Changes in Porosity of Treated Lint Cotton Fibers. I. Purification and Swelling Treatments

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Synopsis

Changes in the internal morphology of lint cotton fibers during purification and swelling treatments were investigated by measurement of nitrogen adsorption at liquid nitrogen temperature. Surface areas and pore size distributions were calculated from the adsorption isotherms and compared with findings from measurements of changes in crystallinity and in fibrillar aggregation as shown by electron micrographs. The adsorption measurements were made on fibers which were either preswollen in water or taken from the rinse water after treatment and solvent exchanged through methanol and *n*-pentane to helium. The large changes found in surface area, pore size distribution, and fibrillar aggregation were accompanied by changes in crystal structure in fibers treated with 5.0M sodium hydroxide. Large changes following treatment with phosphoric acid occurred in pore structure and fibrillar aggregation without concomitant change in crystallinity.

INTRODUCTION

The surface area and porosity of solids, in particular those used in catalytic reactions, have been extensively studied by measurements of adsorption of inert gases.[1,2] Adsorption by celluloses, especially the cotton lint fiber, has been much less extensively explored. The purpose of the present investigation was to extend previous morphologic studies of cotton by exploration of fiber porosity.

In 1953, Forziati investigated nitrogen adsorption by cotton lint fibers after several different processing treatments.[3] Using solvent exchange procedures developed by Assaf, Haas, and Purves,[4] she determined the large increase in area developed by water swelling and solvent exchange, from the level of 0.3–0.8 m²/g to the level of 23–34 m²/g. Following a variety of treatments, surface areas ranged from 4 to 148 m²/g. Similar work has been reported by Klenkova,[5–8] who also obtained data for pore size measurements following swelling treatments and solvent exchange. Odincovs and Erins included mercerized cotton in investigations of porosity of various celluloses by use of several adsorbate gases and concluded that "elementary" capillaries of 18 to 20 Å in radius were distinctive

for all the celluloses which were studied.[9] They further stated that during normal drying these "elementary" capillaries completely close. Two forms of formaldehyde-crosslinked cotton fibers were studied by Iyer and Rao who used both nitrogen and dye adsorption on water-swollen, solvent-exchanged samples.[10] Surface area values varied inversely with formaldehyde content, but the variation was small for treatment in aqueous solution compared to values determined on fibers treated in a nonaqueous solution. Chedin measured surface areas of several dry-cure, crosslinked cottons by use of nitrogen and krypton as adsorbates.[11] He found that large decreases in areas of crosslinked cottons were a function of extent of reaction; no comparable changes were measured in parallel X-ray diffraction studies.

Sommers[12] reported adsorption studies of cotton lint fibers, designed to determine the value of minimizing the surface tension of the final nonpolar solvent used in the solvent-exchange technique of sample preparation. He used carbon dioxide as a gas above its critical temperature to remove solvent from the cotton and found no increases in surface area but increased pore volumes in samples prepared by this method. Wagner[13] used gas adsorption to study the changes in surface area of cotton fibers that were not water swollen and solvent exchanged. He reported increased external areas after various steps of purification processes and some decreased area after application of certain soil-release and crosslinking reagents. Barber[14] has described the energy site distribution for adsorption of argon in water-swollen, solvent-exchanged lint cotton obtained by interpretation of his data by the methods of Ross and Olivier.[15] He reported that the surface is very heterogeneous and possesses adsorptive potentials lower than that of argon. Surface areas calculated by the methods of Ross and Olivier were from 2.25 to 3.07 times those calculated by the Brunauer-Emmett-Teller (BET) method,[2] which was used in most of the studies discussed above.

In studies where fibers are preswollen in water and solvent exchanged to the adsorbate gas, the problem of solvent retention within the fiber should be considered. Some liquid will be retained within the pores of cotton fibers despite exchange to a nonpolar solvent and drying even at high temperatures.[16] This means that a small but significant fraction of the fiber internal surface is not available to the inert gas used, and surface areas and pore volumes are larger than measured. However, careful control of solvent-exchange techniques should permit useful comparative measurements. Apparently characteristics of the surface of pores filled by solvent are little different from those containing the adsorbate gas. Barber reported that changes in adsorptive potentials, or in their distribution, were minor for differences in sample surface areas.[14]

Pore properties of celluloses are currently being measured also by techniques of solute exclusion, a reverse gel permeation technique, used on pulpwood celluloses or on decrystallized or chopped (or both) lint cottons in the form of sols or gels. Stone and Scallan[17] have concluded that, in the water-swollen gels of bleached pine sulfate pulp, half the water is held in

pores 25 to 300 Å in width, the remainder in pores less than 25 Å wide, and that 12% of the water in the cell wall is inaccessible to the 8-Å-diameter glucose molecule. Martin and his co-workers[18] found that only 5% of the internal water volume consisted of nonsolvent water in their solute exclusion studies of Wiley-milled, unmodified lint cotton, but they did not project their findings to give a range of pore sizes. A mercury intrusion technique, developed by Skau and his co-workers[19] to measure the size of pores between the fibers in cotton fabrics, was found inadequate for measurement of pore sizes within the cotton fiber. Low-angle x-ray scattering and electron microscopy have been used by Heyn[20,21] principally to describe the solid structures, the microfibrils, which compose the solid adsorption surfaces within the cotton fiber. In addition, he reported a predominance of 20- to 30-Å-wide spaces between the elementary microfibrils observed in negatively stained samples which were prepared for electron microscopy.

The techniques of optical and electron microscopy permit the most rigorous examination of the fibrillar structures within the cotton fiber.[22] Unfortunately, most methods of sample preparation for electron microscopy distort the pore structures, and it is difficult to make exact comparisons of pore size by this technique with the sizes calculated from gas adsorption data. Despite such difficulties, it has been possible to relate changes in pore structures to changes in the aggregation of the microfibrils following various treatments of cotton. It will also be shown that changes in fibrillar aggregation and in porosity can occur without concomitant changes in findings by x-ray diffraction.

A preliminary report on some of the data given in this paper gave some typical results of comparative BET surface areas and pore sizes from the desorption isotherm.[23] The more complete data in this paper include estimates of pore size distributions found by analysis of both branches of the isotherms.

MORPHOLOGY OF THE COTTON LINT FIBER

One currently acceptable model of cotton lint fiber morphology is based on the concept of a crystalline "elementary" fibril, approximately 30 to 60 Å wide, composed of antiparallel chains of anhydroglucose units.[22,24,25] There is evidence of slip planes, or regions of disorder, in crystal structure along the length of this elementary fibril.[26] These elementary fibrils coalesce along their length and, in native cottons, this aggregation appears as a series of concentric fibrillar aggregates, or lamellae, with many discontinuities along their perimeters. Each lamella is composed of several layers of coalesced elementary fibrils. Longitudinally, the fibrils spiral about the fiber axis at angles of 20 to 35 degrees, with frequent reversals of direction of the spiral. The concentric lamellae, approximately 20 per fiber, constitute 95% of the fiber cellulose. The structure of the outer cellulose layers consists of fibrils interwoven to form a basketweave-type structure in the outermost layer and a loosely constructed, intermediate
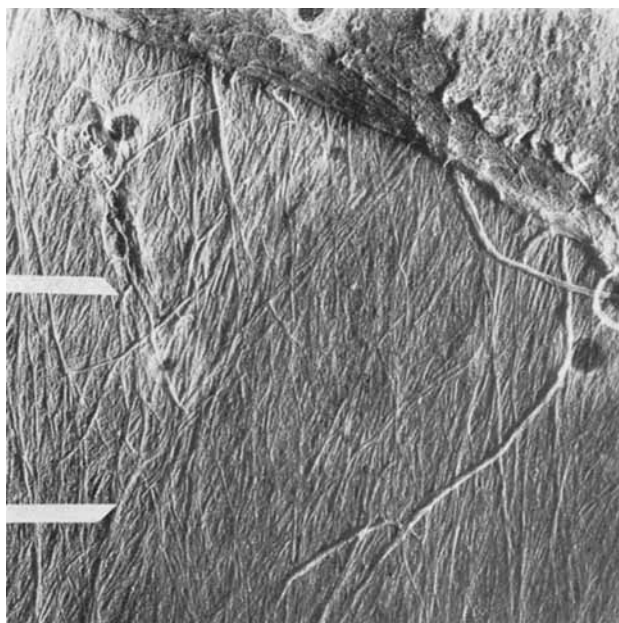
Fig. 1. Electron micrograph of fragment of cell wall of an untreated cotton fiber showing parallelized microfibrils in the lamella just beneath the two outer layers.   Note the difference in fibrillar texture in the layers in the upper right-hand corner.   Distance between markers is 1 micron.

layer in which fibrils spiral in only one direction.   The electron micrograph of a fragment of a fiber, shown in Figure 1, contains these two outer layers folded back from the underlying lamella of parallelized microfibrils.   This fragment was produced by beating a few fibers in water in a blendor.

Accessibility to reactants and liquids has been reported often to be a function of lateral disorder of the cellulose chains within the microfibrils. However, recent chemical studies using various reactions with hydroxyl groups by reagents which do not penetrate the crystal structure show that end products can be accounted for by considering the reactions to occur with the hydroxyl groups on the surface of a crystalline elementary fibril which is calculated, from these studies, to be 40 to 60 Å in width.[25]

Heyn[21] and later Hebert,[27] among others, have recently demonstrated the existence of pores between elementary fibrils in thin longitudinal layers of microfibrils by using heavy-metal staining.   The tortuosity of the pores is apparent in their electron micrographs.

EXPERIMENTAL

Samples and Instrumentation

The cotton, a Deltapine variety, used for most of the experiments on treated samples was in the form of an 80 × 80 print cloth which had been desized,

scoured, and bleached.   Unless noted otherwise, a 2-g or 3-g sample of this untreated fabric, usually 7 in. long and 4 or 6 in. wide, was used as a control sample for each adsorption experiment.   Treated samples examined included: (1) dewaxed and scoured cottons;   (2) cottons swollen in sodium hydroxide and in ethylenediamine;   (3) cottons swollen in phosphoric acid of different concentrations;   and (4) cottons swollen in representative inorganic salts.

In preparation for gas adsorption studies, both control and treated samples were soaked for a minimum of 16 hr in distilled water at room temperature, except when treated samples had been kept in rinse water. Samples were removed from the water, rolled along the 7-in. axis in such a manner that most of the excess water was pressed out, then placed in $1/2$-in.-diameter stainless steel sample tubes.   Glass wool was placed at each end of the rolled samples to prevent threads or loose fibers from being carried into the gas flow channels.   When yarn or fiber samples were used, preparation for solvent exchange was identical, except that the wet yarns were wrapped around a glass rod approximately 7 in. long and pressed to exclude most of the excess water; wet sliver and loose fiber samples were wrapped around wire.   The rod or wire was removed before placing the sample in the sample tubes.   In all samples, care was taken to leave a small opening through the center of the sample to permit an uninterrupted flow of gas through the tube.

Anhydrous, absolute methanol, reagent grade, and "pure" grade normal pentane (from Phillips Petroleum Company) were used for solvent exchange.   These reagents were stored in approximately 600-ml aliquots over Linde Type 4A molecular sieve for periods varying from one to several weeks before use, to remove residual traces of water.   No detectable isomers of n-pentane were found when this reagent was distilled.   After sample tubes were attached to the manifold, ten 30-ml portions of methanol, followed by eight 30-ml portions of n-pentane, were admitted to the control and test samples at intervals of a minimum of 20 min.   Samples were dried in a 50 ml/min flow of dry helium for approximately 64 hr at room temperature, capped and removed from the manifold while in the gas flow, then uncapped and attached to the Isorpta analyzer under the same conditions.

All adsorption experiments were done on the Isorpta analyzer, a gas flow-type instrument which is a modification of the instrument described by Haley.[28]   A mixture of 10% nitrogen in helium was used and adsorption measurements were made at liquid nitrogen temperature.   Calibration was done by using pure helium in the sample channel.   Frequent instrument checks were made by using samples of bone char or other adsorbents previously calibrated and available from the American Instrument Company.

Measurements of solvent retention were made by weighing the sample after the gas adsorption test, then soaking the sample in a minimum of three changes of 50-ml volumes of distilled water, for at least 24 hr at room temperature for each change, drying overnight in a vacuum oven at 60°C,

and reweighing. This final weight was used to calculate the volume of nitrogen adsorbed per gram of cotton. Solvent retention was calculated as the ratio, expressed as a percentage, of the difference in the two weights to the final weight. Cumulative retention values were: 20% of the samples less than 1%; 52% less than 1.5%; and 76% less than 2%. Only wrinkle-resistant treated samples, described in the second part of this paper, consistently showed higher than average values; 50% of these samples had retentions between 2% and 3%. These values are probably higher than actual values existing during tests because of frequent exposures of dried samples to ambient humidities when attempting to detach adapters from the sample tubes for sample removal.

Samples were prepared for electron micrographs by the methods described by Mühlethaler,[22] unless otherwise indicated. Methods for x-ray diffraction have been described by Patil.[29] X-Ray data were obtained on samples which were rinsed, then dried at 60°C after adsorption tests.

Interpretation of Adsorption Measurements

The method of Brunauer, Emmett, and Teller (BET method) was used to calculate surface area.[2] The value used for the area of an adsorbed nitrogen molecule was 16.3 Å². Areas were calculated from graphs of data taken at relative pressures between 0.12 and 0.27. Deviations from a straight-line BET plot, when encountered, appeared attributable to inaccuracies of measurement. Surface area values were checked by regression line analyses. Because of the variability in values of surface areas of samples from any lot of cotton caused by the variabilities encountered in all native fibers and by differences in extent of exchange of water to helium, all surface area data are given as per cent of the control sample. The C values from the BET equation, which are a function of the energy of adsorption of the adsorbate gas, were calculated, and 83% were between 40 and 70, and 50% were between 50 and 60, when all treated cottons and controls were examined. These values are within the range of values reported for milk powders and certain polymers discussed by Berlin.[30]

The method of Cranston and Inkley,[31] developed to obtain pore size distribution, was applied to data on complete adsorption–desorption isotherms. Other values of layer thickness than those given by Cranston and Inkley may have been more appropriate because of the low C values for cotton, but their tables seemed applicable for purposes of comparing distributions among the various cottons. The pore size distributions were obtained from each branch of the isotherm by plotting the values calculated for the pore volume, after correction for layer thicknesses, as a function of pore diameter and reading the values of $\Delta V/\Delta D$ from the fitted curves. Except for Figures 2 and 3, values of $\Delta V/\Delta D$ were scaled to permit display of several distributions in the same figure in order to compare the shapes of the pore size distributions. Pore size distributions obtained from the desorption branch when nitrogen is the adsorbate are known to be unreliable at relative pressures below approximately 0.50[32] or, by the Cranston

and Inkley method, at 37.5–42.5 Å diameters. Although desorption isotherms for most cottons abruptly decreased in this region, an interesting shift between these diameters was encountered often, and distribution data from the desorption branch of the isotherms are included. Average pore diameters were calculated from the cumulative pore volumes and surface areas, derived from the adsorption branch of the isotherm, as described by Cranston and Inkley.

RESULTS AND DISCUSSION

Untreated Cottons of Different Varieties and Controlled Growth Environment

The yarns described in Table I, each spun from a single genetic variety of cotton and wound in skeins, were purified by Soxhlet extraction in 99% ethanol for a total of 52 cycles (approximately 5 hr). Two skeins, air dried after rinsing in distilled water, were set aside for adsorption studies; the remaining portions were air dried also and then purified by scouring in 2% sodium hydroxide for approximately 6 hr, rinsed, neutralized with acetic acid, and air dried. There was a sufficient quantity of the Pima S-2 variety to permit studies of porosity on samples not dried after rinsing. The fiber samples which were grown in a controlled environment[33] were hand-picked from the bolls and similarly purified. The control scoured fabric was used as a control sample for the yarns; for the fibers, a Deltapine cotton grown under normal field conditions and similarly purified was used.

Fiber fineness values given in Table I for each variety of cotton correlate with fiber perimeter measurements or cross-sectional area.[34] Average values of cross-sectional areas of dry fibers (in square microns) have been reported as 93 for Pima cotton, 136 for a coarse Upland cotton (similar to Deltapine), and 166 for a Rowden cotton.[35] The differences found in

TABLE I
Surface Areas of Three Varieties of Cottons and of Two Cottons
Grown in a Controlled Environment

Sample	Maturity	Fineness micrograms per in.	Surface area,[a] % control	
			Dewaxed	Scoured
Rowden yarn	84	5.48	78	111
Deltapine yarn	92	4.39	70	120
Pima S-2 yarn	90	3.24	90	126
Pima S-2 yarns				
undried after dewaxing			108	
undried after dewaxing, scoured and air dried				149
undried after dewaxing, scoured and undried				255
Deltapine fibers, grown 85°F, 70% R.H.				
constant illumination			116	196
13 hr light, 11 hr dark, alternating			202	216

[a] Surface area of control scoured fabric samples was approximately 20 m²/g.
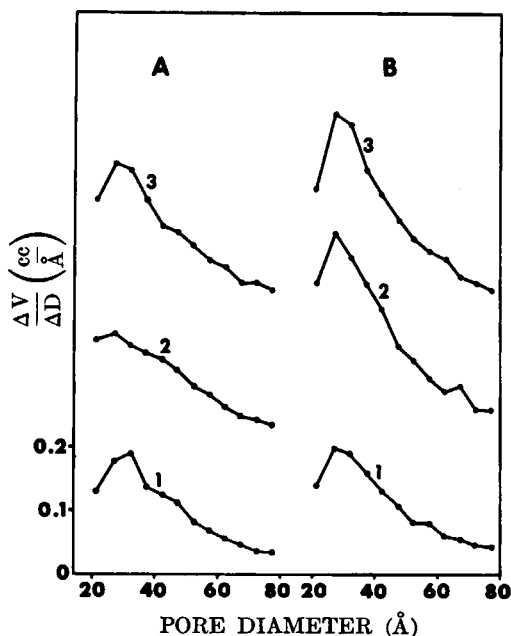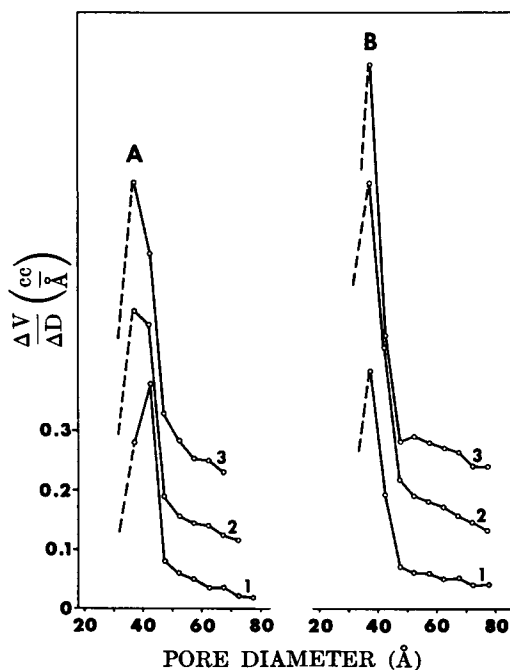
Fig. 2. Pore size distribution in untreated cotton lint fibers from the adsorption branch of the isotherm: (a) dewaxed fibers; (b) dewaxed and scoured fibers; (1) Rowden variety; (2) Deltapine variety; (3) Pima variety. Ordinate values shifted 0.2 units for successive distributions.

surface area measurements (Table I) are smaller, but these differences persisted in duplicate tests. The difference in surface area between fibers grown under constant illumination and with alternating light and darkness is significant in the dewaxed fibers. Scouring increases the surface area of each cotton and reduces the differences in area among the three varieties of cotton and between the two samples grown under different controlled growth conditions. The maximum change in surface areas was produced by purification of the Pima cotton without intermediate drying before preparation for adsorption studies. The area of this undried sample was increased twofold.

Pore size distribution data (Figs. 2 and 3) show no large differences in distribution among the three varieties of cottons, although there is a suggestion of a slightly larger proportion of large pores in the Rowden variety. Calculations of average pore diameter gave a maximum difference of only 3 Å among varieties when unscoured and of only 2.4 Å after scouring (44.8 to 45.7 Å from adsorption, 42.8 to 45.2 Å from desorption branches). Values of average pore size among the cottons grown under controlled conditions were more variable. The unscoured sample of fiber grown under constant illumination had average pore diameters of 50.6 and 44.7 Å from adsorption and desorption isotherms, respectively, compared to diameters of 41.6 and 40.3 Å for the sample grown under alternating light and dark-

ness.   After scouring, the former sample showed a decrease in diameter
to 37.6 and 38.0 Å, but there was no significant change in the diameter of
the latter sample.   Data plotted in Figure 4 indicate this large pore diame-
ter in the unscoured fibers grown under constant illumination by the shift
to larger diameters in the distributions from both the adsorption and
desorption isotherms.

Electron micrographs of cross sections of untreated cotton fibers are
shown in Figures 5a and 5b.   These sections were prepared from fibers
which were swollen in water when placed in the methacrylate embedding
medium.   It is believed that methacrylate penetrates the fiber and during

Fig. 3. Pore size distribution in untreated cotton lint fibers from desorption branch
of the isotherm: (a) dewaxed fibers; (b) dewaxed and scoured fibers; (1) Rowden
variety; (2) Deltapine variety; (3) Pima variety.   Ordinate values shifted 0.1 units
for successive distributions.

polymerization expands the pores in which it is contained; thus the micro-
graphs picture the expansion by methacrylate as well as water swelling.
However, it is very difficult to observe any details of the fibrillar structures
in cross sections without this additional expansion.   At the high magnifica-
tion in Figure 5b, portions of the fibrillar aggregates have fallen and the
individual microfibrils, whose apparent length indicates the thickness of the
cross section, may be observed within the aggregates.   The separation of
the lamellae, shown in both micrographs, suggests the existence of pores
accessible to water and methacrylate between the lamellae.   The dis-
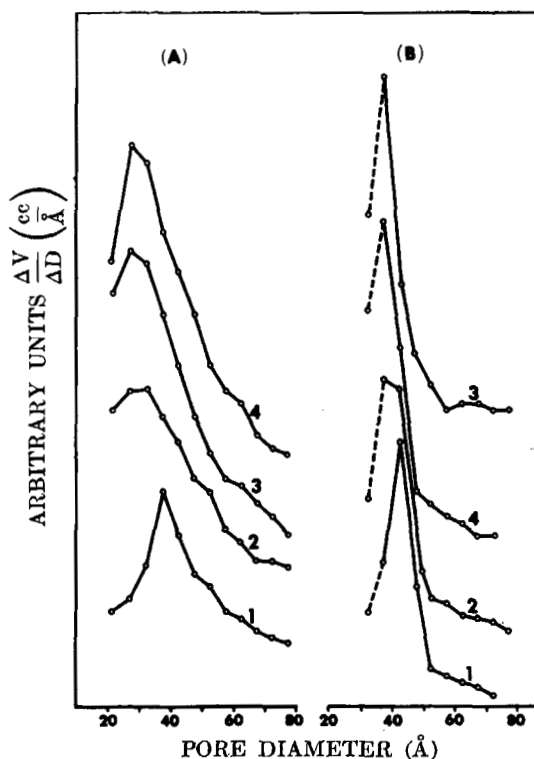
Fig. 4. Pore-size distribution in untreated cotton fibers grown in controlled environments: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) constant illumination, dewaxed; (2) alternating light and dark, dewaxed; (3) constant illumination, dewaxed and scoured; (4) alternating light and dark, dewaxed and scoured. Values on ordinate scaled to permit comparison of isotherm shapes.
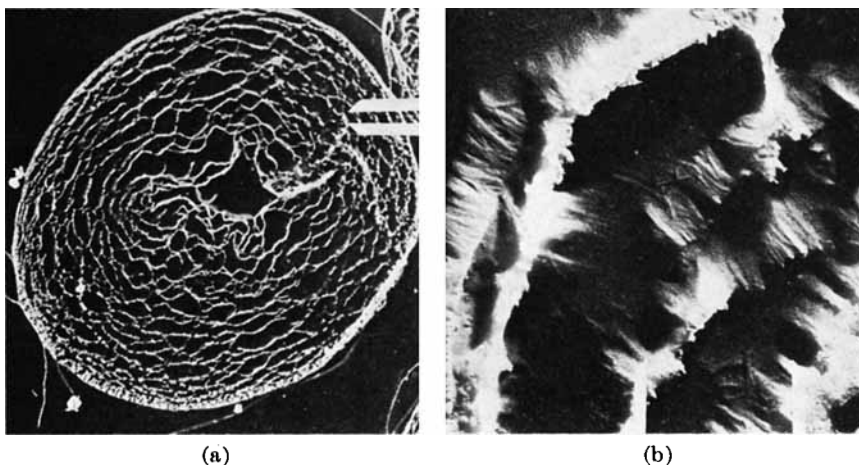

Fig. 5. Electron micrographs of cross sections of water-swollen, untreated cotton fibers embedded with methacrylate: (a) magnification approximately $2250\times$; (b) magnification approximately $27,600\times$. Distance between markers is 1 micron.

continuities along the lamellae show evidence of much smaller pores between the microfibrils within the lamellae or aggregates of fibrils.

Swelling by Various Reagents

Sodium Hydroxide and Ethylenediamine

These reagents, which are frequently employed to produce changes in the crystalline lattice of cotton cellulose,[36-38] produce significant changes in the surface areas of cotton fibers (Table II). Since reagents were used on cotton in the form of fabric, incomplete conversion to the cellulose II crystal structure was observed in samples treated in 5.0M sodium hydroxide. When loose cotton fibers are treated similarly, cellulose I = 7%, cellulose II = 41%, and amorphous = 52%. The large increase in area found in the undried sample, 382% of the control untreated sample, is reduced to 172% if the cotton is air dried and then reswollen in water; treat-

TABLE II
Changes in Surface Area During Swelling by Various Reagents

Sample treatment	Surface area, % control	Crystallinity, %[a]		
		Cell I	Cell II	Amorphous
Sodium hydroxide, 5.0M, 30 min at room temp.				
undried, slack	382	43	18	39
air dried slack	172	41	20	39
air dried, tension	74	52	16	32
Ethylenediamine, 98.9%, 4 hr at room temp.				
rinsed and solvent exchanged at 0°C, undried	133	56	8	36
air dried ands olvent exchanged at room temp.	38	52	6	42
Phosphoric acid, 1 hr, room temp., undried				
Concentration 75%	201	77	7	16
77%	456	79	0	21
81%	798	78	0	22
85%	477	53	3	44
Potassium thiocyanate, 5.0M[b]	154			
Zinc chloride, 5.0M[b]	140	—	—	—
Lithium chloride, 5.0M[b]	160	—	—	—
Boiling distilled water, 30 min	159	—	—	—
Aqueous urea, 50%[c]	166	—	—	—
Aqueous dimethylformamide 50%[c]	121	—	—	—
Aqueous dimethyl sulfoxide 50%[c]	160	—	—	—
Control scoured fabric	100	73	0	27

[a] X-ray diffraction measurements were made on portions of samples used in gas adsorption measurements, then rinsed and dried at 60°C for 16 hr.

[b] Treated 4 hr at room temperature, undried.

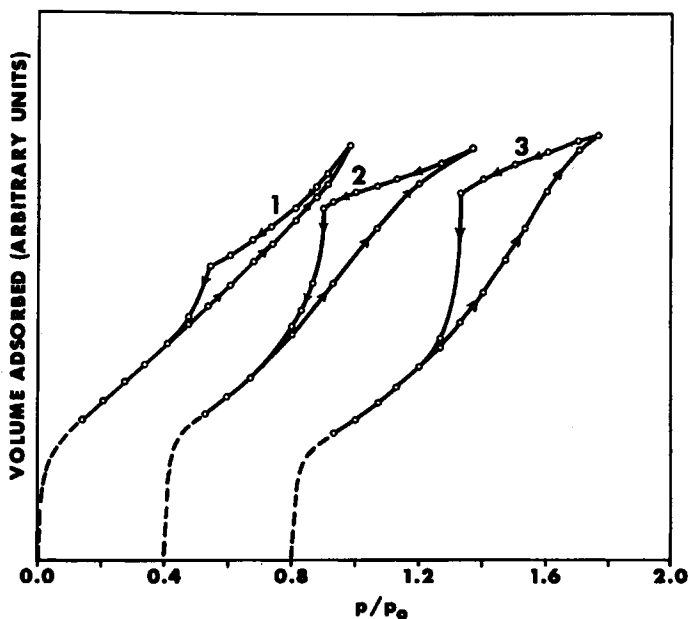[c] Treated 2 hr at room temperature, undried.

Fig. 6. Adsorption isotherms of cotton fabric treated with $5.0M$ NaOH: (1) control, untreated fabric; (2) treated slack, dried; (3) treated slack, undried. Values on ordinate scaled to permit comparison of isotherm shapes. Values on abscissa moved 0.4 p/p_0 to right for successive isotherms.
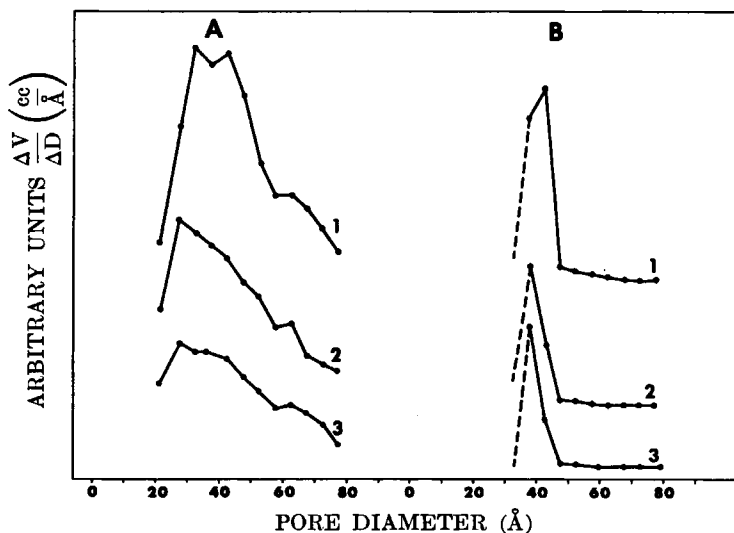

Fig. 7. Pore size distribution in fibers from cotton fabrics treated with $5.0M$ NaOH: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) treated slack and undried; (2) treated slack and dried before reswelling in water for sample preparation; (3) treated and dried with tension. Values on ordinate scaled to permit comparison of shapes of distributions.

ment with the fabric held at constant length during treatment and during rinsing and drying further reduces the area to 74% of the control fabric. Although ethylenediamine has been used to decrystallize cotton, there is much less change in surface area in these samples than in the mercerized cottons. These results are in agreement with similar work reviewed by Warwicker[36]; evidently the hydrogen bonding between the disordered cellulose chains either obliterates or closes off much of the pore structure developed by swelling in the amine, especially when samples were treated at room temperature instead of at 0°C. X-Ray diffraction data show that some decrystallization occurred and a small amount of cellulose II was formed.
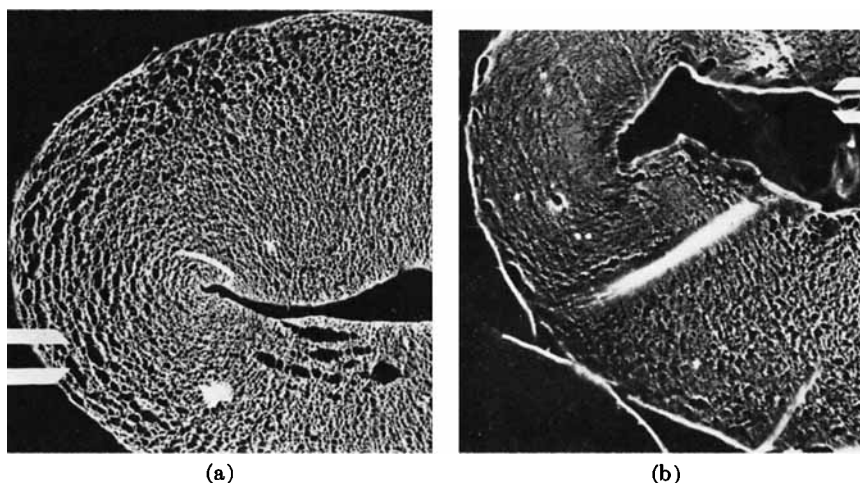

(a)   (b)

Fig. 8. Electron micrographs of cross sections of cotton fibers treated slack with 5.0M NaOH: (a) undried before embedding in methacrylate; (b) dried and reswollen in water before embedding.

Adsorption isotherms for samples treated with 5.0M sodium hydroxide (Fig. 6) show a large difference in hysteresis between the samples undried and air dried before solvent exchange from water. The adsorption branches of the isotherms have decreased slopes at relative pressures above 0.8, which appeared to some extent in all mercerized samples. This finding indicates a shift in pore size distribution to a more uniform pore size. The shape of the hysteresis portion of the isotherm of the undried mercerized sample approaches that suggested by deBoer[1] for "ink bottle" shaped pores. Also, the ratio of the square of the relative pressure during adsorption to the relative pressure during desorption for a given volume adsorbed, $(p/p_0)^2_{ads}/(p/p_0)_{des}$, is slightly larger than 1.00. Linsen and Van den Heuvel[39] propose this result to be indicative of tubular pores in which the radius of the larger portion is greater than, or equal to, twice the radius of the smaller part. In all the other sample isotherms, including the other two samples of mercerized fabric, this ratio was less than 1.00.

Pore size distribution data (Fig. 7) for the sodium hydroxide-treated samples indicate formation of larger pores in the undried mercerized sample in the distributions from both the adsorption and desorption branches. Arbitrary units are used for the ordinate values in order to compare the shapes of the distributions more easily. In the sample treated under tension there is a similar, but less significant, indication of formation of larger pores in the distribution from the adsorption isotherm; the distribution for the sample treated and dried without tension is very similar to that for untreated cotton, as shown in Figures 2 and 3. An average pore diameter of 50 Å was calculated from the adsorption branch data for the undried mercerized sample; otherwise, average pore diameter values for these samples were close to those given for untreated cottons.

Electron micrographs (Fig. 8) of a cross section of a fiber treated with $5.0M$ sodium hydroxide in the fiber form show the characteristic concentric array of ruptured lamellae changed to a more evenly dispersed arrangement of smaller microfibrillar aggregates. This dispersion is more marked in the micrograph of the undried mercerized fiber. These micrographs do not show the disposition of the microfibrils within the aggregates which possibly form much of the pore structure. Electron micrographs of fragments of fibers obtained by beating in water have suggested an increase in the width of elementary fibrils in cottons treated in $5.0M$ sodium hydroxide and a greater number of small fibrillar aggregates.[40] However, it is difficult to obtain evidence of bottle-necked pores from the micrographs which is as positive as that indicated by the gas adsorption studies.

Phosphoric Acid

Surface area data in Table II show a critical dependence on reagent concentration when cottons are swollen in phosphoric acid. Maximum area is measured in the sample treated with 81% phosphoric acid, similar to findings on fiber swelling reported by Warwicker[36] and Betrabet.[41] X-Ray data show significant change in crystalline structure only in the sample treated with 85% phosphoric acid (Table II and Fig. 9). The adsorption isotherms (Fig. 10) show increasing hysteresis for 75% through 81% concentrations of phosphoric acid; at a concentration of 85%, the shape of the desorption portion of the isotherm shows marked changes. The ratio of $(p/p_0)^2{}_{ads}/(p/p_0)_{des}$ for the hysteresis portion of the isotherm in the sample treated with 81% acid is less than 1.00 but never less than 0.96 over the whole hysteresis curve, in contrast to the ratios calculated for most samples which decreased from approximately 0.90 to 0.70 with decreasing relative pressure.

The pore size distributions (Fig. 11) show the breakdown in pore structure which occurs with increasing concentrations of the phosphoric acid. There is no significant change from the distribution for untreated cottons in the sample treated with 75% phosphoric acid. Beginning at a concentration of 77%, the distributions derived from the adsorption isotherms show a continuing shift to larger pore diameters, and the distribution is quite
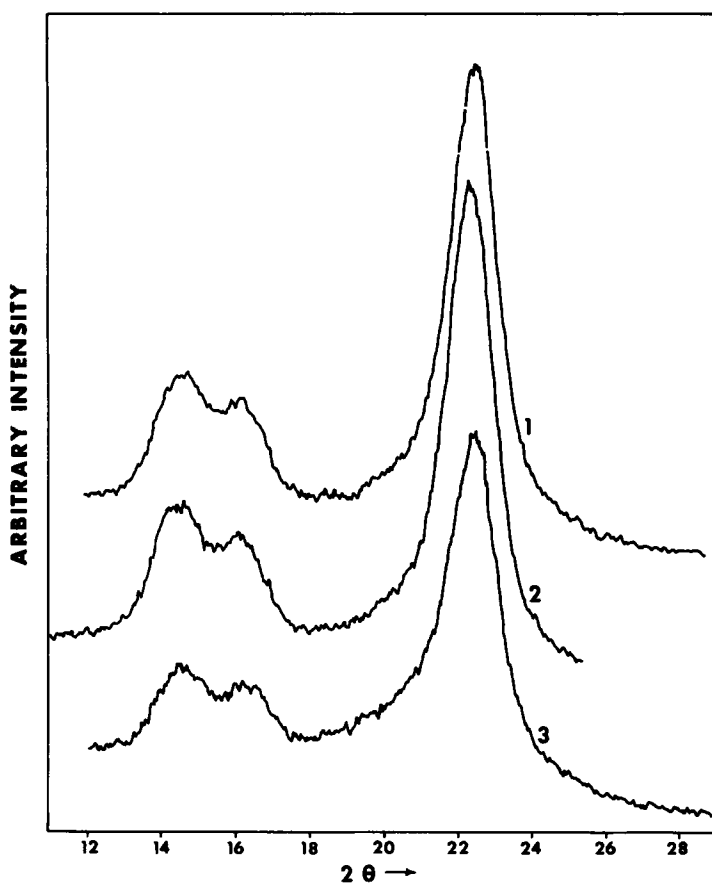
Fig. 9. X-Ray diffractograms of cotton fabrics treated with phosphoric acid: (1) 77% concentration; (2) 81% concentration; (3) 85% concentration. Ordinate values moved up for each successive isotherm to permit comparison of peak heights.

flattened for the sample treated at a concentration of 85%. Distributions derived from the desorption isotherms change from a peak value of 37.5 Å for the sample treated at the lowest concentration to a value of 42.5 Å for samples treated at higher concentrations. The relative peak height at these diameters which is greatly increased at 77% and 81% concentrations diminishes to about 20% of these values for the sample treated at 85% concentration.

Electron micrographs (Fig. 12) were made of sections of single fibers which had been treated as loose fibers, not in the fabric form used for adsorption studies; however, these micrographs illustrate the same features found in a large portion of the fibers from fabric samples. After treatments with an 80% concentration of phosphoric acid, the lamellae appear to be thinner and shorter than seen in the micrograph of the untreated fiber in Figure 5. The whole cross section of the fiber appears swollen, and the
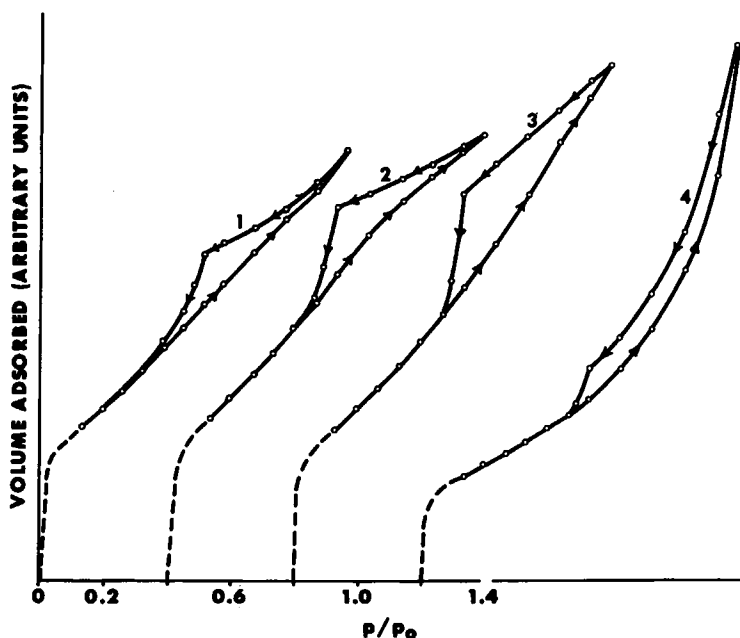
Fig. 10. Absorption isotherms of cotton fabrics treated with various concentrations of phosphoric acid: (1) 75%; (2) 77%; (3) 81%; (4) 85%. Values on ordinate scaled to permit comparison of isotherm shapes. Values on abscissa moved 0.4 p/p_0 for successive isotherms.

outer wall has been ruptured. There is evidence of some degradation in the presence of many separated stacks of microfibrils seen at the left; some beginning fusion of microfibrils may be observed at the top of the cross section. This fibrillar fusion dominates the structure of the sample treated in 85% acid, and evidence of degradation is shown by the torn appearance of the cross section at the lower left. Each of these alterations in fibrillar structure is quite different from the "honeycomb" type of fibrillar array observed after treatment with 5.0M sodium hydroxide and preparation for sectioning without intermediate drying (Fig. 8a).

Other Swelling Agents

The 40% to 60% increases in surface area measured on samples undried from the rinse water after immersion for 4 hr in 5.0M solutions of lithium chloride, zinc chloride, and potassium thiocyanate (Table II) are in agreement with the findings of Jeffries[42] that fiber swelling by aqueous solutions of inorganic salts is only about 50% greater than fiber swelling by water, unless swelling by the former results in changes in fiber crystallinity. There was no significant increase in surface area if the fibers were dried before reswelling in water. It is interesting to find that boiling in distilled water produced as much increase in surface area as did the salt solutions tested. Swelling in the 50% aqueous solution of urea and in 50% solutions of
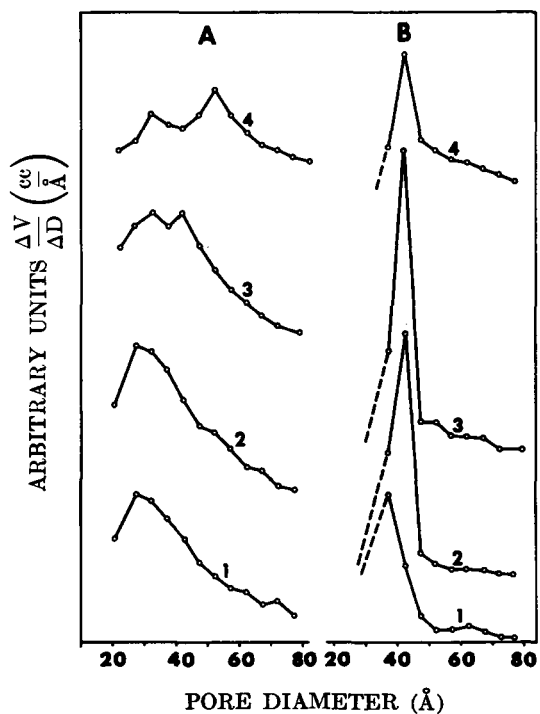
Fig. 11. Pore size distribution in fibers from cotton fabrics treated with various concentrations of phosphoric acid: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) 75%; (2) 77%; (3) 81%; (4) 85%. Values on ordinate scaled to permit comparison of shapes of distributions.
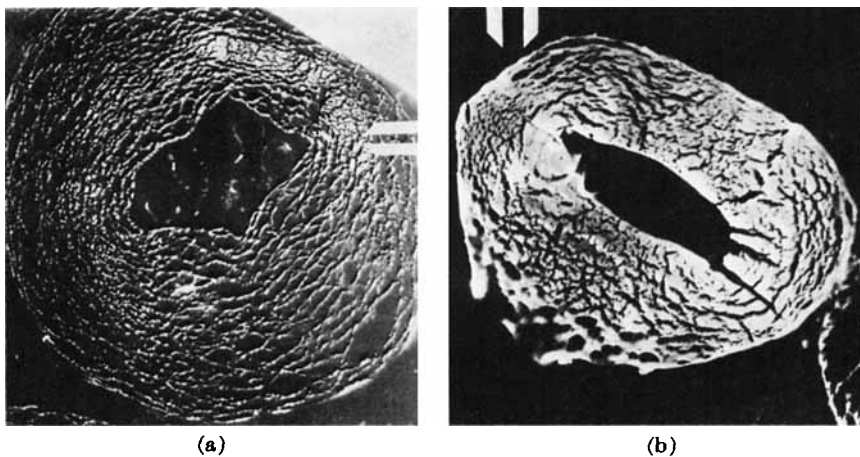

(a)   (b)

Fig. 12. Electron micrographs of cotton fibers treated with two concentrations of phosphoric acid: (a) 80%; (b) 85%. Fibers were dried by solvent exchange, then reswollen in water before being embedded in methacrylate.

dimethyl sulfoxide resulted in approximately 60% increase in area in the samples undried before solvent exchange.

Complete isotherms were run on the samples swollen in the solutions of inorganic salts. However, the pore size distributions did not show any significant differences in pore size or structure between these treated samples and the control fabric.

SUMMARY

Surface area and pore size distribution data show that these parameters may be used to compare changes in fiber morphology accompanying the various treatments. Purification of untreated, alcohol-extracted cottons by removal of pectins reduces to a major extent differences in surface area among the three varieties of cottons and between cottons grown under different controlled growth conditions. There was a significant increase in surface area in each sample after removal of the pectins, although the difference for the sample grown at constant temperature with alternating light and darkness was small; differences in pore size distributions were smaller after pectin removal. Drying after dewaxing and scouring decreased the surface area by significant amounts. In a Pima cotton which was undried between dewaxing and removal of the pectin and then exchanged to helium without drying, the increase in surface area was twice that obtained for the sample dried after each purification process.

A larger increase in area, 382%, was obtained when surface area measurements were made on cottons undried before solvent exchange after treatment with $5.0M$ sodium hydroxide, compared to an increase of 172% in the dried sample. These differences were reflected in pore structures obtained by gas adsorption studies and also in electron micrographs of cross sections of water-wet and of dried fibers. Ethylenediamine-treated samples showed increased area in the undried sample; the surface area of the dried sample was less than the area of an untreated sample.

Comparison of swelling of undried samples treated with $5.0M$ sodium hydroxide with samples treated with 81% phosphoric acid shows significantly more increase in surface area after the phosphoric acid swelling. Phosphoric acid does not change the crystal structure from the cellulose I pattern at this concentration, but definite evidence of formation of cellulose II structure is observed in the sodium hydroxide-treated cotton. The electron micrographs of cross sections of fibers which were treated with $5.0M$ sodium hydroxide and embedded with methacrylate without intermediate drying show a reaggregation of the microfibrils to form a sponge-like texture containing numerous, almost round, holes. These holes presumably result from swelling of pores accessible to the methacrylate during polymerization. In phosphoric acid swelling, the type of microfibrillar aggregation appears similar to that of untreated fibers, except that the lamellar length is greatly reduced and the lamellae appear thinner and much more widely separated. Apparently much of the pore space mea-

sured by gas adsorption is within the lamellae, probably randomly located along the length of the lamellae.

It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

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