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Physical and Fine Structure Properties of Cotton Fibers Swollen with Trimethylbenzylammonium Hydroxide

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Synopsis

Cotton fiber was treated with aqueous trimethylbenzylammonium hydroxide (Triton B) at concentrations over the range 25%–40%. After complete removal of the swelling agent, the samples were evaluated for the extent of swelling, strength and elongation, birefringence, moisture regain, density, crystallinity, x-ray diffraction patterns, and microfibrillar morphology. Electron-microscopical examination and other evaluation of fine structure properties revealed that the nature of swelling is intercrystalline up to 30% concentration of Triton B, and intracrystalline beyond that. Although the swelling as measured by propanol-2 retention after treatment with 30% Triton B is about twice as much as that of the control, the original structure remains almost unchanged except for some gain in strength and elongation and increase in moisture regain. At 32% Triton B concentration and beyond, rapid decrystallization takes place, accompanied by a fall in birefringence, density, and crystallinity index. X-Ray analysis showed significant loss of lateral order and partial conversion of cellulose I to cellulose II at 35% and 40% Triton B concentrations. The results indicate that, used at the critical concentration of 30%, Triton B can be a useful swelling agent for cotton fibers as it opens up the fine structure of cellulose considerably without impairing any important physical properties.

INTRODUCTION

In a series of polarized-light and electron-microscopical observations on the effect of swelling agents on the fine structure of cotton fiber, Betrabet and Rollins[1] compared changes in morphology of ultrathin cross sections in such inter- and intracrystalline swelling agents as mono- and diamines, sodium hydroxide, zinc chloride, phosphoric acid, and sulfuric acid at critical concentrations. The nature of swelling and the extent of decrystallization were found to influence the microfibrillar morphology to a varying degree. In continuation of this investigation, observations were made on the effect of swelling cotton fibers with Triton B (trimethylbenzylammonium hydroxide) obtained from Miles Laboratories at various concentrations from 25% to 40%.

Among the quaternary ammonium bases, Triton B is one of the more

TABLE
Changes in Physical and Fine Structure Properties of Cotton

Triton B, %	Fiber bundle strength, g/tex		Elongation, %	Refractive index for sodium D line at 25°C			Moisture regain, %
	0	1/8 in.		$\eta\parallel$	$\eta\perp$	Birefringence ($\eta\parallel - \eta\perp$)	
Untreated	41.7	24.8	7.0	1.578	1.531	0.047	6.4
25	42.6	25.8	6.4	1.580	1.530	0.050	7.2
30	40.6	30.2	8.9	1.580	1.526	0.054	7.9
32	—	—	—	1.570	1.524	0.046	8.9
35	—	—	—	1.554	1.526	0.027	11.0
40	—	—	—	1.550	1.524	0.026	11.5

[a] For 1 hr at 25°C.

effective swelling agents for cotton. Early investigations on Triton B were mainly concerned with viscosity measurements and x-ray diffraction. Sisson and Saner[2] carried out x-ray studies on cellulose treated with various quaternary ammonium bases and reported a cellulose II pattern for the purified flax fibers treated with 40% Triton B; the results obtained on purified ramie and cotton were similar. They also observed that to get the change in cellulose lattice, the minimum concentration of Triton B should be in the range of 25% to 29%. Brownsett and Clibbens[3] carried out fractional solubilities of chemically modified cotton celluloses in several alkaline solvents including Triton B. They noted two solubility maxima for Triton B at 2.15N and 3.5N, and observed that at any concentration beyond the first maximum the cotton cellulose formed highly swollen gels and that the equilibrium between the phases was slow and difficult to attain. Strepikheev et al.[4] dealt particularly with the mechanism of solvation of cellulose in quaternary ammonium bases. Segal et al.[5] treated cotton fibers with Triton B at different concentrations; they observed no visible fiber damage at 30% concentration. At higher concentrations, progressive gelatinization, decrystallization, and partial solution of cellulose took place, and at 38% concentration complete dispersion occurred. Vigo et al.[6] used Triton B to impart and erase creases in cotton textiles. Recently, Vigo et al.[7] using cotton yarns studied the effect of mixed bases and reported that 35% Triton B by itself did not convert cellulose I to cellulose II, but an addition of a small amount of lithium hydroxide or sodium hydroxide induced such a conversion. They also reported that when fibers of cotton used in their studies were suspended without agitation in the reagent, even 40% Triton B failed to cause disappearance of all the fibers within 100 hr, although microscopical examination showed that tremendous swelling and partial solution had occurred and that the cellulosic material

I
Swollen in Trimethylbenzylammonium Hydroxide (Triton B)[a]

		X-Ray analysis					
Density, g/cm³	Infrared crystallinity ratio	50% x-ray angle, deg	Crystallinity index, %	Crystallite dimension D(002), *l* to plane *hkl*, Å	Cellulose, % I	II	Amorphous
1.548	0.67	31.2	86	48	79	0	21
1.549	0.74	30.1	89	51	83	0	17
1.536	0.68	22.7	88	52	84	2	14
1.530	0.62	—	85	50	67	8	25
1.523	0.42	—	contained		30	18	52
1.522	0.38	—	cellulose II		12	24	64

acquired the same refractive index as the medium. When the fiber bundles, rather than yarn, were treated with 35% Triton B, mixed lattices of cellulose I and II were observed. It is well known that yarns differ significantly

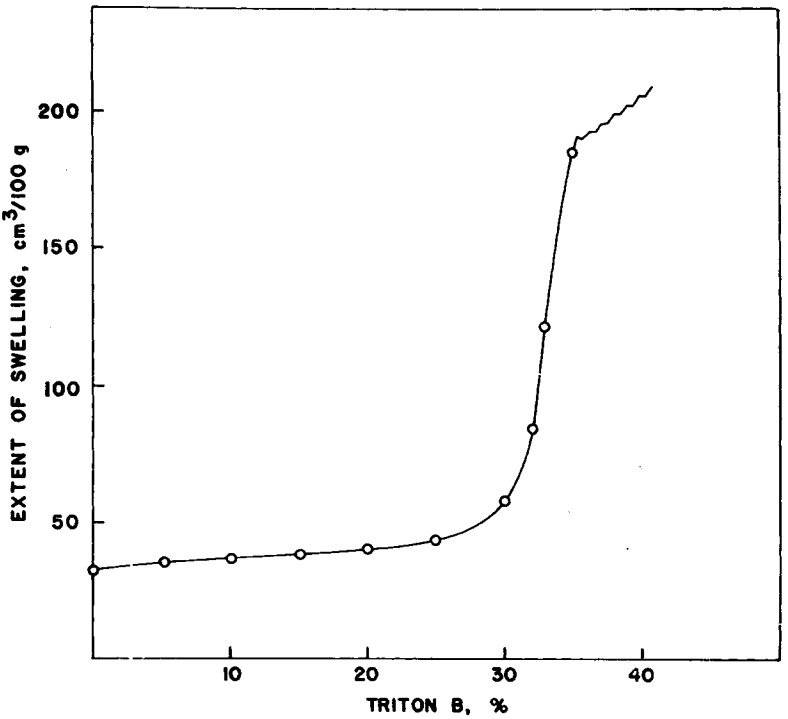


Fig. 1. Extent of swelling of cotton treated with Triton B at different concentrations for 1 hr at 25°C.

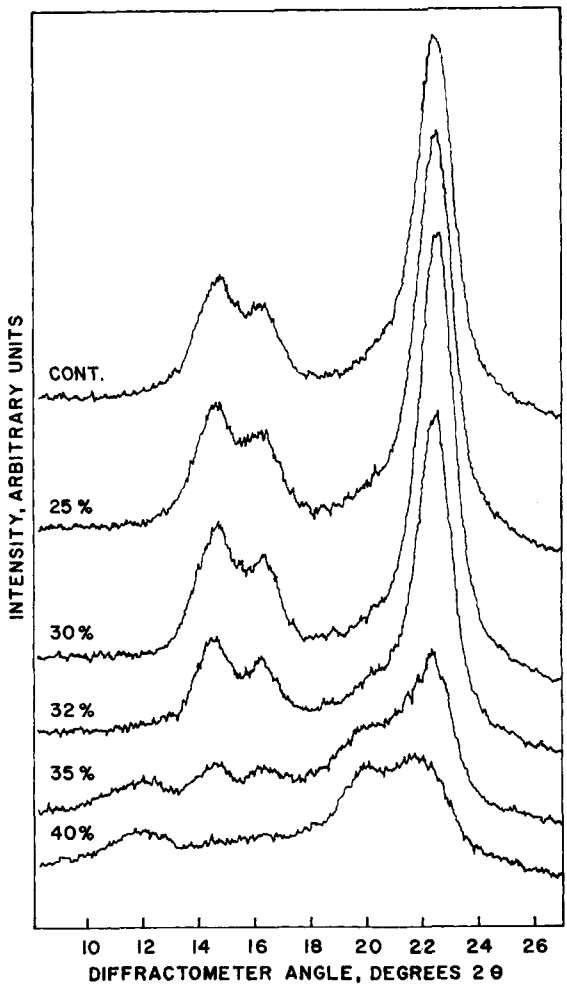


Fig. 2. X-Ray radial tracings of cotton cellulose treated with Triton B at different concentrations for 1 hr at 25°C.

from loose fibers in their response to swelling agents. Yarns were not investigated in the present studies.

EXPERIMENTAL

A good quality Deltapine cotton was purified by a standard procedure[8] and treated in fiber form with aqueous solutions of 25% to 40% (w/w) Triton B (1:50) for 1 hr at 25°C. The treated cotton was repeatedly washed with distilled water, solvent exchanged in dry methanol followed by diethyl ether, and air dried. No external restraint was used during the treatment or drying.

Extent of swelling was determined by the propanol-2 retention technique of Andrews and Oberg[9] for the samples treated with Triton B at ten differ-

ent concentrations from 5% to 40%. This technique is based on the displacement of water-swollen sample with propanol-2, which allows no further swelling and permits removal of extraneous fluid by centrifugation.

Strength of flat fiber bundles was determined at the normal 0 and $^1/_8$-in. gauge along with per cent elongation at break on the Stelometer strength tester.

Refractive indices were determined by the Becke line method[10] using Cargille oils of certified index of refraction in the range 1.520–1.590 and a polarizing microscope.

Moisture regain of the samples was determined at 65% RH and 21°C under conditions of adsorption.

Density was measured in a density gradient column using a mixture of carbon tetrachloride and heptane according to the method of Orr et al.[11] The liquid in the column as well as the samples were carefully dried before determining the density.

Infrared crystallinity ratio proposed by Nelson and O'Connor[12] was calculated from the absorptivity ratio (a_{1372} cm^{-1}/a_{2900} cm^{-1}), obtained from infrared spectra by the potassium bromide-pellet technique of O'Connor et al.[13] using a Perkin-Elmer Model 221 spectrophotometer.

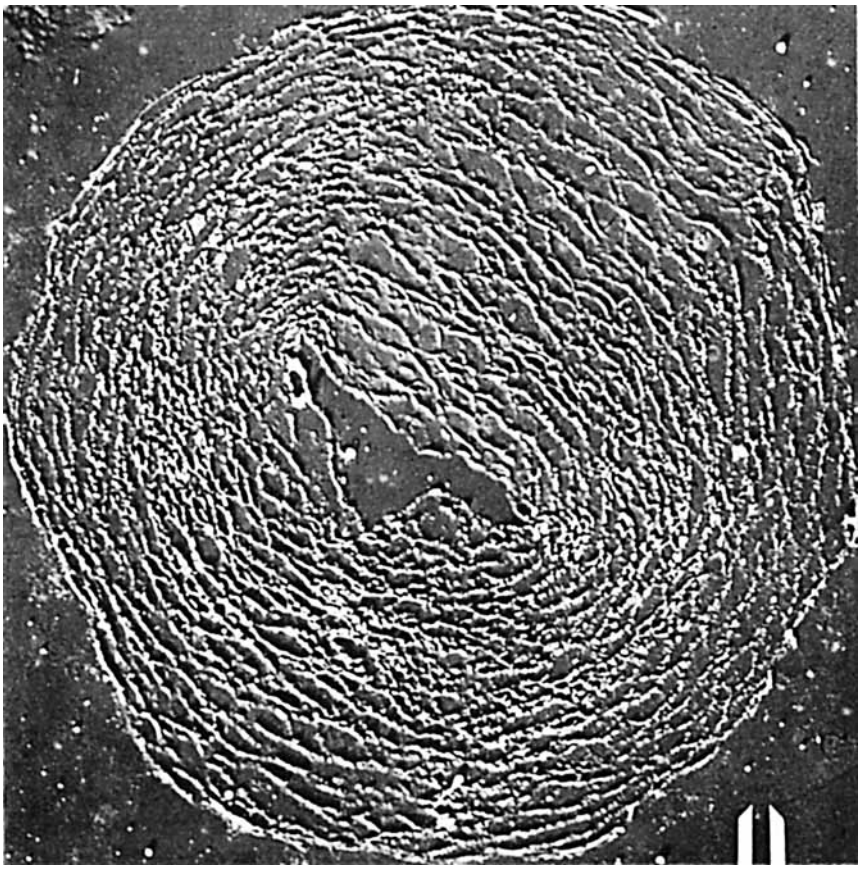
X-Ray data were obtained with a General Electric XRD-5 diffractometer (Cu Kα radiation, parafocusing optics) on pressed pellets of ground samples to record tracings of the diffraction. Crystallinity indices for samples displaying only the cellulose I lattice were calculated according to the method of Segal et al.[14] Degree of crystallinity was also estimated for all of the samples by the regression analysis of Wakelin[15] as extended by Patil and coworkers.[16] The lateral crystallite dimensions were estimated from the width at half-maximum of the recorded 002 interference by the Scherrer line-broadening relationship with appropriate corrections for instrumental conditions. The 50% x-ray angle was measured according to the technique described by Segal et al.[17]

Electron-microscopical examination was carried out by the modified two-step layer expansion technique of Rollins and co-workers[1,18] to observe the microfibrillar morphology. Small fiber bundles of the Triton B-treated samples were soaked in water and embedded appropriately in a 3:2 mixture of partially polymerized methyl and butyl methacrylates. This caused the fibers to swell enormously and the secondary cell wall to form concentric layers. Ultrathin cross sections of the embedded fiber, after removal of the polymethacrylates, were shadowed with platinum and examined under low and high magnification in a Philips EM 200 electron microscope, operated at 60 kV.

RESULTS AND DISCUSSION

The results with respect to the changes in the physical and fine structure properties of cotton swollen in loose fiber state with aqueous Triton B at various concentrations are summarized in Table I. The propanol-2 reten-

tion value a parameter of the extent of swelling, increased from 30% in the untreated control to over 200% in the sample treated with 40% Triton B (Fig. 1). The initial increase in swelling was gradual and reached 57% in the sample treated with 30% Triton B. Fiber bundle strength (Table I) did not change appreciably up to this concentration, and beyond it no strength could be determined as the cotton rapidly lost its fibrous nature, forming a gelatinous mass, especially at 35% and 40% concentrations. Some gain in strength at 1/8-in. gauge test length and elongation at break were noted, however, in the sample treated with 30% Triton B. Birefringence showed a significant initial increase from 0.047 in the untreated sample to 0.054 in the 30% treated sample, indicating an increase in orientation of cellulose chain molecules with respect to the fiber axis (Table I). At 32% concentration, a steep fall in birefringence was noted, eventually reaching 0.026 in the sample treated with 40% Triton B indicating very high disorientation. Vigo et al.[7] in experiments with cotton yarn, have reported considerable increase in crystallite orientation; in their observations the x-ray angle



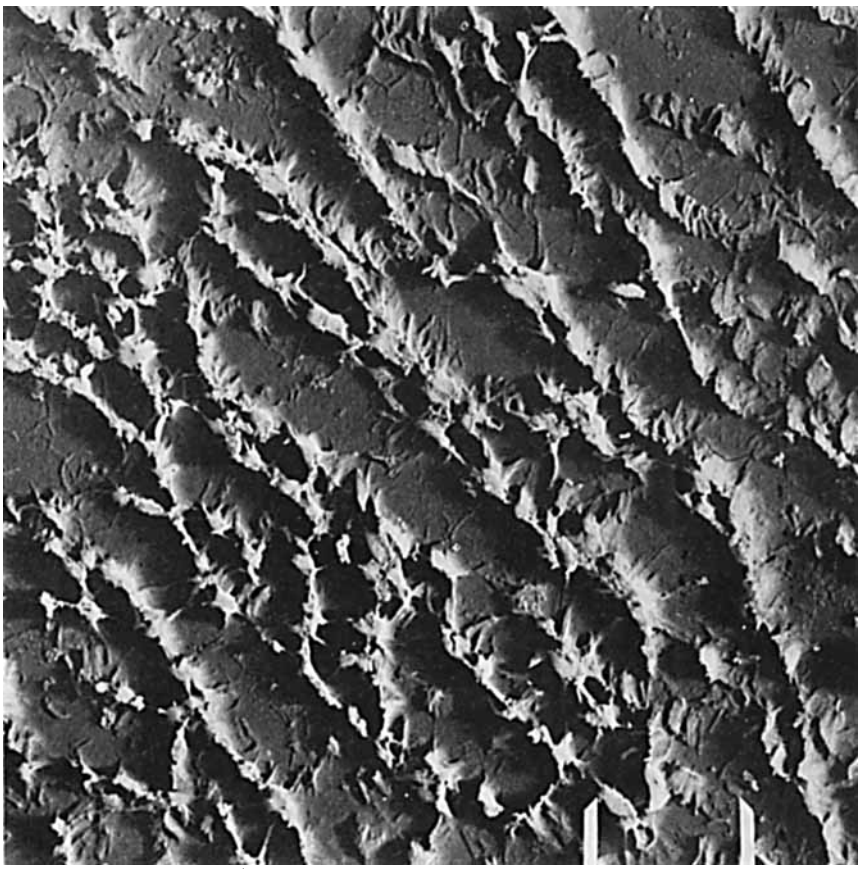
(a)

Fig. 3 (*continued*)

of the untreated control sample was 32°, which was reduced to 23.6° on treating the cotton yarn sample with 35% Triton B for 40 min. The molecular disorientation reflected in the birefringence data in the present study is to be expected as a result of treatment with Triton B at high concentrations under slack conditions, when the cellulose is enormously swollen.

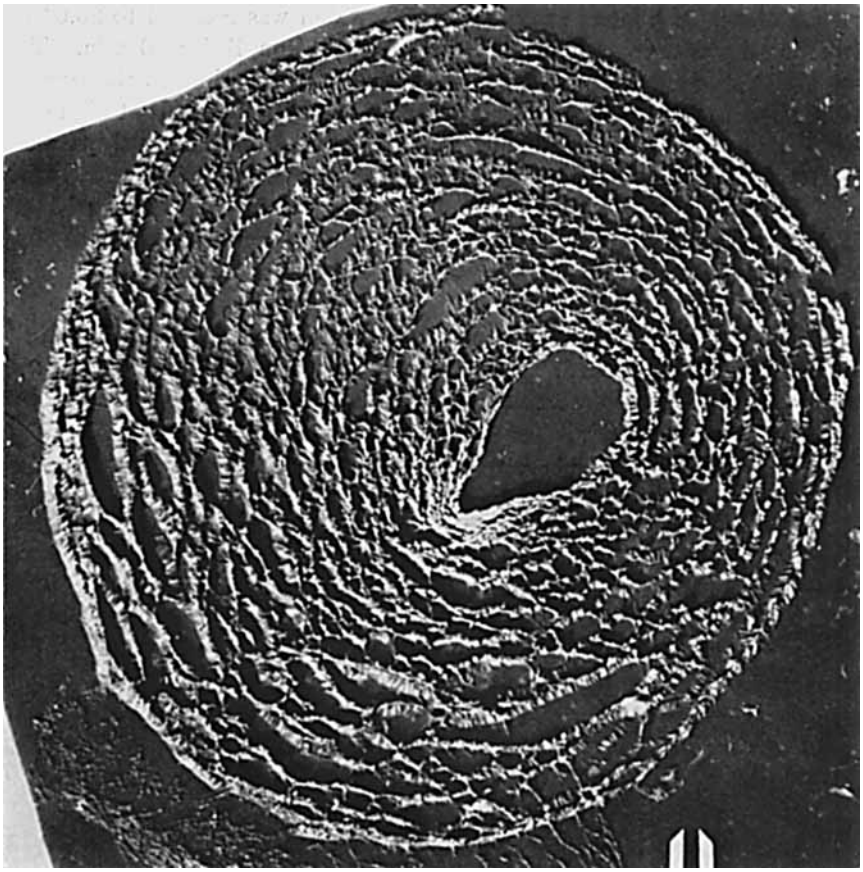
The x-ray angle could be determined only for the samples treated with 25% and 30% Triton B (Table I). The original x-ray angle value of 31.2° in the untreated sample dropped to 22.7° in the sample treated with 30% Triton B. This confirms the increase in orientation observed from birefringence values discussed earlier.

Density of the untreated sample was 1.548. It did not vary much on treating the sample with 25% Triton B. However, beyond this concentration, the density decreased sharply (Table I) to a value of 1.522 in the



(b)

Fig. 3. Cross section of untreated cotton fiber by layer expansion, showing (a) characteristic layers and (b) microfibrils. Distance between vertical lines represents 1 micron.



(a)

Fig. 4 (*continued*)

sample treated with 40% Triton B. There is a definite relationship between the refractive power n and the density d of the fiber, if the fiber is considered as a homogenous mixture of crystalline and paracrystalline regions. According to Hermans,[19] the ratio $(n_{iso}-1)/d$ should be constant, where $n_{iso} = {}^1/_3\,(\eta_\parallel + 2\eta_\perp)$. The refractive index of the fiber in the isotropic state, n_{iso}, is independent of orientation. In the case of all the Triton B-treated samples, the average value of the ratio turned out to be constant at 0.352 ± 0.001, in agreement with such correlation reported to exist between refractive power and density in several types of cellulose fibers.[19] Moisture regain gradually increased from 6.4% to 11.5% (Table I) in keeping with the opening of the cellulose structure owing to decrystallization, particularly at the concentration 32% and beyond.

The infrared crystallinity ratio (Table I) showed an initial increase from 0.67 to 0.74 for the sample treated with 25% Triton B. The decrease in this ratio with increase in concentration of Triton B, especially steep in the 35% and 40% concentration range, indicates substantial decrystalliza-

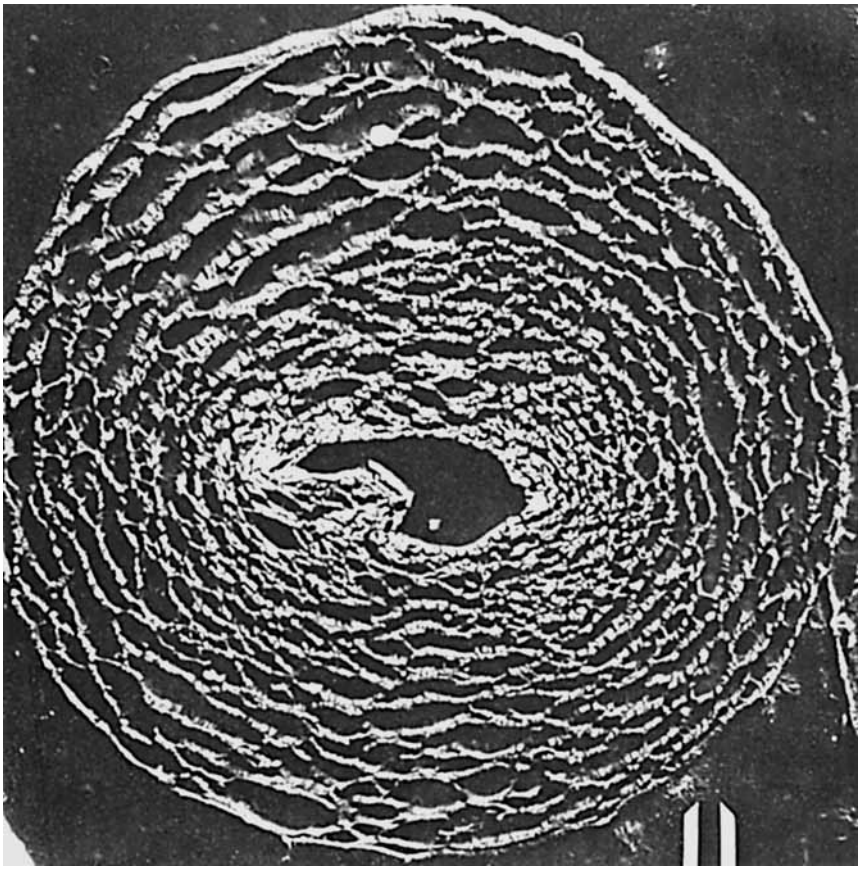
(b)

Fig. 4. Cross section of cotton fiber treated with 25% Triton B examined by layer expansion, showing (a) profuse layering and (b) microfibrils similar to Fig. 3.

tion, the crystallinity indices being 0.42 and 0.38, respectively. Segal et al.[5] had determined the per cent crystallinity of samples treated with Triton B at different concentrations by the acid-hydrolysis residue technique. They did not get decrystallization in the 30%-treated sample. At higher concentrations, viz., 33%, 36%, and 38%, severe damage to the fiber structure was accompanied by strong decrystallization. Our results based on infrared crystallinity indices are in conformity with these observations.

The x-ray crystallinity index developed for cellulose I specimens could not be used for the samples treated with 35% and 40% Triton B, owing to the substantial conversion to cellulose II. However, crystallinity index did not change appreciably up to 30% concentration, nor did the crystallite diameter (Table I). Analysis of the x-ray diffractograms of the treated cellulose to estimate the cellulose I and II crystalline fractions clearly

indicated significant loss of lateral order and partial conversion to cellulose II in the samples treated with 35% and 40% Triton B. The diffraction scans of the Triton B-treated samples (Fig. 2) indicated no substantial change in the pattern in the cottons treated with concentrations lower than 35%. In the sample treated with 35% Triton B, a mixed pattern of cellulose I and II was noted, and in the one treated with 40% Triton B, the 101/10$\bar{1}$ doublet was almost absent. Vigo et al.[7] also observed a mixed pattern of cellulose I and II on swelling the cotton with 35% Triton B in loose fiber form instead of yarn, apparently due to more uniform swelling and better penetration of the swelling agent. That the effect of sample preparation can be a very important factor has been pointed out recently by Manjunath and Peacock.[20] They found that the cellulose I lattice is resistant to alkali attack and difficult to disrupt completely during a single swelling treatment. Only on swelling the native cellulose sample of cotton fibers some five times with fresh alkali, each time at 0°C, did they achieve complete conversion to cellulose II.



(a)

Fig. 5 (*continued*)

The electron micrographs of Triton B-treated fibers brought out vividly the changes at the microfibrillar level. The layer expansion pattern of the sample treated with 25% Triton B resembled the untreated control (Fig. 3 and 4), except that the layering was more profuse in some cross sections of the treated sample. This indicated that the swelling at 25% concentration is intercrystalline in nature. At the 30% concentration, though the swelling is largely intercrystalline, a very unusual layer expansion pattern was observed (Fig. 5). There was loss of microfibrillar character and a parchment-like appearance of the lamellae (Fig. 5b), but no fusion of lamellae occurred; the layers were quite distinct. In none of the electron micrographs of the cotton treated with various inter- and intracrystalline swelling agents, which included mono, and diamines, sodium hydroxide, zinc chloride, phosphoric acid, and sulfuric acid, was such a phenomenon observed

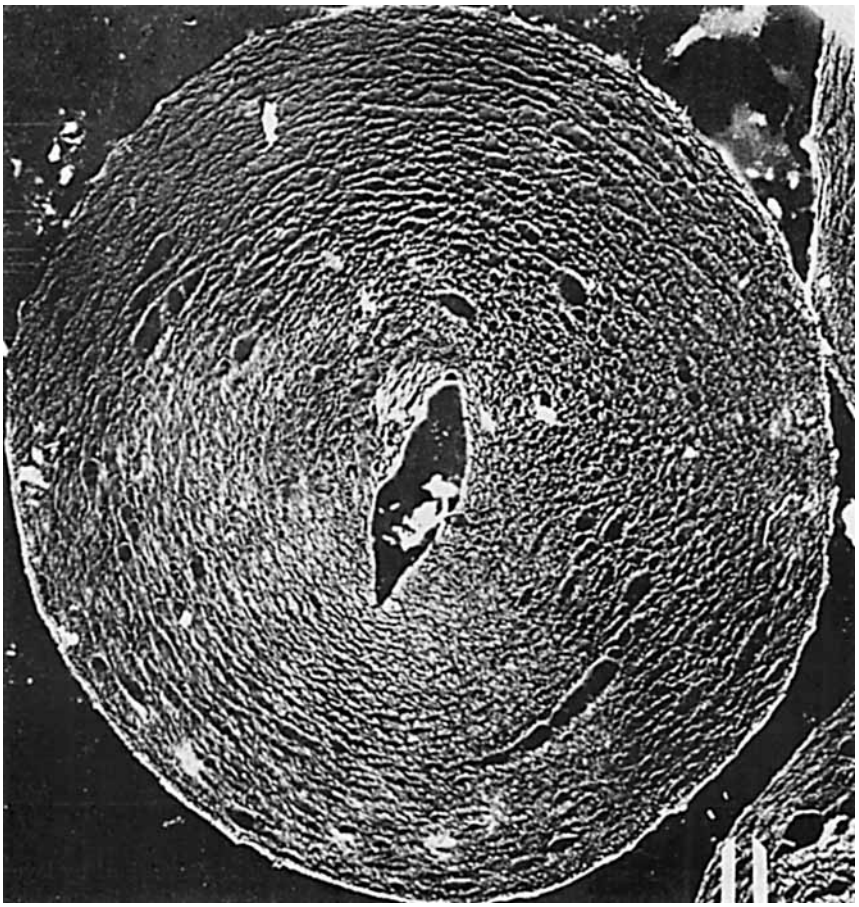
(b)

Fig. 5. Cross section of cotton fiber treated with 30% Triton B examined by layer expansion, showing (a) layering and (b) fusion of microfibrils along the lamellae producing parchment-like effect.

earlier by Betrabet and Rollins.[1] In the 32%-treated sample (Fig. 6), fusion of microfibrils and compactness of lamellar structure were observed, and the pattern came close to the spongy honeycomb structure observed in mercerized cotton.[21] In the fibers treated with 35%, and especially 40% Triton B (Fig. 7), there was a loss of fibrillar structure, fusion of lamellae, and compactness of structure due to strong disordering, which is typical of powerful intracrystalline swelling agents like zinc chloride, phosphoric acid, and sulfuric acid at appropriate concentrations.[1] The action of Triton B at concentrations greater than 32% is quite damaging to the fiber structure and results in partial dispersion of the cellulose at the higher concentrations.

CONCLUSIONS

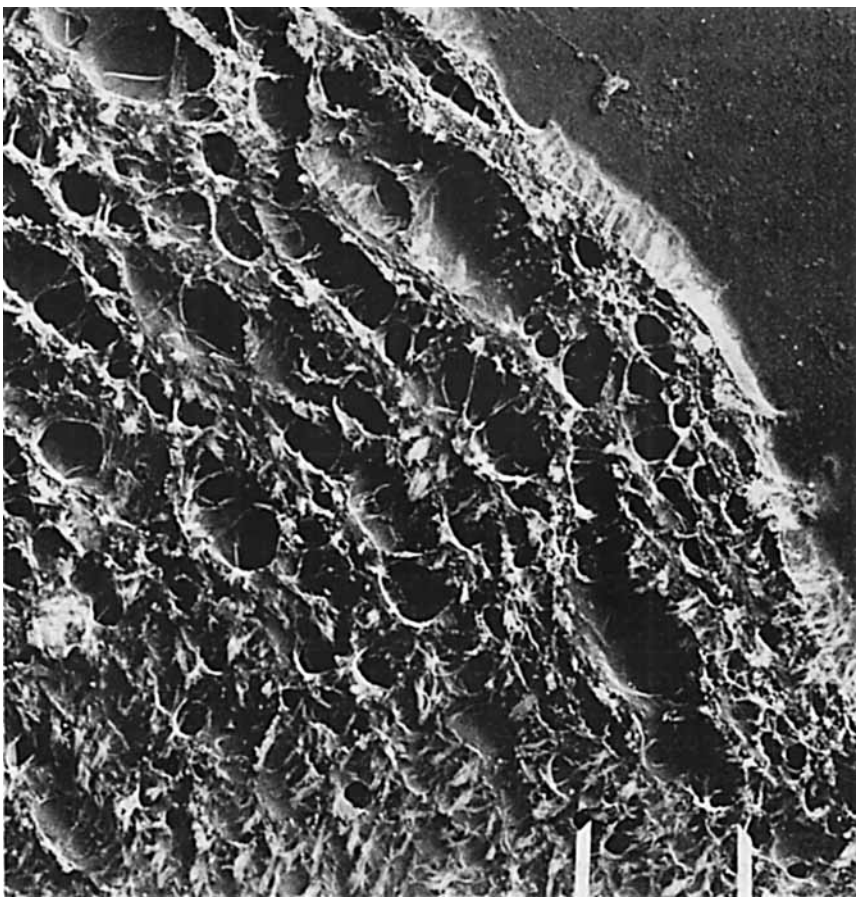
The following conclusions are based on the cotton treated with Triton B in loose fiber form.



(a)

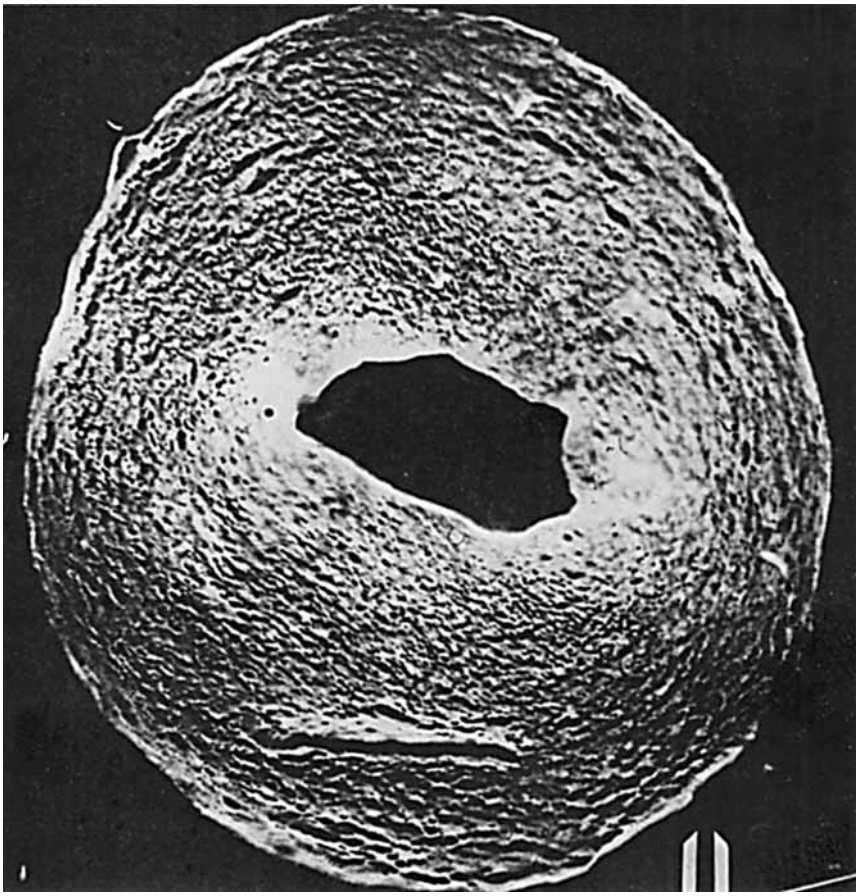
Fig. 6 (*continued*)

Triton B is a powerful swelling agent, and, depending upon its concentration, it can significantly modify the physical and fine structure properties of cotton. The extent of swelling of cotton fibers increases gradually until the 30% Triton B concentration is reached and very rapidly at higher concentrations. Strength, crystallinity, density, birefringence, and x-ray diffraction patterns of cotton fiber do not change appreciably on treating with 25% or 30% Triton B, although there is some gain in strength and significant increase in elongation and moisture regain in the sample treated with 30% Triton B. At 32% Triton B, major changes occur with loose fibers. A sharp decrease in density, birefringence, and crystallinity are noted, and these are accompanied by further increase in moisture regain. The fibers are too fragile for the determination of flat bundle strength at concentrations of 32% and greater. Free fibers treated with 35% and



(b)

Fig. 6. Cross section of cotton fiber treated with 32% Triton B examined by layer expansion, showing (a) spongy structure, loss of layering due to lateral disorder and (b) compactness and fusion of microfibrils.



(a)

Fig. 7 (*continued*)

40% Triton B are very highly swollen and decrystallized. X-Ray analysis indicates substantial amounts of cellulose II, and there is a very sharp decrease in crystallinity, density, and birefringence and considerably higher moisture regain, as compared to values for the untreated control. Electron micrographs reveal that the nature of swelling in cotton is largely intercrystalline for concentrations of Triton B less than 30% and intracrystalline beyond that concentration.

Triton B at an appropriate concentration, viz., 30%, seems to open up the structure of cellulose considerably without significantly altering its basic structure or strength, but increasing its moisture regain and extensibility. Used at this critical concentration, Triton B may prove a very useful swelling agent to impart desirable properties to cotton. Experiments to confirm this are in progress.

The authors are thankful to Miss Dorothy Legendre for providing the fiber strength data, to Miss Rose Babin for her efforts in preparing the photographic prints, to Mr.

(b)

Fig. 7. Cross section of cotton fiber treated with 35% Triton B examined by layer expansion, showing (a) complete loss of microfibrillar pattern and (b) compactness and fusion of lamellae due to high swelling and lateral disorder.

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References

1. S. M. Betrabet and M. L. Rollins, *Text. Res. J.*, in press.
2. W. Sisson and W. R. Saner, *J. Phys. Chem.*, **43**, 687 (1939).
3. T. Brownsett and D. A. Clibbens, *J. Text. Inst.*, **32**, T32 (1941).
4. A. A. Strepikheev, I. L. Knunyants, N. S. Nikolaeva, and E. M. Mogileviskii, *Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk*, 750 (1957).
5. L. Segal, M. L. Nelson, and C. M. Conrad, *J. Phys. Colloid Chem.*, **55**, 325 (1951).
6. T. L. Vigo, R. H. Wade, and C. M. Welch, U.S. Pat. 652,659 (July 10, 1967).

7. T. L. Vigo, R. H. Wade, D. Mitcham, and C. M. Welch, *Text. Res. J.*, **39**, 305 (1969).

8. W. M. Corbett, in *Methods in Carbohydrate Chemistry*, Vol. III, R. Whistler, Ed., Academic Press, New York, 1963, p. 3.

9. C. M. Andrews and A. G. Oberg, *Text. Res. J.*, **33**, 330 (1963).

10. R. Meredith, *J. Text. Inst.*, **37**, T205 (1956).

11. R. S. Orr, L. C. Weiss, H. B. Moore, and J. N. Grant, *Text. Res. J.*, **25**, 592 (1955).

12. M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, **8**, 1325 (1964).

13. R. T. O'Connor, E. F. DuPré, and E. R. McCall, *Anal. Chem.*, **29**, 998 (1957).

14. L. Segal, J. J. Creely, A. E. Martin, Jr., and C. M. Conrad, *Text. Res. J.*, **29**, 786 (1959).

15. J. H. Wakelin, H. S. Virgin, and E. Crystal, *J. Appl. Phys.*, **30**, 1654 (1959).

16. N. B. Patil, N. E. Dweltz, and T. Radhakrishnan, *Text. Res. J.*, **32**, 460 (1962).

17. L. Segal, J. J. Creely, and C. M. Conrad, *Rev. Sci. Instr.*, **21**, 431 (1950).

18. M. L. Rollins, J. H. Carra, E. J. Gonzales, and R. J. Berni, *Text. Res. J.*, **36**, 185 (1966).

19. P. H. Hermans, *Contributions to the Physics of Cellulose Fibers*, Elsevier, Amsterdam, 1946, p. 111.

20. B. R. Manjunath and N. Peacock, *Text. Res. J.*, **39**, 70 (1969).

21. M. L. Rollins, A. T. Moore, I. V. deGruy, and W. R. Goynes, *J. Roy. Microscop. Soc.*, **84**, Pt. 1, 1 (1964).

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