierung war zur Aufrechterhaltung des hochgradig dekristallisierten Zustandes von nie getrockneter, mit Äthylamin behandelte und mit Pyridin extrahierter Baumwolle notwendig. Aus Hygroskopizitätsmessungen wurde der Anteil an amorpher Zellulose im nie getrockneten Material zu 0,71 bestimmt. Die Werte für getrocknete, mit Äthylamin behandelte und mercerisierte Baumwolle waren 0,51 bzw 0,57. Ein Vergleich der Röntgendiagramme von Baumwolle und mit Äthylamin behandelte, mit Pyridin gewaschener acetylierter Baumwolle (Acetylgehalt 8,5 bis 10,6%) zeigte, dass die Basis des Beugungsmaximums der (002)-Ebene beim behandelten Material breiter war; Maxima entsprechend den (101), (10 $\bar{1}$ ) kristalline Reflexe waren nicht mehr vorhanden. Ein Vergleich der elektronenmikroskopischen Aufnahme dieser Materialien zeigt, dass die Mikrofibrillen in der Sekundärwand der dekristallisierten Fasern weitgehend parallel, jedoch schwach gekräuselt blieben. Andererseits waren die Mikrofibrillen bei mercerisierter Baumwolle gequollen und gekräuselt und es trat eine beträchtliche Desorientierung auf. Mercerisierungsbehandlung und Äthylaminbehandlung mit darauffolgender Pyridinextraktion und partieller Acetylierung erhöht die Festigkeit der Baumwolle um ähnliche Beträge. Erstere Behandlung führte auch zu einer merklichen Zunahme der Bruckdehnung der Fasern, während letztere keine signifikante Zunahme erzeugte.

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