

Action of Alkali Metal Hydroxides on Cotton

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Synopsis

The swelling of cotton increased continuously as the concentration of LiOH solution was raised progressively to saturation. In contrast, the swelling of cotton treated with NaOH or KOH leveled off at higher concentrations after increasing initially. The maximum swelling achieved with NaOH was higher than that obtained with LiOH, which was higher than that given by KOH. Accessibility of cotton treated with LiOH solutions, as indicated by sorption ratios, was lower than that of cotton treated with NaOH or KOH solutions of similar concentrations. The level-off degree of polymerization (LODP) of cotton treated with similar concentrations of alkali decreased in the order LiOH, NaOH, KOH. The reactivity, as indicated by acetylation, of cotton treated with alkali metal hydroxides, washed with water, and never dried was measured. At concentrations between 5.5*N* and 8.2*N*, the rate of increase of reactivity was relatively low for cotton treated with NaOH, and no increase was observed for cotton treated with KOH. The reactivity of LiOH-treated cotton continued to increase sharply up to treatment with a saturated solution of the alkali. A limited number of observations were also made on cotton treated with CsOH and RbOH. Accessibility, reactivity, extent of swelling, and LODP values, together with x-ray data, are discussed in relation to the fine structure of the alkali-treated fiber.

INTRODUCTION

The swelling of cellulose by aqueous solutions of NaOH is of technological importance, especially in the mercerization process used by the cotton industry. Because of its importance, the action of NaOH on cotton has been studied in depth by many workers. However, the effect of this alkali on the fine structure of cotton is not understood completely. Investigations with other alkali metal hydroxides have been fewer. A comprehensive review of the action of alkali metal hydroxides on cotton has been provided by Warwicker and co-workers.¹

The purpose of the present investigation was to compare the effect of LiOH, NaOH, and KOH on the properties of cotton in order to establish a better understanding of the action of the alkalis on the fine structure of this fiber. A less comprehensive study of the effect of RbOH and CsOH on cotton was also made.

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, N. C. Other chemicals, except CsOH and RbOH, 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 30 min at 21°C. The alkali was then filtered off, and the sample was washed in several changes of distilled water before it was steeped 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 were kept in water. The remaining samples were dried overnight in an oven at 55°C and then conditioned in the laboratory.

Acetylation. Samples (5 g) of material to be acetylated were washed in 125 ml pyridine. With air-dry samples, the washing was repeated three times; with samples wet with water, the washing was repeated four times. The final portion of pyridine was adjusted to 125 ml by weighing, and 125 ml acetic anhydride was added. The mixture was shaken well and kept at 25°C for 24 hr. Then the acetylation mixture was decanted, and the product was washed with distilled water until free from acid. The sample was dried by exposure to the atmosphere at room temperature.

Characterization of Product

Acetyl Content. The method used has been previously described.²

Hygroscopicity. Moisture regains were determined by drying samples (1.0 g) of the materials in an oven at 110°C for 3 hr and then exposing them at 59% R.H. (obtained by means of a saturated solution of sodium bromide) at 21°C until they reached a constant weight. In order to convert the moisture regains to sorption ratios, the moisture regain of the starting cotton was determined under the same set of conditions. 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.

Level-Off Degree of Polymerization. Cellulosic samples (1 g per 50 ml solution) were hydrolyzed in 2.5*N* hydrochloric acid at the boil for 15 min, using a procedure essentially similar to that of Battista.³ Allowance was made for the moisture present in the air-dry samples when they were being weighed out for hydrolysis.

After the hydrolysis had been terminated, the samples were dried in an air oven at 105°C for 90 min. The residues were then calculated as a percentage of the dry weight of the starting material. Finally, the samples were conditioned in a constant environment room at 65% R.H. and 21°C.

The intrinsic viscosity of the hydrolyzed products was determined with Cannon-Fenske viscometers in cupriethylenediamine hydroxide, using a

method essentially the same as ASTM D1795-62.⁴ Intrinsic viscosity was converted to degree of polymerization (DP) using the relation of Immergut et al.⁵:

$$DP = 124[\eta] \quad \text{where } DP < 300.$$

Following customary nomenclature, the degree of polymerization of the hydrolyzed residue will be called the level-off degree of polymerization (LODP).

Cellulose Swelling

1. *2-Propanol Retention.* In this technique, the extent of swelling of cellulose is obtained by displacing water from the water-swollen sample with 2-propanol, and then determining the amount of 2-propanol retained by the sample after excess fluid has been removed by centrifuging. Yarn cut into 1/2-in. lengths was used. The procedure followed was based on that of Andrews and Oberg.⁶

An International clinical centrifuge with a no. 215 head and 50-ml tubes was used to remove the excess 2-propanol. A no. 3 rubber stopper with a hole of 7/16-in. diameter was placed in the bottom of the tube (Fig. 1), followed by a piece of Tygon tubing, 13/16 in. in diameter and 1/4 in. in length. Finally, 18-mesh wire was placed on the Tygon tubing. The sample was placed on the wire for centrifuging and then the tube was closed with Parafilm. The samples were centrifuged for 30 min at 900 g, weighed, dried in an oven at 100°C for 15 min, and weighed.

The extent of swelling (cm³ per 100 g) was calculated from the formula

$$\frac{W_1 - W_2}{W_2 \times 0.786} \times 100$$

in which W_1 is the weight of sample immediately after centrifuging, W_2 is the weight of dry sample, and 0.786 is the specific gravity of 2-propanol.

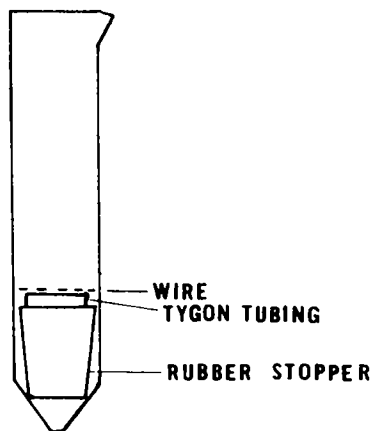


Fig. 1. Centrifuge tube.

2. *Water Retention.* Centrifuging conditions were similar to those used in the 2-propanol retention experiments. However, the samples were dried for 3 hr at 110°C to determine the dry weights. The water retention value (%) was calculated from the formula

$$\frac{W_1 - W_2}{W_2} \times 100$$

in which W_1 is the weight of sample immediately after centrifuging and W_2 is the weight of dry sample.

X-Ray Diagrams. Samples were held in thin-walled, cellulose acetate capillaries, and the photographs were taken with nickel-filtered copper K_α radiation.

RESULTS AND DISCUSSION

Swelling

The extent of swelling of the cotton yarn treated with alkali metal hydroxide and never dried was measured by 2-propanol retention. As the concentration of LiOH was increased up to saturation (5.05*N*), swelling of the cotton increased progressively (Fig. 2). In contrast, the swelling of cotton treated with NaOH or KOH leveled off at higher concentrations after increasing initially. The maximum swelling achieved with NaOH was higher than that obtained with LiOH, which was higher than that induced by KOH.

Water retention values for cotton treated with alkali and never dried also indicated that, at optimum concentrations, NaOH caused more swelling of cellulose than did LiOH, and that KOH caused the least amount of swelling (Table I). The water retention values were greater than the 2-propanol retention values because of the higher surface tension of water.

TABLE I
Determination of Extent of Swelling by 2-Propanol Retention and by Water Retention of Cotton Treated with Alkali Metal Hydroxides and Never Dried

Swelling agent	Swelling agent concn., <i>N</i>	2-Propanol retention, cm ³ /100 g	Water retention, g/100 g
—	0	34	41
LiOH	4.0	74	84
	4.5	78	92
	4.9	84	98
	5.0	88	103
NaOH	6.6	88	102
	7.5	91	108
	5.0	74	90
KOH	6.0	76	91
	7.6	77	92

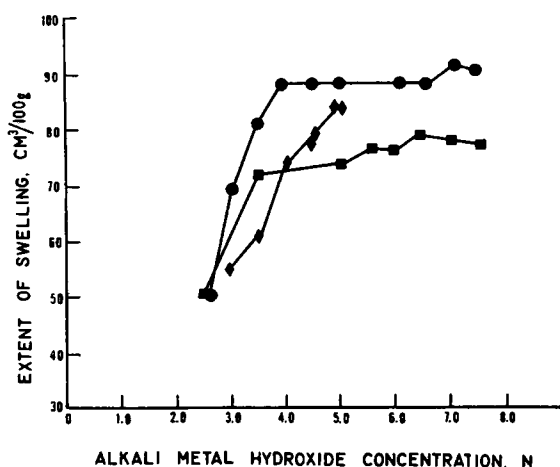


Fig. 2. Effect of aqueous solutions of alkali metal hydroxides at 21°C on the swelling of cotton as measured by 2-propanol retention: (●) NaOH; (◆) LiOH; (■) KOH.

Heuser and Bartunek⁷ have presented data which indicate that the capacity of alkali metal hydroxides, at optimum concentrations, to swell cotton decreases in the order LiOH, NaOH, KOH. They claim that swelling induced by LiOH passes through a maximum at a concentration of 9.5 vol-% (about 4*N*). We found no indication that the swelling of cotton passed through a maximum with increasing concentration of LiOH. Also, in our study, LiOH was less effective than NaOH in swelling cotton. The discrepancy between the two sets of data may reflect the differences in the experimental techniques and swelling conditions used. Heuser and Bartunek determined the degree of swelling by measuring fiber widths, in the presence of alkali, through a microscope. It is difficult to obtain an accurate measure by this technique, as cotton fibers are not of uniform width.

TABLE II
Effect of Drying on the Extent of Swelling of Cotton
Treated with Alkali Metal Hydroxides*

Swelling agent	Swelling agent concn., <i>N</i>	2-Propanol retention, cm ³ /100 g.	
		Never-dried	Dried
LiOH	3.5	61	48
	4.0	74	49
	4.5	78	49
NaOH	4.5	88	50
	6.1	88	51
	7.1	91	46
KOH	5.6	77	50
	6.5	79	53
	7.0	78	53

* 2-Propanol retention of untreated cotton was 34 cm³/100 g.

In addition, their cross-sectional shapes change on swelling. It should be noted, also, that in the present work the swelling measurements were made after extraction of the alkali by water. The ability of the cotton fiber to swell might be affected when the alkali is displaced by water and the change might vary with the alkali used to cause the initial swelling.

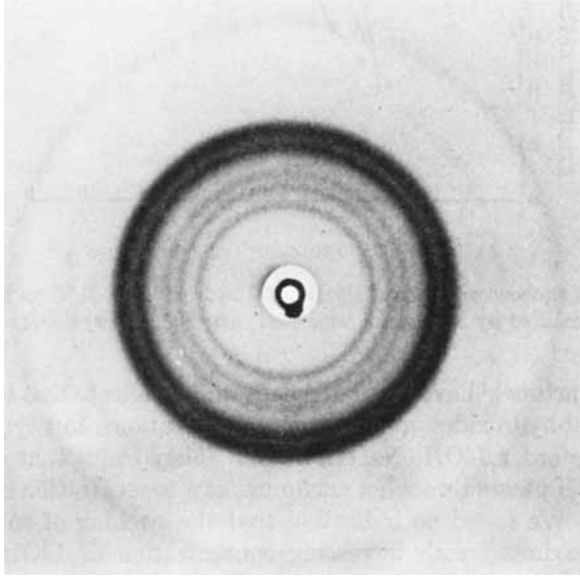


Fig. 3. X-Ray diagram of cotton treated with 5.05*N* LiOH and then hydrolyzed for 15 min in boiling 2.5*N* HCl.

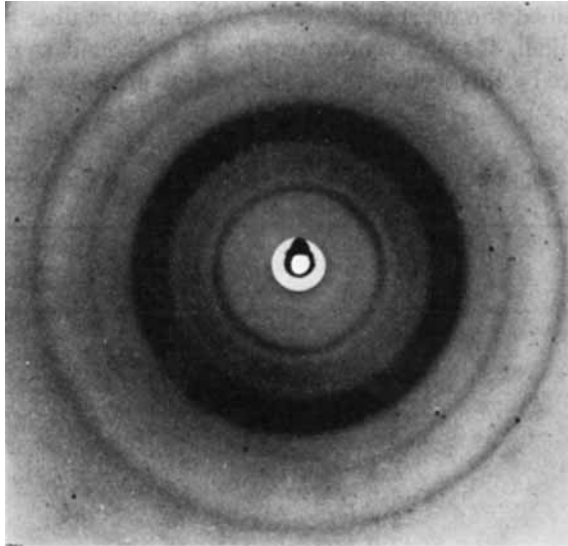


Fig. 4. X-Ray diagram of cotton treated with 7.3*N* KOH and then hydrolyzed for 15 min in boiling 2.5*N* HCl.

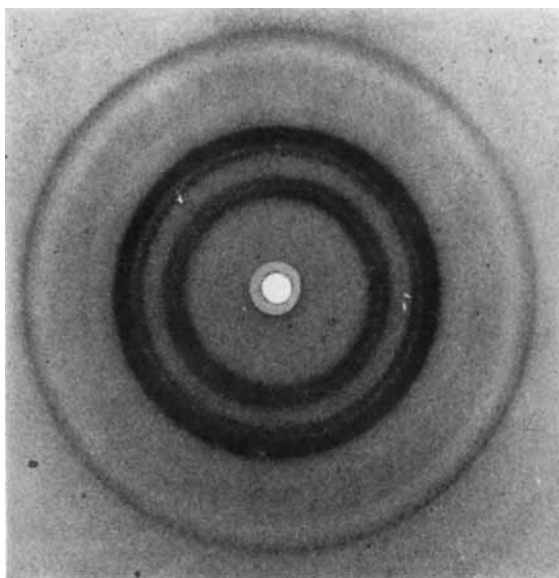


Fig. 5. X-Ray diagram of starting cotton hydrolyzed for 15 min in boiling 2.5*N* HCl.

A marked decrease in the extent of the swelling occurred when alkali-treated cotton was dried (Table II); the decrease reflected a collapse in fiber structure and formation of hydrogen bonds between cellulosic chains. However, the swellability of the dried samples remained greater than that of the starting cotton.

It is well known that aqueous NaOH can penetrate the crystalline regions of cellulose. At 20°C the cellulose crystal form changes progressively from cellulose I to cellulose II as the strength of the NaOH solution is increased above 2.4*N*.¹ Information on the effect of KOH or LiOH on the crystal structure of native cellulose is much more limited.

X-Ray photographs were taken of cellulosic samples which, after treatment with alkali, had been washed with water and dried before being hydrolyzed with 2.5*N* HCl for 15 min at the boil. The x-ray diagram of a sample treated with 5.05*N* LiOH indicated the presence of both cellulose I and II (Fig. 3), whereas that of a sample treated with 7.3*N* KOH revealed almost complete conversion to cellulose II (Fig. 4). For comparison, x-ray photographs of hydrolyzed cotton showing cellulose I (Fig. 5) and of cotton treated with 8.0*N* NaOH and then hydrolyzed showing cellulose II (Fig. 6) are presented. Essentially similar x-ray diagrams were obtained with unhydrolyzed samples that had been ground in a Wiley mill to pass a 20-mesh screen.

Vigo et al.⁸ treated cotton yarn at room temperature and found that 32% KOH (7.5*N*) did not cause complete conversion of cellulose I to cellulose II. They also found 9.5% LiOH caused little, if any conversion of cellulose I to cellulose II. In contrast to Heuser and Bartunek,⁷ who

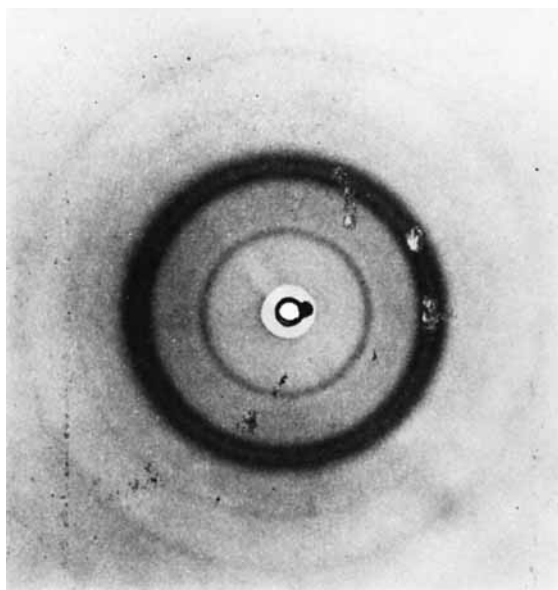


Fig. 6. X-Ray diagram of cotton treated with 8.0*N* NaOH and then hydrolyzed for 15 min in boiling 2.5*N* HCl.

gave their concentrations in vol-%, Vigo et al. used the units of wt-%. Thus, the concentrations used by the latter authors are roughly 10% larger than those determined by Heuser and Bartunek to produce optimum swelling.⁹ Our results indicate partial conversion of cellulose I to II by 5.05*N* LiOH. It appears, therefore, that the higher the concentration of LiOH, the greater the conversion of cellulose I to cellulose II.

For samples that had not been dried after preparation, the swelling of cotton treated with a saturated solution of LiOH was lower than that of cotton treated with NaOH at concentrations between 3.9*N* and 8.0*N* (Fig. 2). As different workers have used various swelling techniques and methods of measurement, it is difficult to define an exact concentration at which NaOH will complete the transition of cellulose crystallites from cellulose I to II. However, the conversion will have been substantially completed within the range of 3.9 to 8.0*N*.^{1,10} If the swelling power of LiOH could be increased in some manner, such as by lowering the temperature, it is possible that it too could cause complete conversion of the crystallites in cotton from cellulose I to II. It should be noted, however, that 5.05*N* LiOH caused greater swelling of cotton than did 7.3*N* KOH, but greater conversion to cellulose II occurred in the KOH-treated cotton. The low level of conversion of cellulose I to II by LiOH may have resulted from the Li ions penetrating into the cellulose crystallites but causing little configurational change, so that when the Li ions are extracted, the crystals of the product revert primarily to the cellulose I form, as suggested by Vigo and co-workers.⁸ Another possibility is that the crystallites present in

cellulose vary in their degree of perfection and that LiOH is not capable of penetrating the crystalline regions of highest order, and mainly causes intercrystalline swelling. It has been pointed out by Warwicker¹¹ that considerable swelling of cotton cellulose can be obtained with reagents that do not penetrate the crystalline fibrils. However, there is evidence to indicate that intracrystalline swelling probably occurs with LiOH solutions of concentration approaching saturation. Cotton which has been given a high swelling capacity by means of an intracrystalline swelling treatment will retain some of the additional capacity after drying. In contrast, the extent of swelling of samples treated with an intercrystalline swelling agent and then dried will not differ much from that of the control.¹² In our study, cotton dried after treatment with LiOH of concentration 3.5*N* or higher retained a markedly higher swelling capacity than did the cotton control (Table II), an indication of intracrystalline swelling. Further evidence comes from sorption ratio results. Sorption ratios give a measure of the degree of accessibility, or fraction of amorphous material, present in cellulose.¹³ The sorption ratio of cotton treated with 5.05*N* LiOH was 44% higher than that of the control. An increase of this magnitude supports the contention that the LiOH had penetrated and disrupted crystalline regions.

Sorption Ratios

The sorption ratio of LiOH-treated cotton increased progressively with increasing concentration of alkali (Fig. 7). In contrast, the sorption ratio of cotton treated with NaOH or KOH leveled off at higher concentrations. Under optimum conditions, the sorption ratio of LiOH-treated cotton was less than that of NaOH- or KOH-treated cotton. These results contrast sharply with the swelling results (Fig. 2). For a given concentration greater than 4.0*N*, the swelling capacity of LiOH-treated cotton was higher than that of KOH-treated cotton if the samples were not dried after treatment. In addition, although the extent of swelling of cotton treated with NaOH was 13% higher at optimum conditions than that of KOH-treated cotton, the sorption ratios differed by only 3%. Thus, as measured by hygroscopicity, the increase in accessibility resulting from treatment with a swelling agent may not reflect fully the swelling power of the reagent. Under optimum conditions, the swelling capacity of cotton treated with LiOH, NaOH, or KOH and never dried was increased 155%, 170%, and 133%, respectively, whereas the sorption ratio of the products was increased 44%, 64%, and 59%, respectively.

Level-Off Degree of Polymerization

LODP can be used to give an indication of the length of the crystallites in cellulosic materials.^{14,15} The untreated cotton had an LODP of 131. The LODP of cotton treated with LiOH solution of increasing strength fell progressively (Fig. 8) to a value of 87 with a saturated solution of LiOH. In contrast, the LODP of cotton treated with NaOH or KOH solutions of

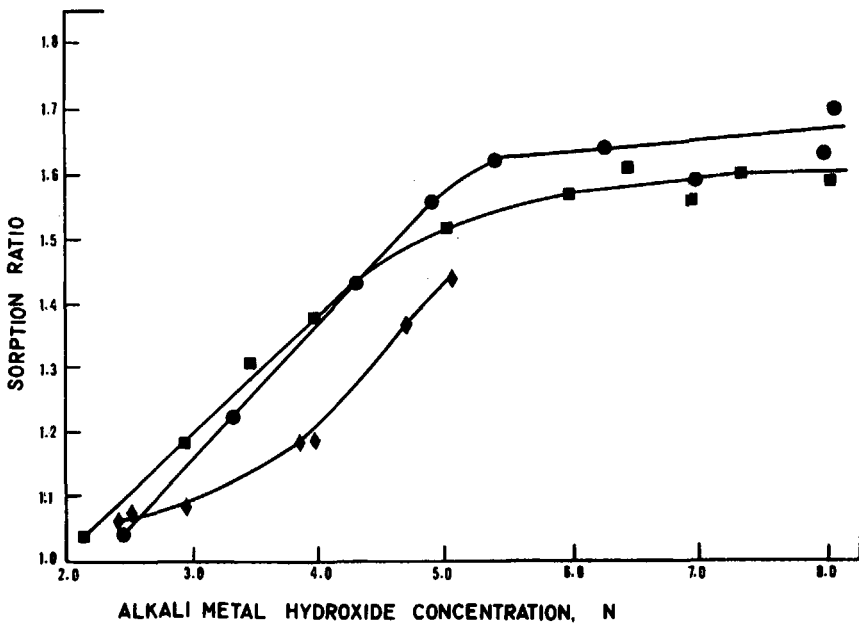


Fig. 7. Sorption ratio of cotton treated with aqueous solutions of alkali metal hydroxides at 21°C: (■) KOH; (●) NaOH; (◆) LiOH.

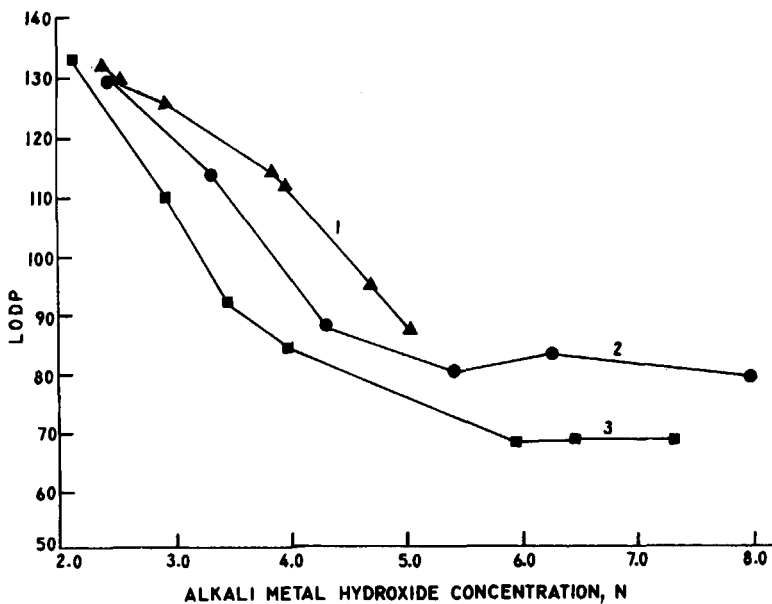


Fig. 8. The level-off degree of polymerization (LODP) of cotton treated with aqueous solutions of alkali metal hydroxides at 21°C: (1) LiOH; (2) NaOH; (3) KOH.

increasing strength fell initially, and then became constant with values of 81 and 69, respectively. Thus, under optimum conditions, the crystallite lengths in cotton were reduced most by KOH and least by LiOH. As indicated earlier, the swelling power of KOH was less than that of NaOH or LiOH. Therefore, it might initially have been expected that KOH would not reduce the LODP of cotton as much as would NaOH or LiOH. However, it appears that the alkali metal hydroxides affect the fine structure of cotton differently.

Current ideas on the structure of cotton have been discussed recently by Warwicker and co-workers.¹⁶ They suggest that any disorder in cotton must be either on the surface of the elementary fibrils or periodically disposed along their length; and that the important factor in the reactivity of cellulose is accessibility to the surface of the fibrils. They also consider the regions where lattice imperfections extend across the fibril to be short in length. The imperfections are not considered as noncrystalline regions into which molecules can readily enter, but rather are envisaged as becoming centers at which acid can attack fibrils.

Based on this model for the fine structure of cotton, LODP would be a measure of the length of the crystallites between the lattice imperfections. Evidence has been presented that acetylation can occur at lattice imperfections after cellulose has been swollen with an intracrystalline swelling agent.¹⁷

As noted earlier, there was a marked drop in LODP of cotton after swelling with alkali metal hydroxides at optimum concentrations. Weight loss after hydrolysis was not affected as much, being 6% for untreated cotton and not greater than 10% for cotton treated with LiOH, NaOH, or KOH at optimum swelling conditions. In previous work¹⁷ it was suggested that treatment of cotton with NaOH of mercerizing strength had produced additional sites of lattice imperfection along the length of the fibrils, thus explaining the lower LODP of cotton after mercerization. The present results can be explained in similar terms. At optimum conditions, the LODP of KOH-treated cotton was less than that of the NaOH-treated samples. It appears, therefore, that KOH, with its larger cation, can cause greater disorder at the lattice imperfections than can NaOH.

The increased swelling capacity retained by cotton that had been dried after treatment with an alkali metal hydroxide solution of sufficient strength to cause intrafibrillar swelling is difficult to explain simply in terms of additional sites of lattice imperfections. In addition to an increased number of these imperfections, other modifications may have occurred to the fine structure of the cotton after the alkali treatment and drying. These could include a disordering of the chain molecules in the surface layers of the microfibrils, or development of fissures or cleavages in the microfibrils along the (101) plane.

The latter possibility can provide a satisfactory model for explaining the increased swelling capacity of the alkali-treated cellulose. It can be used also to explain other facets of the behavior of mercerized cellulose.

For example, from hygroscopicity measurements it can be calculated, using Valentine's relation,¹² that the crystallinity of cotton on mercerization falls from 62% to about 37%, whereas the crystallinity as determined by acid hydrolysis is reduced only from 90% to 72%.¹⁸ In terms of the present model, the increased hygroscopicity on mercerization could be due to sorption of water in the fissures or cleavages. The acid hydrolysis probably occurs first at the lattice imperfections and later at the ends of the crystallites. It would not occur on fissures surface. Sharples¹⁹ has shown that the glucosidic bonds in the surface of crystallites, although accessible to hydrolyzing acid, are remarkably resistant to degradation. The possibility of fissures occurring in microfibrils is consistent also with the theory put forward by Warwicker and Wright²⁰ to explain the swelling of cellulose by NaOH. They proposed that the fundamental reacting unit is a sheet of cellulose chains and that the sheets are separated along the (101) plane. Thus, when the sample is washed and dried after the swelling treatment, it is possible that changes in configuration of the cellulose molecules within the sheets could cause strains within the dried microfibrils and that these strains could precipitate formation of fissures.

Reactivity

Reactivities were determined by acetylation measurements. It should be emphasized that the dried samples were not treated with water prior to acetylation. The reactivity of cotton treated with LiOH solution

TABLE III
Acetyl Content of Cotton Treated with Alkali Metal Hydroxide at 21°C

Swelling agent	Swelling agent concn., <i>N</i>	Acetyl content of never-dried sample, ^a %	Acetyl content of dried sample, ^b %
—	—	—	7.5 ^c
LiOH	3.96	13.5	5.0
	4.96	15.4	1.3
	5.05	17.7	—
NaOH	5.40	—	1.3
	5.50	17.1	—
	5.77	17.4	—
	6.25	—	1.4
	7.96	—	1.0
KOH	8.21	19.0	—
	5.98	16.9	1.2
	6.45	16.9	1.1
	7.33	16.7	1.3

^a After treatment with the swelling agent the sample was washed with water and then solvent exchanged with pyridine before acetylation.

^b After treatment with the swelling agent the sample was washed with water, dried in an air oven at 55°C, and then conditioned in the laboratory before acetylation.

^c The starting cotton was conditioned in the laboratory before acetylation. However, unlike the alkali-treated samples, it was not dried in the air oven.

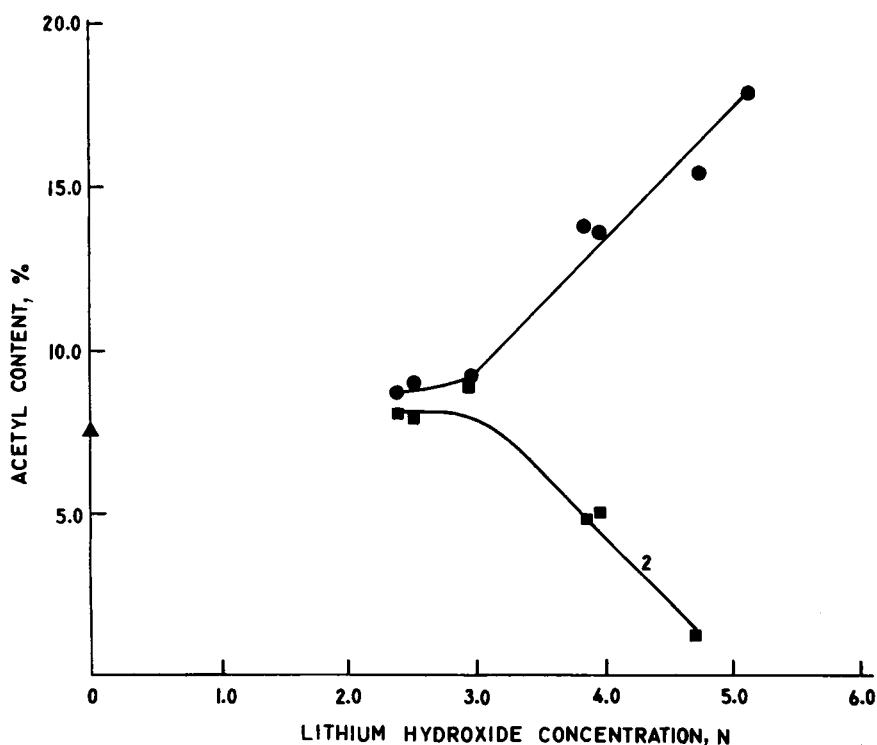


Fig. 9. Effect of aqueous solutions of LiOH on the reactivity of cotton as measured by degree of acetylation: (1) cotton never dried; (2) cotton dried, after treatment with alkali; (▲) starting cotton.

at concentrations up to $3N$ was higher than that of the untreated control, irrespective of whether the sample had been dried or not (Fig. 9). The reactivity of the never-dried samples was only slightly higher than that of the dried samples at this stage. As the concentration of LiOH was increased from $3N$ to $5.05N$, the reactivity of the never-dried samples increased progressively. In contrast, the reactivity of the dried samples became lower than that of the untreated control.

Reactivity determinations on NaOH-treated and KOH-treated cotton were limited to samples treated with alkaline solutions at concentrations yielding maximum swelling (Table III). At concentrations between $5.5N$ and $8.2N$, the rate of increase of reactivity of samples that had been treated with NaOH and never dried was relatively low, and no increase was observed with KOH-treated samples. The reactivity of cotton was increased most by treatment with $8.2N$ NaOH. In both the NaOH-treated and KOH-treated samples there was a sharp lowering in reactivity after drying, with acetyl contents markedly less than that of the untreated control.

Acetylation would be expected to occur initially at the most accessible hydroxyl groups, and increases in reactivity would be due to additional

hydroxyl groups becoming available. Based on the microfibril model given in the previous section, acetylation of untreated cotton takes place initially on the fibril surfaces. If such a sample is treated with a solution of an alkali metal hydroxide at a concentration capable of causing intrafibrillar swelling, and then is washed with water and never dried, additional hydroxyl groups within the microfibrils become available, and thus the reactivity of the sample becomes higher. Accessibility of the hydroxyl groups within the microfibrils can be varied by using a solvent other than water for extracting the alkali.²¹ If the alkali-treated sample is dried before acetylation, the fiber structure collapses and the hydroxyl groups become inaccessible to the acetylating reagent. The results with LiOH (Fig. 9) indicate that the greater the reactivity of the never-dried product, the greater the subsequent collapse of fiber structure on drying.

RbOH and CsOH

A limited number of experiments were done using RbOH and CsOH. According to Heuser and Bartunek,⁷ maximum swelling of cotton by RbOH and CsOH occurs at concentrations of 3.7*N* and 3.0*N*, respectively. X-Ray photographs were taken of hydrolyzed cotton that had been treated with 3.7*N* RbOH (Fig. 10) and with 2.9*N* CsOH (Fig. 11). It can be seen that the crystallites remained in the cellulose I form for the CsOH-treated cotton, but there was an indication of the presence of cellulose II in the RbOH-treated cotton. At the normalities studied (Table IV), the sorption ratios of RbOH-treated and CsOH-treated cotton were roughly similar to the sorption ratio of NaOH-treated and KOH-treated cotton

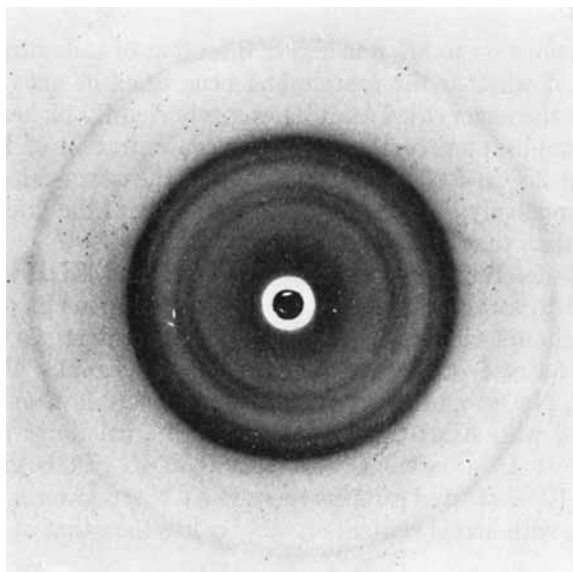


Fig. 10. X-Ray diagram of cotton treated with 3.7*N* RbOH and then hydrolyzed for 15 min in boiling 2.5*N* HCl.

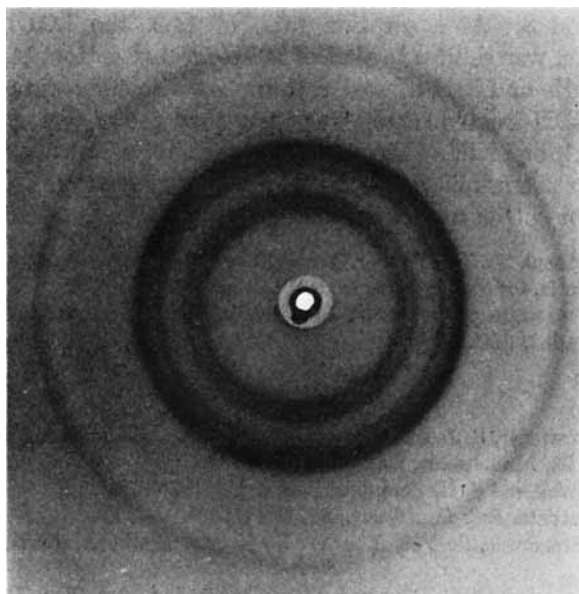


Fig. 11. X-Ray diagram of cotton treated with 2.9*N* CsOH and then hydrolyzed for 15 min in boiling 2.5*N* HCl.

(Fig. 7). Also, the LODP of RbOH-treated cotton was close to the value obtained with KOH-treated cotton (Fig. 8, curve 3). In contrast, the LODP of CsOH-treated cotton was lower for a given normality than that of KOH-treated cotton. The LODPs of cotton treated with 2.9*N* CsOH and 3.7*N* RbOH were 95 and 87, respectively. The value for the CsOH-treated sample was higher than the LODP of cotton treated with KOH, NaOH, or LiOH (69, 81, and 87, respectively) at optimum swelling conditions. However, the LODP of RbOH-treated cotton was similar to that of cotton treated with LiOH.

Instead of comparing LODPs for alkali metal hydroxide treatments at optimum swelling conditions, the samples can be compared at equivalent accessibilities (as measured by sorption ratio) by interpolation from

TABLE IV
Effect of RbOH and CsOH on Sorption Ratio and
Level-Off Degree of Polymerization (LODP) of Cotton

Swelling agent	Swelling agent concn., <i>N</i>	Sorption ratio	LODP ^a
RbOH	3.0	1.15	109
	3.7	1.33	87
CsOH	2.3	1.07	124
	2.9	1.20	95

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

Figures 7 and 8. At a sorption ratio of 1.33, the LODP of RbOH-treated cotton was similar to that of KOH-treated cotton, but lower than that of NaOH- or LiOH-treated cotton. At a sorption ratio of 1.20, the LODP of CsOH-treated cotton was lower than the of cotton treated with KOH, NaOH, or LiOH. Thus, there does not appear to be a direct relation between accessibility and LODP. This observation had been made previously for cotton modified by other methods.¹⁷

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