

Effect of Low Temperatures on Polymorphic Structures of Cotton Cellulose

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Synopsis

Effects of low temperatures upon fine structures of cotton pretreated with either liquid ammonia or caustic of mercerizing strength were investigated. Temperatures of cotton after impregnation with liquid ammonia were lowered by (1) liquid nitrogen, (2) acetone-Dry Ice, (3) acetone, or (4) simple evaporation. With alkali-impregnated fabrics, temperature was lowered by immersion in liquid nitrogen. Changes in fine structure of ammonia- and alkali-celluloses were evaluated by x-ray diffraction before and after removal of each swelling reagent. After treatment with either ammonia or caustic soda, extent of crystalline modification was increased as temperature was reduced. X-ray diffractograms taken while liquid ammonia was still present indicated that the cellulose I structure of cotton sheeting was converted to cellulose III at liquid nitrogen temperatures; extent of conversion was approximately that obtained when a looser yarn structure was treated with liquid ammonia and the ammonia was removed by evaporation. When ammonia was removed with water, the cellulose I lattice was regenerated. In the presence of 23% NaOH, diffractograms indicated a significant decrease in order after a similar drop in temperature, but patterns were not of cellulose II until the NaOH was removed with water. Conversion to cellulose III or to cellulose II was achieved instantaneously when ammonia- and alkali-impregnated fabrics were immersed in liquid nitrogen.

INTRODUCTION

Cellulose I, the major constituent of cotton fibers, can be converted selectively into cellulose II, III, or IV polymorphs. Conventional mercerization with aqueous 23% NaOH produces cellulose II, and treatment with liquid ammonia results either in retention of the cellulose I lattice or in conversion to cellulose III. Both reagents cause a major expansion of the unit cell between (101) planes, but, comparatively, cause very little change in distances between (10 $\bar{1}$) or (002) planes. Thus, differences between swelling in NaOH and in liquid ammonia must be associated with the nature of the swelling complexes formed and their modes of decomposition.

A comparison of 23% NaOH and liquid ammonia as pretreatments in chemical modification of cotton¹ indicated that changes in lattice structure were related to heat changes occurring in the cotton substrate. In formation of cellulose II from the cellulose-NaOH complex, heat changes at the cotton surface, due primarily to dilution of NaOH, are negligible. In contrast, cellulose I is regenerated when the ammonia-cellulose complex is quenched with water, and the heat changes of the cellulose are large and endothermic due to exothermic heats of

formation of ammonium hydroxide. When cellulose III is formed by vaporization of ammonia, heat changes at the cotton surface are exothermic. Therefore, removal of ammonia from cotton at even colder temperatures should increase the extent of conversion to the cellulose III lattice. Experiments reported in this paper were designed to test this latter hypothesis.

EXPERIMENTAL

Cotton specimens included (1) a 3.72 oz/sq yd sheeting which had been desized, scoured, and boiled off with mild alkali and detergent, and (2) a 12/3 scoured yarn.

Chemicals used were reagent grade and included (1) liquid ammonia, (2) liquid nitrogen, (3) acetone, and (4) sodium hydroxide.

Generally, fabric and yarn were immersed slack in liquid ammonia and then were slowly transferred to either (1) liquid nitrogen, (2) acetone, (3) acetone-Dry Ice, or (4) water. Fabric specimens measured 4 in. \times 4 in., and yarns were in skeins weighing about 5 g. Specimens were immersed in excess liquid ammonia (-33°C) for 3 sec, and ammonia remained on them for 6 sec longer before they were immersed for 5 min in one of the quenching reagents. Upon removal from the preselected reagent, each specimen (except that transferred to water) was placed in a polyethylene bag and, while wet, immediately examined by x-ray diffraction. Samples immersed in water are known to have the cellulose I structure and, hence, were dried at 80°C for 7 min. All samples were ground in the Wiley mill for the preparation of x-ray pellets.

Fabric samples treated with NaOH included a slack mercerized control prepared by immersing native cotton in 23% NaOH at room temperature for 30 min, rinsing in cold tap water for 1 hr, then neutralizing with dilute acetic acid for 10 min followed by another 15-min wash with cold tap water, and air drying for 16 hr. In general, other specimens were immersed in 23% NaOH for 30 sec with NaOH treatment either preceding or following immersion in liquid nitrogen for 1 min, or in liquid ammonia for 1 min followed by liquid nitrogen for 1 min. At completion of each treatment, the "wet" specimen was immediately examined by x-ray diffraction.

X-Ray diffraction patterns were obtained by the method of Segal et al.² on a G.E. XRD-5 diffractometer.

RESULTS AND DISCUSSION

The conversion of cellulose I to cellulose III by treatment of cotton fabric with liquid ammonia is achieved under carefully controlled conditions. Cellulose III is characterized by only two x-ray diffractions, located at $2\theta = 20.6^{\circ}$ and 11.6° . Diffractograms of native cotton before and after treatment with liquid ammonia and subjection to various temperatures during quenching of the ammonia-cellulose reaction are shown in Figure 1.

With the exception of samples C and D which are included to show the degree of conversion to cellulose III when conventional ammonia treatments are used, all samples were milled, pelleted, and subjected to x-ray diffraction immediately upon removal from the preselected quenching reagent. Quenching reagents provided temperatures ranging from room temperature to -196°C . Immersion

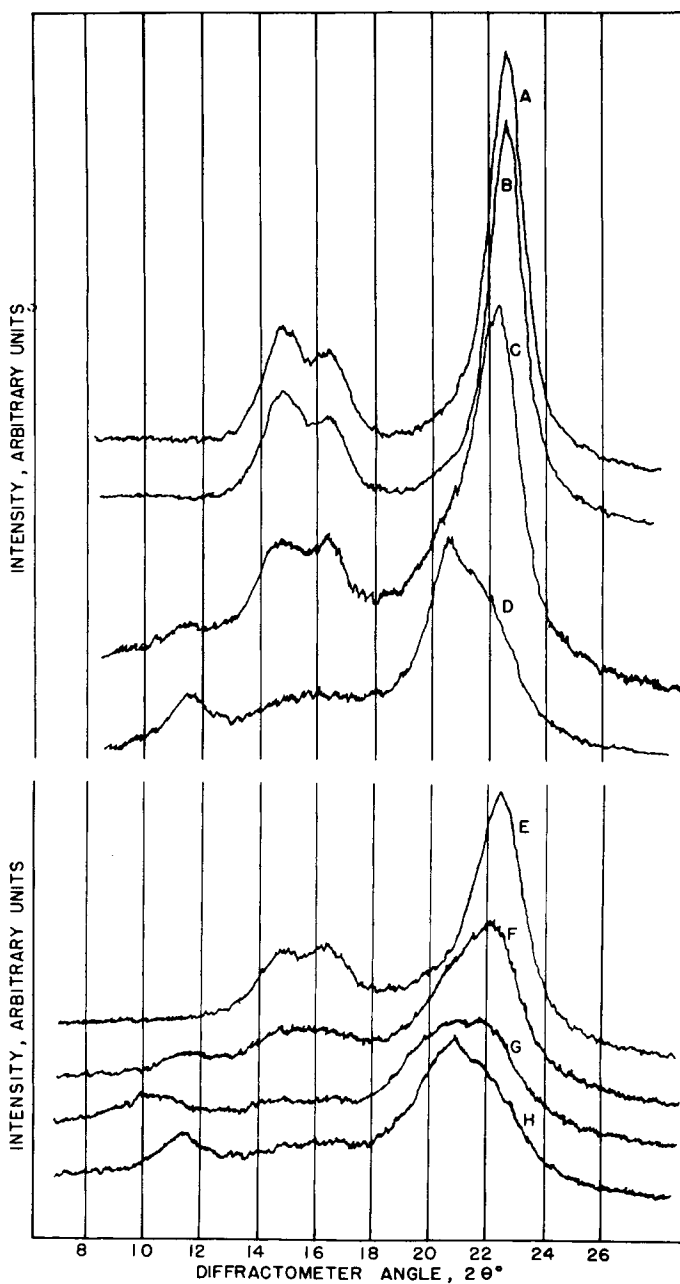


Fig. 1. Effect of temperature on crystalline structure of native cotton treated with liquid ammonia: (A) native cotton fabric control N; (B) N immersed in liquid nitrogen; (C) N treated with liquid ammonia, ammonia removed by evaporation; (D) 12/3 cotton yarn treated with liquid ammonia (75%) and anhydrous ethylamine (25%), reaction quenched with dry acetone; (E) N treated with liquid ammonia, then water; (F) N treated with liquid ammonia, then acetone; (G) N treated with liquid ammonia, then acetone-Dry Ice; (H) N treated with liquid ammonia, then liquid nitrogen.

of native cotton (A) in liquid nitrogen (-196°C) had no effect upon its crystalline lattice (B). The presence of both cellulose I and III diffractions indicate only partial conversion to cellulose III in fabric treated with liquid ammonia followed by evaporative removal (C).

Conversion to cellulose III is indicated for yarn treated in a solution of 75% ammonia/25% anhydrous ethylamine and quenched with dry acetone (D).³ As expected, removal of ammonia with water caused regeneration of cellulose I (E). With acetone (25°C) as the quenching reagent, the presence of some cellulose III was indicated by the shift in (002) diffraction toward $2\theta = 20.6^{\circ}$ and appearance of a broad diffraction at $2\theta = 11.8^{\circ}$ (F). Quenching in an acetone-Dry Ice bath (-78°C) resulted in instantaneous formation of ammonium carbonate. However, diffractograms of a fabric section free of the white substance indicated greater conversion to cellulose III than was observed with acetone alone (G). With liquid nitrogen (-196°C), diffractions characteristic of cellulose I were no longer evident; conversion to cellulose III was greatest (H) and was almost equivalent in extent to that obtained with the yarn and conventional methods (D). Lowering of the temperature from that of liquid NH_3 (-33°C) to that of liquid nitrogen must cause disruption of the cellulose- NH_3 complex and loss of the NH_3 at the lower temperature.

A similar study of ammonia-treated yarns showed that the extent of modification in crystalline lattice also increased as temperature of quenching decreased; when water was used, cellulose I was regenerated. Removal of ammonia from yarn which had been subjected to liquid nitrogen (-196°C) by applying vacuum overnight in a desiccator resulted in some reversion to cellulose I. The more complete conversion to cellulose III required only an "instantaneous" treatment of cotton fabric or yarn with liquid ammonia, provided it was subsequently immersed in liquid nitrogen.

Since the swelling actions of caustic soda and liquid ammonia are similar, a more complete mercerization might be achieved by an instantaneous reaction with NaOH followed by immersion in liquid nitrogen. Studies of the effects of temperature and NaOH concentration upon x-ray diagrams of cotton have been made for a concentration range of 2%–50% and temperatures from -20°C to 100°C .⁴ However, Sisson et al.⁴ immersed cotton fibers in NaOH which had been previously brought to the required temperature in either a water bath or a freezing mixture, and the fibers were subsequently washed with water at the same temperature or with ice water. Under these conditions, three x-ray patterns resulted: (1) native (cellulose I), (2) partially mercerized (celluloses I and II), and (3) completely mercerized (cellulose II). The temperature-NaOH concentration diagrams indicated that the native cellulose lattice was obtained between 0% and 4% NaOH at -20°C and between 0% and 20% NaOH at 100°C . The partially mercerized lattice (I and II) occurs over a very narrow concentration range between -20° and 30°C , but above 60°C it extends over a concentration range of 18%–50% NaOH. Although relationship of temperature and NaOH concentration to extent of mercerization is not simple, these diagrams showed that as the temperature was lowered from room temperature, the concentration of NaOH required for complete mercerization decreased until at -20°C , 5% NaOH was sufficient. Also, between 30°C and -20°C , complete mercerization (cellulose II) was not obtained when NaOH concentration exceeded 35%.

In the present study, native cotton fabric was treated with 23% NaOH at room

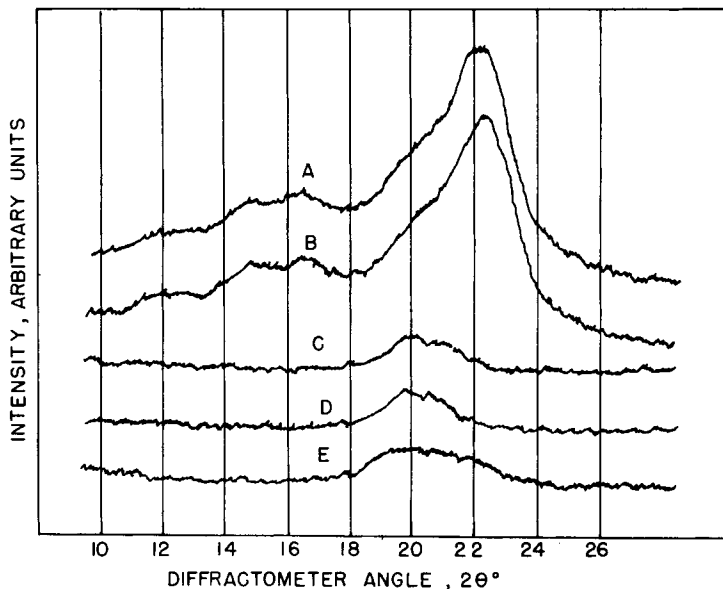


Fig. 2. Effect of temperature on crystalline structure of cotton fabric treated with 23% NaOH: (A) slack mercerized cotton control M; (B) M immersed in liquid nitrogen; (C) native cotton immersed in 23% NaOH, then in liquid nitrogen; (D) native cotton immersed in 23% NaOH, then in liquid ammonia followed by liquid nitrogen; (E) native cotton immersed in liquid ammonia followed by liquid nitrogen and then by 23% NaOH.

temperature and then immersed in either liquid ammonia, followed by liquid nitrogen, or in liquid nitrogen alone. X-Ray diffractograms were made immediately following treatment. For comparison, fabric slack-mercerized with 23% NaOH by the conventional 30-min immersion, souring, etc., process, and fabric pretreated with liquid ammonia/liquid nitrogen to convert it to cellulose III prior to immersion in 23% NaOH were included. Typical diffractograms are shown in Figure 2. As expected, the conventional slack mercerization procedure resulted in partial mercerization (A); when the slack-mercerized specimen was immersed in liquid nitrogen, no further change in crystalline lattice was effected (B). When cotton wet with 23% NaOH was immersed in liquid nitrogen (C) or in liquid ammonia and then in liquid nitrogen (D), other changes were observed. Two very low intensity diffractions at $2\theta = 20^\circ$ and 21° in C and at $2\theta = 19.8^\circ$ and 20.6° in D are evident. In C, the peaks correspond to $(10\bar{1})$ and (002) diffractions of cellulose II at $2\theta = 20^\circ$ and 21.8° , respectively. In D, the peaks correspond to the $(10\bar{1})$ of cellulose II ($2\theta = 20^\circ$) and the (002) of cellulose III at $2\theta = 20.6^\circ$, respectively.

From unit cell dimensions calculated in studies of soda celluloses formed with NaOH at concentrations up to 45% and temperatures of -20° to 100°C , Sobue et al.⁵ concluded that the difference in the six resultant soda celluloses was in their water contents. Petitpas⁶ speculated similarly from his work on soda celluloses from cotton, i.e., only one soda cellulose was formed and the others were different hydrated forms of it. Petitpas⁷ also showed dependence of the threshold of mercerization upon previous history of the cotton. Differences in diffractograms C and D might be attributed to further reaction of some of the available sites remaining after NaOH treatment with the liquid ammonia/liquid

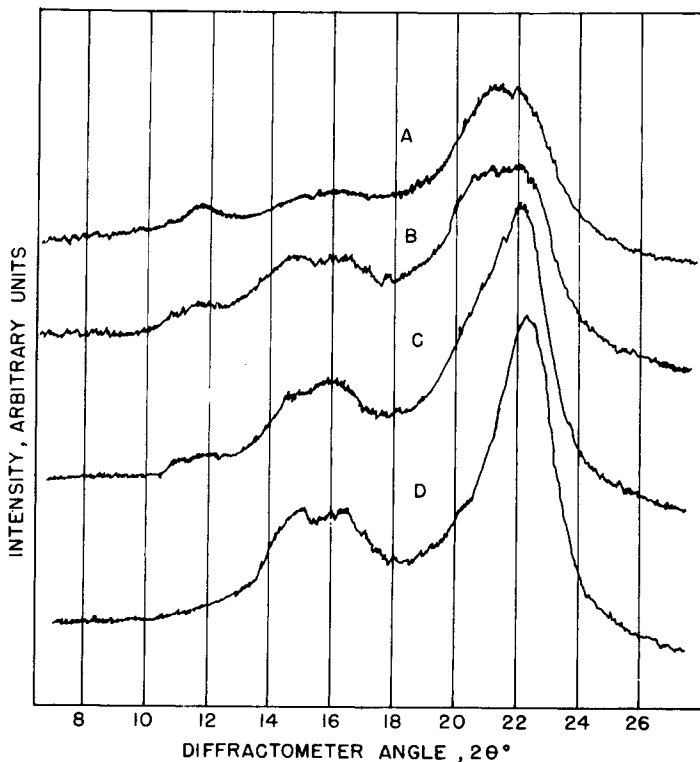


Fig. 3. Effect of storage in polyethylene bags and of washing with water upon structures of cotton sheeting treated with liquid, CAM: (A) CAM immersed in liquid nitrogen after standing 2 days; (B) CAM immersed in acetone-Dry Ice after standing 10 days; (C) CAM immersed in acetone after standing 3 months; (D) all CAM cottons after water washing.

nitrogen to form some cellulose III. When cotton which had been pretreated with liquid ammonia and then immersed in liquid nitrogen was postmercerized with 23% NaOH, only one very low intensity broad diffraction at $2\theta = 18.8^\circ$ – 22.4° was observed (E). The much broader diffraction obtained when NaOH treatment followed immersion in liquid ammonia/liquid nitrogen suggests that conversion of native cotton (I) into the more expanded cellulose III by the pretreatment makes more sites accessible to NaOH. Grinding of NaOH-treated fabrics in preparation for x-ray examination produced a material which was no longer fibrous in nature, but had a fused appearance. Presence of NaOH in the unwashed samples probably masks the characteristic peaks of cellulose and accounts for the apparent amorphous character.

Ammonia pretreated fabrics which had been subjected to decreasing temperatures and then stored in polyethylene bags for various times after pretreatments were reexamined before and after being washed with water. Typical diffractograms are presented in Figure 3. On standing from 2 days to 3 months, ammonia-treated specimens partially reverted to cellulose I. While stored in polyethylene bags, these samples were essentially enveloped by a nitrogen/ammonia atmosphere. No extra precautions were taken to exclude moisture from the atmosphere when samples were put into bags so that as nitrogen and

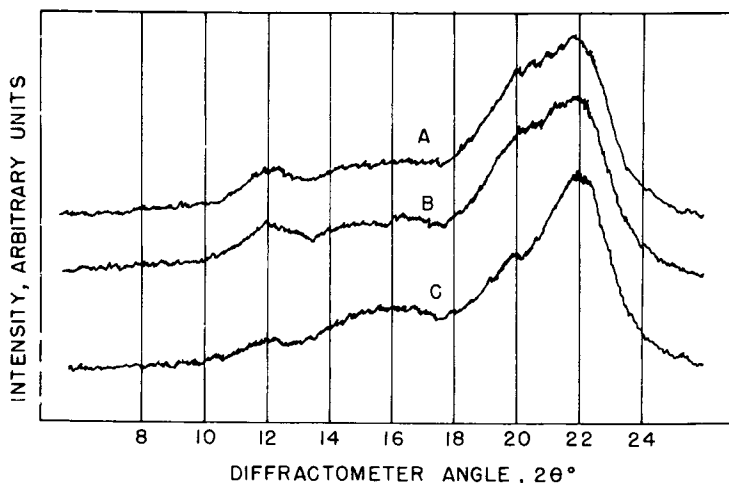


Fig. 4. Effect of washing with water upon structure of cotton sheeting immersed in 23% NaOH, CM: (A) CM immersed in liquid nitrogen then water washed; (B) CM immersed in liquid ammonia followed by liquid nitrogen and then water washed; (C) native cotton immersed in liquid ammonia followed by liquid nitrogen and 23% NaOH, then water washed.

ammonia are lost, any moisture present would cause the observed partial reversion to cellulose I. After washing with water, complete regeneration of cellulose I crystalline lattice was effected (Fig. 3).

Figure 4 shows x-ray diffractograms of stored fabrics pretreated with NaOH after they have been washed with water and air dried. The NaOH-treated fabric which had been immersed in liquid nitrogen was converted to cellulose II when washed with water (A). Fabric treated with NaOH and then immersed in liquid ammonia followed by liquid nitrogen possessed a mixed cellulose I and II lattice after water washing (B). When immersion in liquid ammonia and then in liquid nitrogen preceded an NaOH treatment, a mixed cellulose I and II lattice was also present in the water-washed sample C, but in this case, the cellulose II conversion was greater than in B. As indicated earlier, when liquid ammonia was present, some cellulose III apparently was formed; water washing should revert this to cellulose I and would account for presence of the mixed lattice indicated in x-ray diffractograms. When ground in preparation for x-ray examination, these water-washed samples retained their fibrous nature. Thus, the "fused" nature of those samples ground while wet with NaOH was due to inclusion of the NaOH. More complete conversion to cellulose II after water washing of the NaOH treated fabric which had been subsequently immersed in liquid nitrogen (Fig. 4A vs. Fig. 2A) indicates that the lower the temperature at the cotton surface, the greater the mercerization accomplished with 23% NaOH. This effect is similar to that noted in the production of cellulose III by liquid ammonia treatment.

Borruso⁸ has shown that soda-celluloses are formed at lower alkali concentrations by addition of alcohols, ethylenediamine, or acetone, and Sisson⁴ has shown that complete mercerization is achieved at lower alkali concentrations as the temperature is reduced to -20°C . Thus, at liquid nitrogen temperature, the observed greater conversion can probably be achieved at NaOH concentrations even below that reported by Sisson⁴ at -20°C .

SUMMARY AND CONCLUSIONS

These data indicate that in the presence of liquid ammonia or NaOH swelling reagents, the extent of crystalline modification of native cotton is increased as the temperature at the cotton surface is lowered. The extent of conversion to cellulose III achieved by lowering the temperature from ambient to -196°C when cotton sheeting was treated with liquid ammonia was the same as that obtained when a looser yarn construction was treated conventionally with liquid ammonia. In presence of 23% NaOH, x-ray patterns were not those of cellulose II while NaOH was still present in the sample. Ammonia-swollen cotton reverted to cellulose I, and NaOH-swollen cotton sheeting reverted to either cellulose II or to a mixed cellulose I and II lattice when swelling reagents were removed by water washing. A mixed cellulose I and II lattice occurred only when liquid ammonia was used in conjunction with the 23% NaOH. When ammonia was used, presence of some cellulose III was indicated, and upon water washing, this portion apparently reverted to cellulose I.

The cellulose II lattice was obtained from NaOH-swollen cotton sheeting which had been immersed in liquid nitrogen alone. Crystalline lattice changes occurring in the presence of liquid ammonia resulted from instantaneous treatment with this swelling reagent by lowering the temperature of the cotton surface through use of liquid nitrogen. Whereas conventional mercerization at room temperature necessitated 30 min immersion in caustic soda, only instantaneous (35 sec) immersion in 23% NaOH was required for conversion to cellulose II at the temperature of liquid nitrogen (-196°C).

In conventional procedures, it is difficult to obtain complete mercerization (cellulose II) or conversion to the cellulose III lattice when native cotton is reacted in fabric form with 23% NaOH or with liquid ammonia, respectively. Yet these highly swollen alkali- and ammonia-celluloses are desirable in chemical finishing processes, presumably because of greater accessibility to other finishing reagents. It is conceivable, therefore, that instantaneous formation of these highly swollen celluloses by inclusion of such a temperature-reducing step in processes using these swelling reagents would increase reactivity of cotton cellulose with other modifying reagents and thereby increase the overall efficiency of the textile finishing process.

Mention of companies or commercial products does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

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