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A New Process of Decrystallization and Partial Acetylation of Cellulosic Materials

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Synopsis

A new process of decrystallization of cellulosic materials[8] is described. The process involves the preparation of alkali-cellulose and an interaction between alkali-cellulose and acetic anhydride. The decrystallized products thus obtained are partially acetylated and are designated as SPA (S for swollen, PA for partially acetylated) products. The effect of varying the alkali concentration on the structure and mechanical properties of SPA products is described. Maximum decrystallization is obtained when the swelling is carried out in alkali of intracrystalline swelling strength, prior to treatment with acetic anhydride. Acetylation is instrumental in retaining the highly decrystallized state. The structure of SPA cotton was characterized using chemical analyses, infrared spectroscopy, and x-ray diffraction.

INTRODUCTION

When cotton is treated with aqueous solutions of sodium hydroxide of mercerizing strength, extensive decrystallization of native cellulose takes place.[1] The swelling agent penetrates the fibrillar structure of cellulose and disrupts various intermolecular and interfibrillar H bonds. On the microscopic scale, this results in a high degree of swelling of fibers and adsorption of a considerable amount of alkali. In the swollen state, cellulose forms a complex[2] with alkali, which is generally referred to as "alkali cellulose" or cellulose alkoxide.[3] Subsequent washing with water leads to a decomposition of the complex, removal of excess alkali, and, as a consequence, a collapse of the swollen network of cellulose chains. Drying of washed, mercerized samples in air causes further microfibrillar aggregation and a consolidation of fiber structure.

From the x-ray diffraction viewpoint, treatment with alkali causes not only a decrystallization but also a change in crystal lattice from cellulose I (native cotton) to cellulose II (mercerized cotton) via a "soda-cellulose" lattice. A complete recrystallization of alkali cellulose into cellulose II can be effective only when water is used as a washing medium. Cellulose chains which are quite separate from one another in the alkali-swollen state come close to each other after decomposition of the alkali-cellulose complex with water. Thus, the accessibility gained by cotton upon alkali treatment is at least partially lost upon washing and drying. Loeb and Segal[4] and Zeronian[5] showed that the mercerized but undried cotton possesses a considerably higher reactivity to acetylation than cotton which has been mercerized, water washed, and air dried. It has been

shown that the extent of enhancement of chemical reactivity upon decrystallization is influenced by the way[6] in which the decrystallizing agent is removed. Mercerized cotton, if it is exchanged with organic solvents, possesses a greater disorder[7] and reactivity than when it is washed with water.

The investigations reported here were undertaken with a view to preserve the accessibility of the alkali-cellulose complex and prevent structural collapse during its decomposition. During the present study, it became apparent that in order to achieve maximum decrystallization, a recrystallization of cellulose must be avoided and a few chemical groups should be introduced *while the cellulose molecules are held apart by the decrystallizing sodium hydroxide solution.* Since water is strongly polar and assists in a recrystallization of cellulose, it had to be dispensed with as a medium for washing and decomposition of alkali-cellulose. For the decomposition of alkali-cellulose, a series of nonpolar organic substances, such as formic acid, glacial acetic acid, phthalic anhydride (dissolved in pyridine), acetic anhydride, etc., were tried. The decomposition products thus obtained were studied by means of x-ray diffraction. The decomposition products obtained using the first three compounds showed only slight decrystallization, but the x-ray diffractogram of the decomposition product of alkali-cellulose with acetic anhydride revealed very extensive decrystallization. On chemical and infrared analyses, this product was found to be partially acetylated.

This decrystallization process was standardized and investigated in great detail. Since the process involves swelling and partial acetylation of cellulose, it has been designated as the SPA (S = swollen, PA = partially acetylated) process. Cotton decrystallized using the SPA process has been referred to as SPA cotton. The preparation of SPA products from cellulosic materials will now be described and attempts will be made to characterize them.

EXPERIMENTAL

Materials

Scoured Egyptian Karnak cotton was used as a starting material for various treatments on fibers. Ring-spun grey yarns of 30's counts were used for the SPA treatment on cotton in yarn form. The cotton fabric selected for a similar study was a bleached poplin (128 × 60; 39's/39's). Other substrates employed in the decrystallization process were ramie, jute, viscose, paper, and pulp.

Methods of Treatment

Swelling in Alkali. Cotton, 1 g, was immersed in 100 ml alkali of the required concentration for 30 min. For obtaining the mercerized product, alkali-swollen cotton was thoroughly washed first with running (tap) water and then with distilled water and air dried. For obtaining a decrystallized product, the following procedure was employed.

Decrystallization of Alkali-Swollen Cotton. The alkali-swollen cotton was centrifuged for about 5 min to obtain approximately 200% pickup (by weight) of aqueous alkali. It was then immersed for 30 min in acetic anhydride. After

the completion of the immersion time, the products were subjected to a thorough wash in water and air dried.

Description of the SPA Treatment. A 1:100 material-to-liquor ratio was employed in various stages of this process. The treatment,[8] which was carried out on cellulosic substrates in fiber, yarn, fabric, pulp, or sheet form, can be divided into the following stages: (1) swelling in a suitable concentration of an aqueous solution of alkali for 30 min at room temperature; (2) centrifuging the swollen cellulose to adjust the weight for about 200% pickup of alkali solution; (3) immersion of the centrifuged alkali-cellulose in acetic anhydride for 30 min; (4) thorough washing of the product in water; and (5) drying of the washed product.

The following alkali metal hydroxides were employed in stage (1) of the treatment to establish the extent of acetylation with acetic anhydride: 9% (w/w) lithium hydroxide, 40% (w/w) potassium hydroxide, and 10–36% (w/w) solutions of sodium hydroxide. The effect of changing the immersion time in stage (3) on the acetyl content of decrystallized products was also studied.

Characterization of Products

Acetyl Content. Acetyl values were measured according to the standard chemical method[9] using duplicate samples. The method involves the saponification of finely cut acetylated material in an excess of 0.5*N* sodium hydroxide. After the completion of saponification, the excess alkali is titrated with 0.5*N* hydrochloric acid. Similar treatment was applied to the blank (unacetylated) material also, and from the titration readings the percentage acetyl content was calculated.

Hygroscopicity. Duplicate samples (1 g each) of the material were conditioned by exposing them to an atmosphere of 65% R.H. at 27°C for 48 hr. These were then dried at 110°C to constant weight (attained in approximately 4 hr) in an oven. The moisture content of the sample was calculated from the difference in weights of the conditioned and the dried materials.

Dye Uptake. Cotton, 0.5 g, was immersed in 50 ml Chlorazol Sky Blue FF dye solution in a conical flask fitted with a ground-glass stopper. The flask was placed in a thermostatically controlled water bath at 50°C for 48 hr and was continuously shaken mechanically. The dye adsorbed was estimated from the concentration of the equilibrium dye bath.

Infrared Spectroscopy. Infrared absorption spectra of SPA and other acetylated cottons were obtained using a Perkin-Elmer IR spectrophotometer (Model 221) employing the KBr pellet technique. The degree of acetylation can be correlated with the following band ratio:

$$\text{IR band ratio} = \frac{\text{absorbance of band at } 1750\ \text{cm}^{-1}}{\text{absorbance of band at } 2900\ \text{cm}^{-1} \times \text{absorbance of band at } 3600\ \text{cm}^{-1}}$$

X-Ray Diffraction. Equatorial x-ray diffractograms were obtained from a parallelized pad of fibers using a Philips x-ray diffractometer employing transmission geometry. Effective focussing of the divergent transmitted x-rays was achieved by means of a curved crystal focalizer, an accessory to the diffrac-

tometer, which considerably reduces instrumental broadening. The diffracted beam was monitored by a scintillation counter in conjunction with a pulse-height discriminator. The slit system used employed a divergence slit of 1°, a receiving slit of width 0.3 mm, and no scatter slit. The diffractograms were recorded on a chart using a scanning speed of 0.5°/min and a chart speed of 200 mm/hr.

Mechanical Properties. (a) **Fiber Bundles.** Breaking strength and the extension at break at ⅛ in. gauge of fiber bundles was determined using an Instron tensile tester. The preparation of a parallelized bundle of fibers was carried out on Stelometer jaws, which were mounted on the Instron and extended at a rate of 62.5%. Cross-head speed used was 0.2 cm/min, and the full-scale sensitivity was 5 kg.

(b) **Fabric.** ASTM standard methods[10] were used for the determination of dry crease recovery (Test D 1295-67), breaking load, and elongation by the raveled-strip method (Test D 1682-64), tear resistance (Test D.1424-63), and abrasion resistance (D-1175-64T). Fabric shrinkage after chemical or swelling treatment was deduced from a determination of the density of the ends and picks using a low-power microscope.

RESULTS

The reaction between acetic anhydride and various alkali-celluloses was observed to be exothermic in nature.

Alkali-celluloses were prepared by swelling Egyptian Karnak in aqueous solutions of three different alkalis, namely, the hydroxides of lithium, sodium, and potassium. After removing the excess alkali, each alkali-cellulose was reacted with acetic anhydride for 30 min at room temperature. The reaction products were washed with water and dried. Table I shows the acetyl contents of these products. It can be seen that acetylation took place to an appreciable extent in each case.

In all the subsequent work reported in this paper, sodium hydroxide was employed for the preparation of alkali-cellulose, and this was subsequently reacted with acetic anhydride to obtain the decrystallized SPA products. For a typical cotton sample, Table II shows the effect of reaction time on the acetyl contents of the products. In order to have reproducible results, a reaction time of 30 min was chosen for the preparation of SPA samples.

SPA products were prepared from different cottons, ramie, and jute by swelling them in 24% (w/w) NaOH, squeezing, and reacting with acetic anhydride for 30 min. Table III shows the acetyl contents of various SPA products which lie in

TABLE I
Acetyl Contents of Decrystallized Products Obtained Using Different Alkalis[a]

No.	Alkali used in preparing alkali-cellulose complex	Acetyl content of decrystallized product,[b] %
1	9% (w/w) LiOH	12.2
2	24% (w/w) NaOH	16.7
3	40% (w/w) KOH	18.9

[a] Cotton: Egyptian Karnak.
[b] Obtained by the reaction of alkali-cellulose with acetic anhydride.

TABLE II
Effect of Immersion Time in Acetic Anhydride on Acetyl Content of SPA Cotton

No.	Time of immersion of alkali-cellulose in acetic anhydride, min	Acetyl content of SPA cotton product, %
1	5	9.9
2	10	11.8
3	15	17.2
4	30	17.2
5	45	17.2
6	60	17.2

TABLE III
Acetyl Contents of SPA Products Prepared from Various Cellulosic Fibers

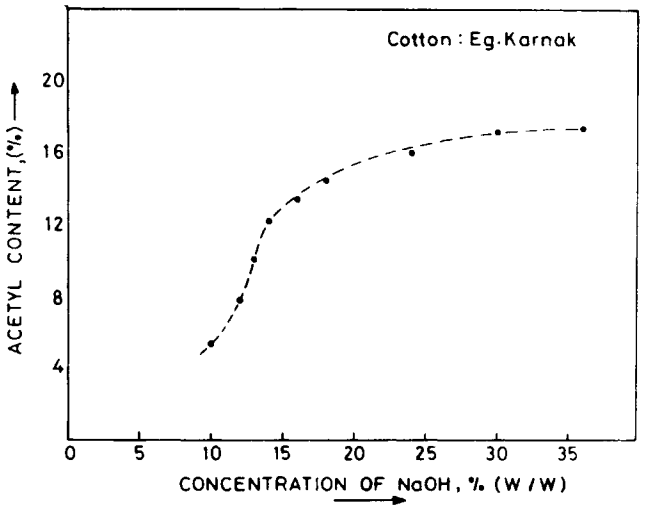
No.	Starting material	Percent mature fibers, Pm	Acetyl content of SPA (24%) product, %	Moisture regain of SPA (24%) products, %
1	Cotton 947[a]	45	17.2	7.64
2	Cotton 805[a]	83	14.5	7.34
3	Cotton Egyptian Karnak	90	16.1	6.53
4	Cotton 888[a]	96	14.0	7.63
5	Cotton 875[a]	98	14.0	7.66
6	Ramie	—	18.9	—
7	Jute	—	17.8	—

[a] USDA cottons.

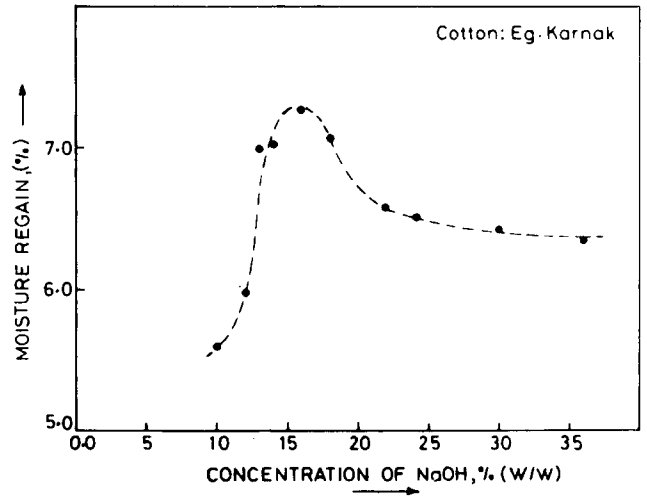
TABLE IV
Effect of NaOH Concentration on Acetyl Content and Moisture Regain of SPA Cotton Products[a]

No.	Concentration of NaOH used in the SPA treatment, % (w/w)	Designation of sample	Acetyl content, %	Moisture regain, %
1	—	Raw cotton	0	5.50
2	24	Mercerized[a]	0	7.90
3	10	SPA (10%)	5.4	5.59
4	12	SPA (12%)	7.8	5.99
5	13	SPA (13%)	10.1	7.00
6	14	SPA (14%)	12.2	7.04
7	16	SPA (16%)	13.4	7.29
8	18	SPA (18%)	14.5	7.08
9	22	SPA (22%)	15.4	6.60
10	24	SPA (24%)	16.1	6.53
11	30	SPA (30%)	17.2	6.45
12	36	SPA (36%)	19.4	6.36

[a] Cotton: Egyptian Karnak.
[b] In this case, alkali-cellulose was washed directly with water; no treatment was given with acetic anhydride.



(a)



(b)

Fig. 1. Effect of varying the concentration of NaOH on (a) acetyl content and (b) moisture content of SPA products.

the range 14% to 19%. The SPA products have a moisture regain of approximately 7%.

The effect of varying the concentration of NaOH on the acetyl content and moisture content of SPA cotton has been studied and is shown in Table IV and Figures 1(a) and 1(b). The moisture regain of SPA cotton increases, passes through a maximum, and decreases as the NaOH concentration is increased [Fig. 1(b)]. Untreated, mercerized, and SPA (24%) cotton have moisture contents of 5.50%, 7.90%, and 6.53%, respectively (Table IV).

Infrared spectra of various SPA cotton samples were obtained using the KBr pellet technique. Figure 2 shows typical spectra obtained for two different SPA samples, where three absorption bands at 3400, 2950, and 1750 cm^{-1} corre-

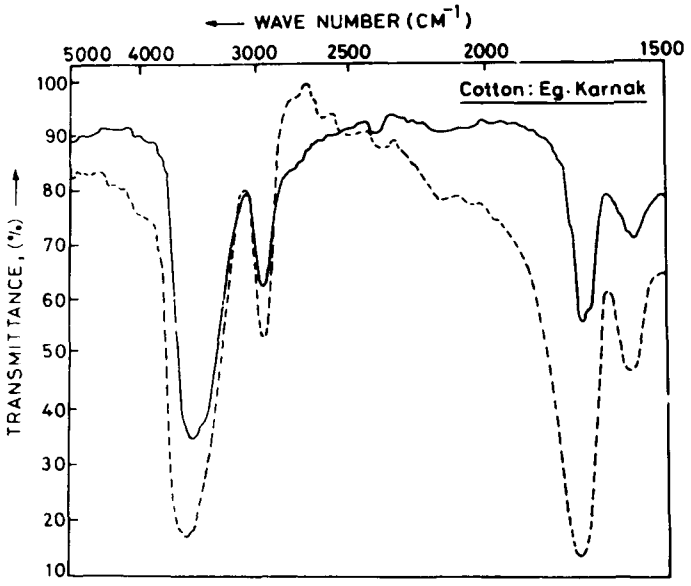


Fig. 2. Infrared spectra of SPA (10%) cotton (—) and SPA (24%) cotton (- - - - -).

sponding to the vibration of —OH, —CH_2, and —C=O groups can be identified.

The absorption at 1750 cm^{-1} was found to be proportional to the acetyl content of the SPA products. From the observed spectra of various samples, the infrared band ratio was calculated. This ratio increased in magnitude with increasing acetyl content of the SPA products (Table V).

Equatorial x-ray diffractograms of various SPA cotton samples are shown in Figure 3, as a function of increasing concentration of NaOH used in the decrystallization process. With increasing concentration of NaOH, progressive decrystallization occurs. The x-ray pattern of SPA (10%) cotton is similar to that of raw cotton. The pattern of SPA (14%) cotton resembles that of mercerized cotton, as 101, $10\bar{1}$, and 002 peaks can be identified. However, in the pattern of SPA (16%) cotton, only one peak is visible in place of $10\bar{1}$ and 002 peaks, due

TABLE V
Fine Structural Parameters of SPA Products
Prepared Using NaOH Solutions of Various Concentrations[a]

No.	Sample	Infrared band ratio	Width of 002 x-ray peak, degree 2θ
1	SPA (10%) Cotton	0.012	1.3
2	SPA (12%) Cotton	0.013	1.3
3	SPA (14%) Cotton	0.019	
4	SPA (16%) Cotton	0.021	3.8
5	SPA (18%) Cotton	0.023	4.0
6	SPA (24%) Cotton	0.022	4.8
7	SPA (30%) Cotton	0.025	5.1
8	SPA (36%) Cotton	0.030	6.0

[a] Cotton: Egyptian Karnak.

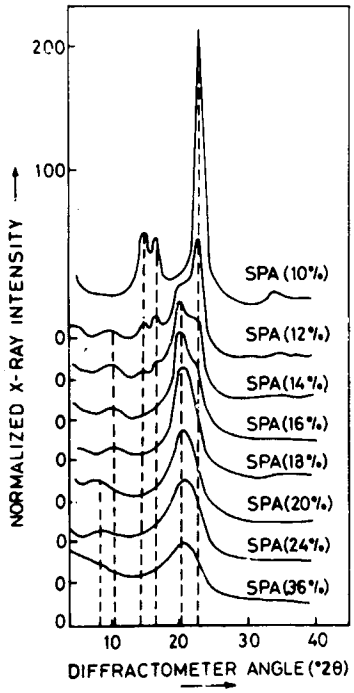


Fig. 3. Normalized equatorial x-ray diffractograms of various SPA cotton products.

to a broadening and overlap of diffraction lines. With a further increase in the concentration of NaOH, there is an extensive broadening of the diffractogram, indicating a destruction of lattice. The diffractograms of SPA (18%) and SPA (24%) cottons resemble the x-ray pattern of a commercial diacetate rayon. In these diffractograms, there is a peak at 8.5 (deg. 2θ) which is produced by the acetylated cellulosic portions of treated cotton. The half-width of the diffraction envelopes located in the region 20–23 (deg. 2θ) of the x-ray diffractograms of

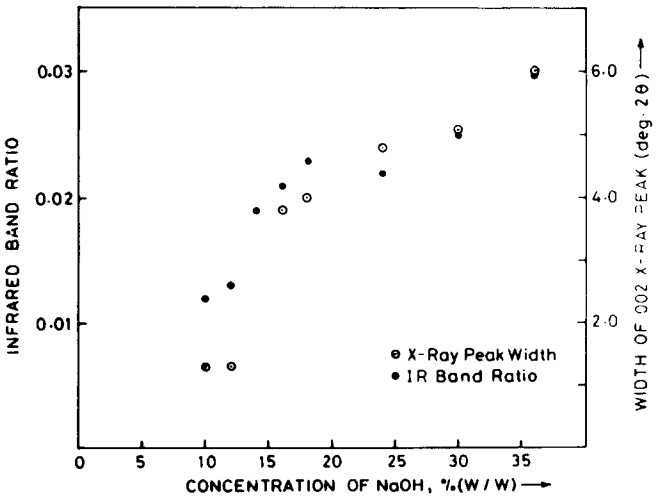


Fig. 4. Plot of infrared band ratio and x-ray half-width vs concentration of NaOH, for various SPA cotton products.

TABLE VI
Mechanical Properties of Untreated, Slack Mercerized, and SPA Cotton[a]

No.	Sample	Bundle breaking strength A, g/tex	Bundle extension at break B, %	Stiffness A/B, g/tex
1	Untreated cotton	24.3	11.9	2.04
2	SPA (10%) cotton	25.8	12.5	2.06
3	SPA (12%) cotton	25.3	12.6	2.01
4	SPA (14%) cotton	25.0	22.4	1.11
5	SPA (16%) cotton	24.2	22.0	1.10
6	SPA (18%) cotton	24.5	23.2	1.05
7	SPA (24%) cotton	22.5	19.0	1.18
8	SPA (30%) cotton	20.1	17.0	1.18
9	SPA (36%) cotton	21.5	15.6	1.38
10	Mercerized (24%)	24.5	21.8	1.12

[a] Cotton: Egyptian Karnak.

Figure 3 has been estimated and is listed in Table V. This half-width increases with increasing concentration of NaOH used in the treatment. Figure 4 shows a plot of the two fine structural parameters of SPA cotton infrared band ratio and x-ray half-width against the concentration of NaOH used in the treatment. Both the parameters can be seen to increase with increasing concentration of NaOH. The increase in the infrared band ratio reflects the increase in acetyl content of the SPA products, whereas the increase in x-ray half-width indicates the increasing extent of decrystallization of the products.

The mechanical properties of untreated cotton, mercerized cotton, and various SPA cotton products are summarized in Table VI. It can be seen that the properties of SPA (24%) cotton lie closer to those of mercerized cotton than those of untreated cotton. With increasing concentration of NaOH, the extensibility of SPA cotton increases, passes through a maximum value of 23.2%, and then falls (a similar trend was observed in the case of moisture regain). Stiffness

TABLE VII
An Intercomparison of Properties of
Untreated, Slack-Mercerized, and SPA-Treated Poplin

No.	Property	Untreated poplin	Slack-mercerized (24%) poplin	SPA (24%) poplin (slack)
1	Shrinkage along warp, %	0	21.1	24.6
2	Breaking load, kg	28.6	34.4	32.0
3	Breaking extension, %	15.1	38.8	39.2
4	Work of rupture, units	100	222	207
5	Elmendrof tear, warp	1008	1248	816
	Strength, g, weft	752	928	672
6	Flex abrasion resistance, warp, cycles	1159	5642	1187
7	Dry crease recovery, (W + F)°	150	174	154
8	Uptake of Chlorazol Sky Blue, (moles/kg) × 10^3	11.3	33.0	65.0

follows the reverse trend. Acetyl content as well as the extent of decrystallization govern the mechanical behavior of SPA samples.

In order to test the resistance to high temperatures, slivers of untreated and SPA (24%) cotton were subjected to treatment in boiling liquid paraffin for 10 min. While charring took place in untreated cotton, the SPA cotton was unaffected by virtue of its acetyl content. Cotton yarns treated by the SPA process could be dyed with disperse dyes. It was also observed that in dyeing experiments using several reactive dyes, the SPA cotton achieved a deeper shade of color than either the untreated or mercerized cotton.

The SPA treatment was also carried out on a cotton poplin fabric in the slack state, employing NaOH of 24% (w/w) concentration. Various properties of the SPA fabric are compared with the properties of untreated and slack-mercerized cotton fabrics in Table VII. The mechanical properties of the SPA fabric are superior to those of the untreated fabric and compare well with the values for the slack-mercerized fabric. However, the tear strength of SPA fabric is slightly lower than the other two on account of the presence of acetyl groups. The SPA fabric has a considerably higher direct dye uptake than the untreated and slack-mercerized fabrics, thus showing an appreciable gain in accessibility as a result of treatment.

DISCUSSION

The general principle underlying the SPA treatment[8] is to prevent the recrystallization of cellulose chains and the collapse of the swollen cellulose structure after the intracrystalline swelling in an alkali (e.g., NaOH) has taken place. This is achieved by neutralization of alkali-cellulose with an acetylating agent, such as acetic anhydride. Acetic anhydride absorbs all the water which is present in the fiber or fabric sample as well as causes acetylation of cellulose. The product obtained is highly decrystallized since the recrystallization of cellulose is not allowed to occur.

The SPA treatment renders the cellulosic substrate amorphous and hence more reactive to subsequent chemical treatment. It also leads to an improvement in the mechanical properties of the material. The SPA treatment has been successfully used for the decrystallization of cotton, viscose, ramie, jute, and paper. The extent and nature of the decrystallization of cellulose are dependent upon the concentration of alkali used in the swelling step of the process. This concentration should preferably be greater than the concentration of alkali at which intracrystalline swelling of the cellulosic material begins to take place, in order to obtain maximum benefits in the accessibility of the products.

The decrystallized SPA cellulosic products have better breaking strength and considerably higher breaking elongation and work of rupture than the untreated materials. They have greater moisture regain, heat resistance, and dye uptake than untreated or the corresponding mercerized products. They are more uniform as regards accessibility as well as in microscopic appearance than the untreated controls. The products are in a particularly reactive form with considerably enhanced accessibility to all chemical reagents in general. Similar decrystallized products were prepared and reported by Zeronian[11] using ethylamine.

A great advantage of SPA products is that they can be dyed with direct, re-

active, and even disperse dyestuffs. This phenomenal feature of SPA cellulose can have considerable application, for instance, in dyeing blends of untreated and SPA cottons in a single bath containing a reactive and a disperse dye to obtain beautiful cross-dyeing effects. Two-shade effects may be obtained upon disperse dyeing blends of polyester and SPA cotton or nylon and SPA cotton.

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