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Further Studies on the Action of Alkali Metal Hydroxides on Cotton*

S. H. ZERONIAN and K. E. CABRADILLA, *Department of Consumer Sciences, University of California, Davis, California 95616*

Synopsis

X-Ray diagrams revealed that the conversion of the lattice structure from cellulose I to cellulose II is substantially complete in cotton treated at 0°C with LiOH, NaOH, or KOH of approximately 5*N* concentration. With concentrations less than 5*N*, there were marked differences in the ability of these reagents to cause lattice conversions in cotton. Below a minimum concentration which is dependent on both the alkali and the treatment temperature, conversion from cellulose I to cellulose II cannot take place in cotton irrespective of the swelling caused by the reagent. We suggest that extensive swelling by one of these alkalis is not sufficient by itself to cause conversion from cellulose 1 to cellulose II and that the concentration of the alkali is of prime importance. There was no direct relation between the swelling induced in cotton by treatment with LiOH, NaOH, or KOH at 0°C and the sorption ratio of the resulting product. Also, although treatment with 5*N* KOH caused less swelling than that obtained with either 5*N* NaOH or LiOH, KOH reduced the level-off degree of polymerization (LODP) of cotton most, indicating the importance of the size of alkali cation in reducing crystallite length. In additional experiments, cotton was treated at 21°C with a solution of 4.7*N* NaOH to which boric acid had been added. Although the swelling of the cotton was little affected, the addition of the boric acid caused the sorption ratio of the product to decrease, whereas the LODP increased. Also conversion of the lattice structure from cellulose I to cellulose II was inhibited.

INTRODUCTION

We have discussed previously the fine structure of cotton treated at 21°C with aqueous solutions of alkali metal hydroxides.[1] We found that the maximum swelling achieved with NaOH, as measured by 2-propanol retention, was higher than that obtained with LiOH, which, in turn, was higher than that from KOH. Also, we found that the level-off degree of polymerization (LODP) of cotton treated with similar concentrations of these alkalis decreased the most with KOH and the least with LiOH. In addition, after the cotton was treated at 21°C with aqueous solutions of alkali at concentrations giving optimum swelling, the extent of conversion from cellulose I to cellulose II was greatest with NaOH and least with LiOH. Our results indicated that the changes that occur in crystal struc-

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ture and in crystallite length, as measured by LODP, when cotton is treated with alkali metal hydroxide solutions are not easily explained solely in terms of the swelling caused by the alkali.

To clarify the role of the cation in changes in crystal structure and in crystallite length, we have studied the properties of cotton treated with alkali metal hydroxides at 0°C. In addition, we have examined the effect of boric acid on the properties of cotton treated with an aqueous NaOH solution to which the acid had been added.

EXPERIMENTAL

Materials

Commercially kier-boiled cotton yarn (80/2's filling twist) was used as starting material. Cupriethylenediamine hydroxide solution was obtained from Ecusta Paper Div., Olin-Matheson Chemical Corp., Pisgah Forest, North Carolina. Other chemicals were reagent grade. The normality of the alkali metal hydroxide solutions was obtained by titration with standardized 0.1*N* hydrochloric acid, using phenolphthalein as indicator.

Methods of Treatment

Treatment with Alkali Metal Hydroxides. Cotton was immersed in the alkali metal hydroxide solution (5 g per 250 ml of solution) in a stoppered, ground-glass bottle for 1 hr at 0°C. After the alkali was filtered off, the sample was washed in several changes of distilled water at room temperature and then stepped in 10% acetic acid for 15 min. The cotton was rewashed in distilled water, with the water being changed periodically until it was free of acid. Samples which were to be retained in the never-dried state for 2-propanol retention determinations were kept in water at room temperature. The remaining samples were dried overnight in an oven at 55°C and then conditioned in the laboratory.

Treatment with NaOH Solution with Added Boric Acid. Cotton was immersed for 30 min in a 4.73*N* NaOH solution (5 g per 250 ml of solution) at 21°C to which various amounts of boric acid had been added. The procedure described in the previous section was used to terminate the reaction and to obtain samples in the never-dried state or in the air-dry state.

Characterization of Product

Descriptions have been given previously[1] of the procedures used to determine the following: moisture regains of samples at 59% R.H. and 21°C; LODP of the air-dry samples; and swelling of never-dried materials, using 2-propanol retention. The procedure used to obtain x-ray diagrams of hydrolyzed cellulosic samples has been described previously also.[1]

RESULTS AND DISCUSSION

Swelling

The extent of swelling of cotton yarn treated with an aqueous solution of alkali metal hydroxide at 0°C, then washed with water and never dried, was measured by 2-propanol retention (Figs. 1 and 2). The 2-propanol retention of the untreated cotton was 34 cm^3/100 g. As the concentration of LiOH was increased progressively up to 5.0*N*, the swelling of the cotton increased initially and then levelled off at 3*N* (Fig. 1). The swelling of cotton treated with NaOH passed through a maximum at a concentration of 3*N* and then remained roughly constant up to the highest concentration examined (Fig. 2). Warwicker[2] has found that the width of cotton hairs immersed in NaOH at 0°C passes through a sharp maximum at a concentration of 3*N*. He has attributed it to bursting of the primary wall of the fiber. The maximum swelling of cotton achieved with LiOH was approximately the same as that obtained with NaOH. At optimum concentrations, KOH did not cause as much swelling as either LiOH or NaOH.

For LiOH and NaOH, the effect on cotton of lowering the treatment temperature from 21°C[1] to 0°C was to lower the concentration at which swelling of the fibers increased sharply and to increase the swelling at optimum concentrations. In addition, the swelling of cotton in LiOH solution at 21°C[1] increased progressively up to treatment with a saturated solution of the alkali; whereas at 0°C, swelling did not continue to increase after the concentration of LiOH reached 3*N*. With KOH, our results indicate that the effect on cotton of lowering the treatment temperature from 21°C[1] to

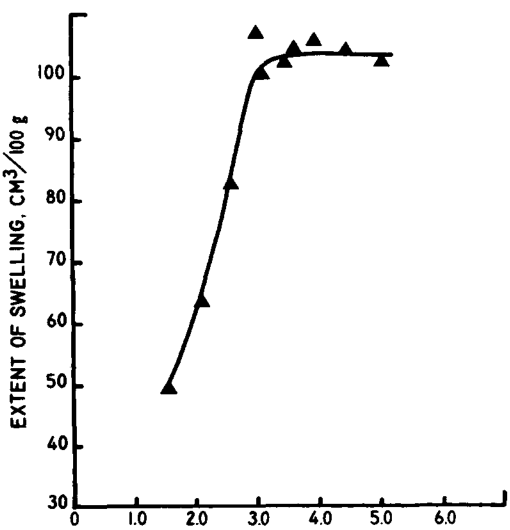

Fig. 1. Effect of aqueous LiOH solution at 0°C on the swelling of cotton, as measured by 2-propanol retention.

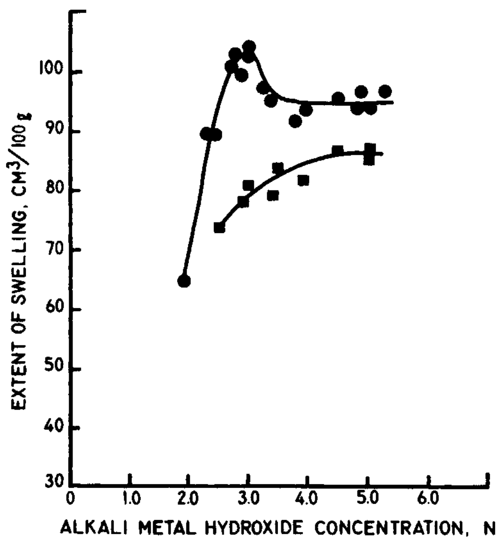

Fig. 2. Effect of aqueous solutions of alkali metal hydroxides at 0°C on the swelling of cotton, as measured by 2-propanol retention: (●) NaOH; (■) KOH.

0°C was to lower the concentration at which extensive swelling of the fibers occurs and to increase the swelling at optimum concentrations.

X-Ray Diagrams

X-Ray photographs were taken of air-dry cellulosic samples which, after treatment with alkali, had been washed with water and dried before being reduced to a powder by hydrolysis for 15 min with 2.5*N* HCl at the boil. The x-ray diagrams revealed that the conversion of the lattice structure from cellulose I to cellulose II was substantially complete in cotton treated at 0°C with LiOH, NaOH, or KOH of approximately 5*N* concentration. In both the LiOH- and KOH-treated samples, weak 101, $10\bar{1}$ reflections indicative of cellulose I were evident on the x-ray diagrams (Figs. 3 and 4). These additional 101, $10\bar{1}$ reflections were fainter on cotton treated with NaOH (Fig. 5).

X-Ray diagrams of cotton treated at 0°C with alkali metal hydroxide at concentrations less than 5*N* revealed marked differences in the ability of the alkalis to cause lattice conversion from cellulose I to II. The swelling of cotton caused by 2.55*N* LiOH was roughly similar to that caused by 3.41*N* KOH (Figs. 1 and 2). However, x-ray diagrams indicated considerable conversion to cellulose II in the KOH-treated cotton (Fig. 6), whereas no conversion was apparent in the LiOH-treated sample. Also, no conversion to cellulose II was obtained by treating cotton with 3.06*N* LiOH at 0°C (Fig. 7), although at this concentration the swelling of the LiOH-treated cotton was markedly higher than that obtained with KOH in the concentration range examined (Figs. 1 and 2). The swelling of cotton at 0°C by LiOH leveled off as the concentration of the alkali was increased

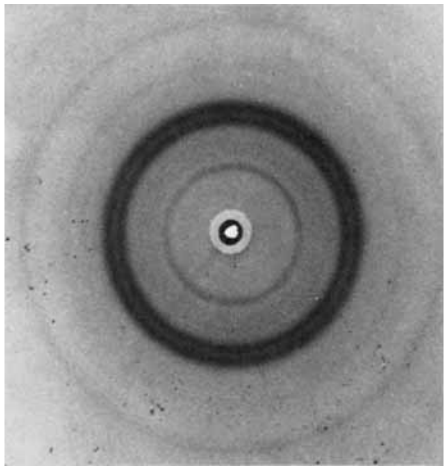

Fig. 3. X-Ray diagram of cotton treated with 5.01N LiOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

above 3N LiOH. However, x-ray diagrams indicated only partial conversion to cellulose II for cotton treated with 3.57N LiOH (Fig. 8), whereas treatment with 4.44N LiOH caused substantially complete conversion to cellulose II, as did treatment with 5N LiOH (Fig. 3). The swelling of cotton treated at 0°C with 2.46N NaOH was greater than that obtained with 5.04N KOH (Fig. 2); but the former treatment caused only a small degree of lattice conversion to cellulose II (Fig. 9), whereas the degree of lattice conversion to cellulose II was substantially complete in the latter case (Fig. 4). Thus, it can be concluded that the cation size of the alkali

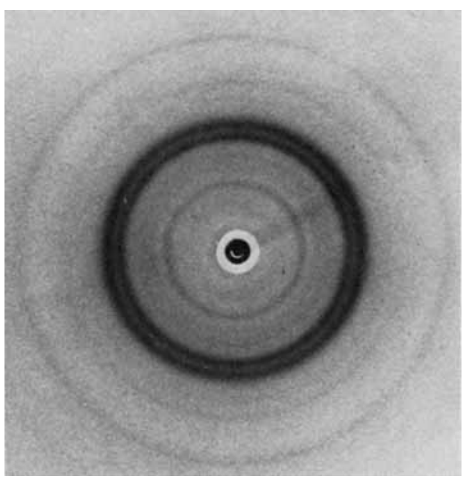

Fig. 4. X-Ray diagram of cotton treated with 5.04N KOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

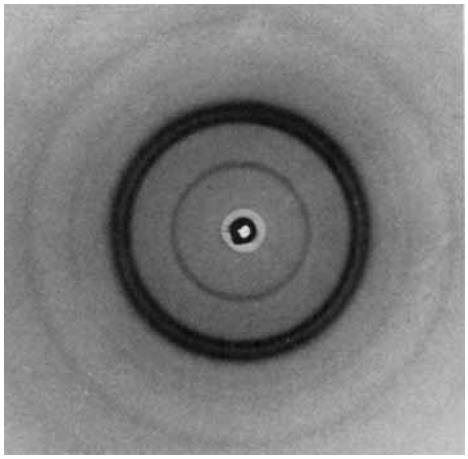

Fig. 5. X-Ray diagram of cotton treated with 5.00N NaOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

metal hydroxide has a marked influence on the amount of swelling required for lattice conversion of the cotton to occur.

As indicated earlier, the swelling of cotton treated with NaOH at 0°C passed through a maximum at 3N concentration. However, at this concentration, there was only partial lattice conversion in the cotton (Fig. 10). Again, with swelling treatments at 0°C, only partial lattice conversion was found at 3.28N NaOH (Fig. 11), but at 4N NaOH, conversion to cellulose II was substantially complete.

Swelling of the crystalline regions of the cotton is necessary for penetration of alkali metal hydroxide to occur, with subsequent conversion of the

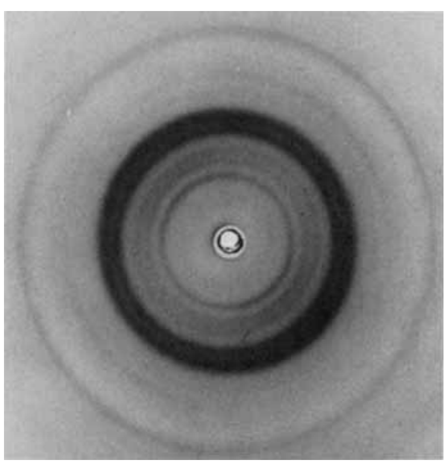

Fig. 6. X-Ray diagram of cotton treated with 3.41N KOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

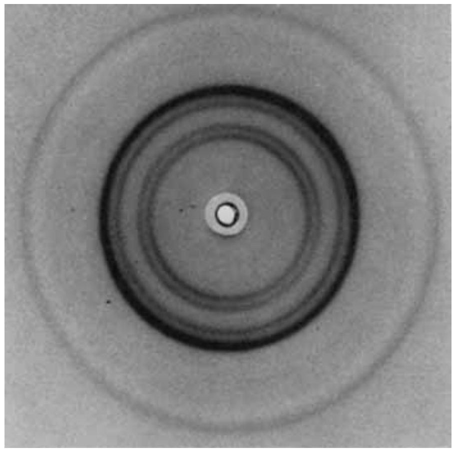

Fig. 7. X-Ray diagram of cotton treated with 3.06N LiOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

lattice structure to cellulose II. However, it appears from our results that extensive swelling of cotton by one of the three alkalis examined is not sufficient by itself to cause conversion from cellulose I to cellulose II. The concentration of the alkali is of prime importance. Below a minimum concentration, which is dependent on both the alkali metal hydroxide and the treatment temperature, conversion from cellulose I to cellulose II does not take place.

For a given concentration and a given alkali metal hydroxide, the swelling induced by the solution can affect the degree of lattice conversion. For example, we have shown previously[1] that the extent of swelling of cotton

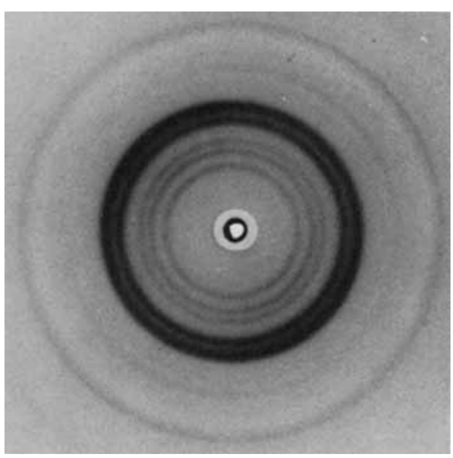

Fig. 8. X-Ray diagram of cotton treated with 3.57N LiOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

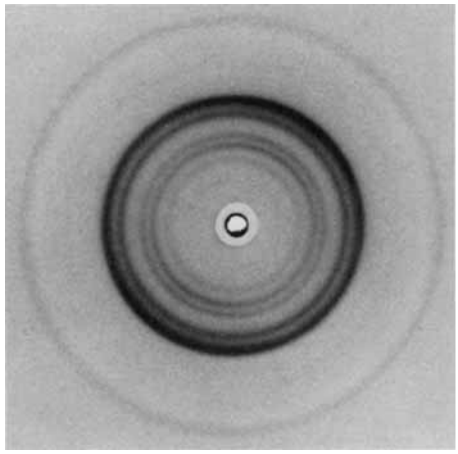

Fig. 9. X-Ray diagram of cotton treated with 2.46N NaOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

treated with 5N LiOH at 21°C is 84 cm^3/100 g, as measured by 2-propanol retention, and that this treatment causes only partial conversion of the lattice structure from cellulose I to cellulose II. If essentially the same treatment is given at 0°C, the swelling of the cotton increases to 102 cm^3/100 g, and conversion to cellulose II is substantially complete.

Other workers[3] treated cotton yarn with 9.5% LiOH at room temperature and found little if any conversion to cellulose II. They suggested that their results may indicate that swelling inside the cotton crystallites can increase certain interchain spacings without causing configurational changes, and that in such a case the lattice formed after removal of the

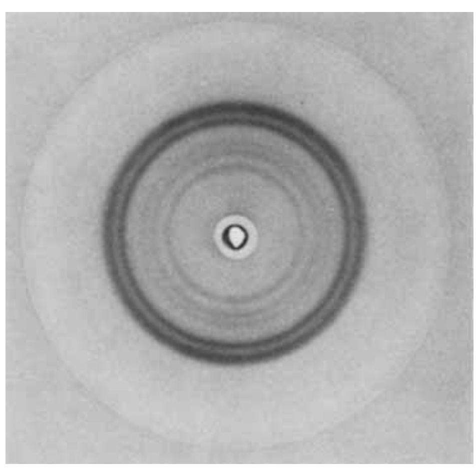

Fig. 10. X-Ray diagram of cotton treated with 3.02N NaOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

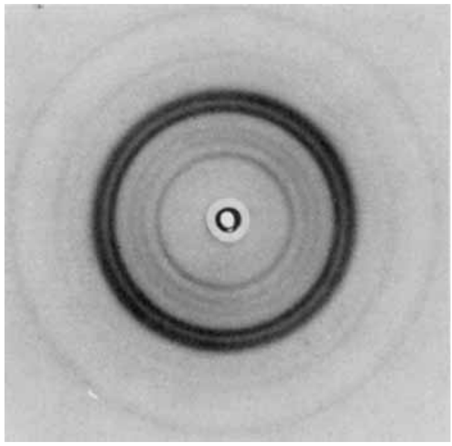

Fig. 11. X-Ray diagram of cotton treated with 3.28N NaOH at 0°C and then hydrolyzed 15 min in boiling 2.5N HCl.

swelling agent can be the same type as that present prior to swelling. Our results indicate, however, that under appropriate treatment conditions LiOH can induce a change in lattice structure of cotton. Warwicker and Wright[4] have suggested a mechanism for the swelling of cotton by NaOH and for the lattice conversion of cotton by NaOH from cellulose I to cellulose II. It is possible that a similar mechanism also holds for LiOH and KOH.

Sorption Ratios

Sorption ratio is defined as the ratio of moisture regain of a cellulose to that of the starting cotton at the same relative humidity and temperature. In our study, moisture regain of the starting cotton was 6.06%. Sorption ratio can be used as a measure of the fraction of amorphous material in a

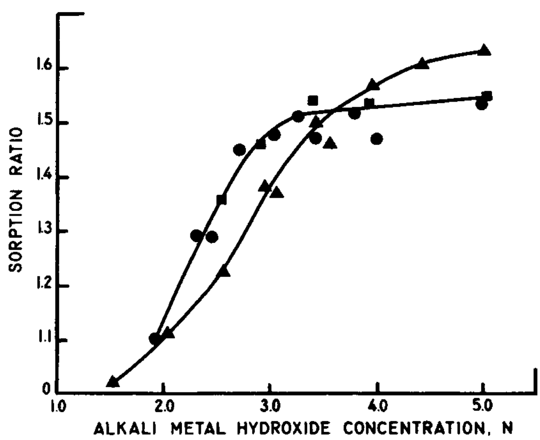

Fig. 12. Sorption ratio of cotton treated with aqueous solutions of alkali metal hydroxides at 0°C: (▲) LiOH; (●) NaOH; (■) KOH.

cellulose[5] or as a measure of the accessibility of the cellulose. The relation between the sorption ratio of cotton and the concentration of the alkali metal hydroxide treatment at 0°C was similar for NaOH and KOH (Fig. 12). At concentrations lower than 3*N*, the sorption ratio of cotton treated with LiOH was less than that of cotton treated with NaOH or KOH (Fig. 12), but the sorption ratios of LiOH-treated cotton became clearly higher than those of NaOH- or KOH-treated samples at concentrations greater than 4*N*.

Although the swelling of cotton at 0°C by NaOH reached a maximum at 3*N* concentration, a maximum was not found in the sorption ratio at this concentration for the NaOH-treated product. Also, the swelling of cotton at 0°C by LiOH became constant at concentrations greater than 3*N*, whereas the sorption ratio continued to increase sharply and only began to level off at concentrations greater than 4*N*. Thus, no direct relation was observed between the swelling of cotton as a result of the alkali metal hydroxide treatment at 0°C and the sorption ratio of the product. This is not unexpected. Swelling was determined on cotton that had not been dried after the alkali treatment. At higher alkali concentrations, the measurements reflect penetration by the alkali of the crystalline as well as of the amorphous regions. In contrast, hygroscopicities were determined on dried samples. Thus, the sorption ratios are measuring the accessibility of the treated cotton after collapse of the fiber structure and after crystallization has taken place. The increase in sorption ratio that occurred after immersion of the cotton in alkali indicates that the treatment changed the fine structure of the fiber in a manner causing an increase in accessibility or in amorphousness. In the case of LiOH, it is interesting also that the increase in accessibility continued above a 3*N* concentration, although further increases in swelling did not occur. It appears that, as in the case of lattice conversion, the concentration of LiOH is of prime importance in causing a change in the amorphousness of the cotton fiber.

For all three alkalis, lowering the treatment temperature from 21°C[1] to 0°C lowered the concentration at which the sorption ratio increased sharply. In addition, the gradient of the initial portion of the sorption ratio–concentration curves increased with the lowering in temperature. Also, the sorption ratio of cotton treated with LiOH at 21°C increased progressively up to a value of 1.44 on treatment with a saturated solution of LiOH.[1] In contrast with treatment at 0°C, the sorption ratio of cotton increased to 1.44 by 3.2*N* LiOH and reached a value of 1.63 on treatment with a saturated solution of LiOH. Our results thus indicate that, in the range of concentrations measured (2 to 5*N*), the accessibility of cotton treated with LiOH was further increased when the treatment temperature was lowered from 21°C to 0°C.

Level-Off Degree of Polymerization (LODP)

LODP can be used to provide an indication of the length of the crystallites in cellulosic materials.[6,7] The LODP of cotton treated at 0°C with

5N KOH was lower than that of cotton treated at 0°C with 5N NaOH or LiOH (Table I). The swelling of cotton at 0°C caused by these alkali metal hydroxides at 5N concentration was greatest with LiOH and least with KOH (Figs. 1 and 2). Thus, although KOH caused the least swelling, it decreased the LODP of cotton most. We suggested previously[1] that KOH, with its larger cation, causes greater disorder at lattice imperfections than does NaOH and consequently reduces crystallite lengths by a greater amount. This suggestion is reinforced by our present finding that LiOH also has less effect on crystallite length than does KOH.

TABLE I
Level-Off Degree of Polymerization (LODP) of Cotton Treated with Alkali Metal Hydroxide at 0°C

Swelling agent	Swelling agent concn., N	LODP[a]
—	—	131
LiOH	2.55	120
	3.06	107
	3.57	84
	4.44	71
	5.01	74
NaOH	2.46	100
	2.73	89
	2.98	87
	3.28	76
	4.00	79
	5.00	75
KOH	3.41	65
	3.92	63
	5.04	64

[a] Level-off degree of polymerization determined after 15 min of hydrolysis with boiling 2.5N HCl.

As noted earlier at 5N concentration, treatment at 0°C with any of the three alkali metal hydroxides investigated will substantially convert the crystal structure of cotton from cellulose I to cellulose II. Our results, in agreement with those of earlier workers,[8] indicate that as cotton is treated with aqueous NaOH of progressively increasing concentration, the crystal lattice of the fiber changes gradually from cellulose I to cellulose II (Figs. 9, 10, 11, and 5) and the LODP also falls gradually and then becomes roughly constant (Table I). However, it should be noted that the decrease in LODP ceased before full conversion of the lattice structure to cellulose II had occurred. The LODP of cotton remained roughly constant for treatments with concentrations of alkali of 3.28N and above (Table I), whereas the lattice structure of cotton treated with 3.28N NaOH was only partially converted from cellulose I to cellulose II (Fig. 11), and that of cotton treated with NaOH of concentrations of 4N and above was substantially converted to cellulose II.

When cotton was treated with LiOH, there was no conversion of the crystal lattice from cellulose I to cellulose II as the concentration of the alkali was increased to 3.06*N* (Fig. 7). However, the LODP had already begun to fall (Table I). At concentrations of this alkali of 4.44*N* and higher, when the conversion of the crystal lattice from cellulose I to cellulose II was substantially complete for the treated cotton (Fig. 3), the LODP also had become constant (Table I).

Previously, the decrease in LODP with increasing concentration of NaOH has been used to determine the mercerization transition range.[8] Although such use may be valid, our results with alkali metal hydroxides indicate that the LODP of the mercerized material will depend on the reagent used to convert the crystal structure from cellulose I to cellulose II.

Effect of Boric Acid on the Swelling of Cotton by NaOH

Cotton was treated at 21°C with aqueous NaOH to which boric acid had been added to determine the effect the addition of boric acid to the reaction solution had on the fine structure of the fiber. An initial NaOH concentration of approximately 4.7*N* was used. The concentration was selected because it is at the start of the range in which further increases in concentration do not cause additional decreases in the LODP of the product.[1] Also, after treatment with 4.7*N* NaOH at 21°C, the conversion of the lattice structure to cellulose II is substantially complete (Fig. 13). The swelling of cotton by 4.7*N* NaOH was little affected as the amount of boric acid added to the NaOH solution was increased progressively to 6% (Table II). However, significant changes were observed in the fine structure of the product. The sorption ratio fell, indicating a reduction in accessibility of the treated product; and the LODP increased, indicating that the addition of boric acid had inhibited the reduction of the crystallite lengths in the

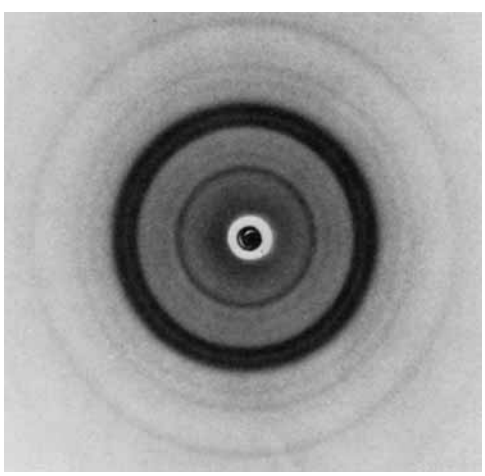

Fig. 13. X-Ray diagram of cotton treated with 4.73*N* NaOH at 21°C and then hydrolyzed 15 min in boiling 2.5*N* HCl.

TABLE II
Effect of Treatment with Alkaline Borate Solutions at 21 °C on the Properties of Cotton[a]

Amount of boric acid added to solution, wt-%	Sorption ratio	2-Propanol retention,[b] cm^3/100 g	LODP[c]
—	1.49	92	80
4.16	1.45	89	75
4.50	1.43	91	74
4.99	1.41	90	91
5.49	1.40	87	91
5.99	1.40	86	96

[a] Alkaline borate solutions prepared by addition of boric acid to 4.73N NaOH.
[b] 2-Propanol retention measured on never-dried sample.
[c] Level-off degree of polymerization determined after 15 min of hydrolysis with boiling 2.5 N HCl.

cotton by the NaOH solution (Table II). Also, the addition of boric acid inhibited conversion of the crystal lattice of the cotton from cellulose I to cellulose II (compare Figs. 13 and 14). The greater the amount of boric acid added, the lesser the conversion.

The fact that changes caused in the fine structure of cotton by treatment with 4.7*N* NaOH are lessened by addition of boric acid to the solution although there is little reduction in swelling supports the contention we made earlier in this paper; namely, that extensive swelling by itself is not sufficient to cause conversion from cellulose I to cellulose II and that for a given alkali metal hydroxide, and a given treatment temperature, the concentration of the alkali rather than the degree of swelling determines when initiation of conversion begins. In the case of boric acid addition to the solution

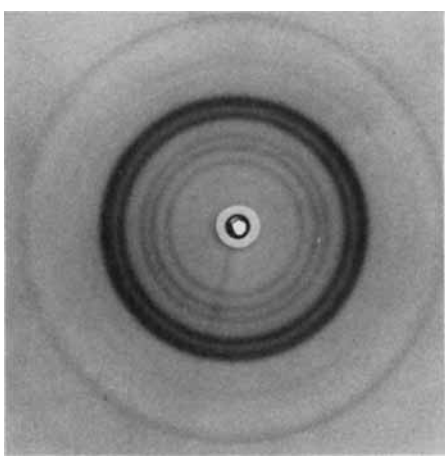

Fig. 14. X-Ray diagram of cotton treated at 21 °C with a solution of 4.73*N* NaOH to which boric acid (6%) had been added and then hydrolyzed 15 min in boiling 2.5*M* HCl.

of NaOH, it appears that the boric acid reduced the amount of sodium hydroxide available to complex with the cellulose, and, as a result, less conversion to cellulose II occurred.

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