

Changes in Porosity of Treated Lint Cotton Fibers. II. Treatments for Chemically Modifying Cotton

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Synopsis

Changes in the internal morphology of chemically modified lint cotton fibers 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 of fibrillar aggregation as shown by electron micrographs. Fibers were either preswollen in water or taken from the rinse water and solvent exchanged through methanol and *n*-pentane to helium before adsorption measurements were made. Unless reacted in the presence of water, the wrinkle resistance treatments studied caused losses in surface area of 55% or greater. Changes in surface area and porosity of cottons reacted with monofunctional reagents designed to give protective and other types of finishes were dependent on the type of reaction used.

INTRODUCTION

Part I of this paper described the use of gas adsorption methods to determine changes in porosity of cotton fibers during purification treatments and treatments with reagents which are purported to swell the fibers.¹ In this part similar studies of cottons during and after treatment with reagents used to chemically modify the cellulose will be reported.

EXPERIMENTAL

Treated samples examined include:

1. Cottons treated by wrinkle resistance treatments such as (a) formaldehyde crosslinking in processes where reaction is completed at ambient temperatures in the processing liquid; (b) formaldehyde crosslinking in dry-cure, wet-fix, and poly-set processes where crosslinking occurs principally in the padded fabric at high temperatures; (c) treatments using butadiene diepoxide (BDO), tris(1-aziridiny)phosphine oxide (APO), and stearyl chloride, which stabilize the fibrillar elements.
2. Cottons that are chemically modified by acetylation, cyanoethylation, aminization, and phosphonomethylation.

Details of the methods of preparation of treated samples will be described or referenced in the report of test results. The experimental procedures and analytical methods were described in part I.¹

RESULTS

Porosity Changes in Cottons in Formaldehyde Treating Solutions

Wrinkle resistance is believed to result from crosslinking the fibrillar elements within the fiber when a bifunctional reagent such as formaldehyde is used. Other mechanisms have been postulated for some reagents but the end-product properties are assumed to result from fixation of fibrillar structures.

Although many reactions with reagents used to produce wrinkle-resistant cottons take place in partially dried fabric or during the "cure" stage of the reaction, usually at about 160°C, four methods of crosslinking with formaldehyde in which the reaction occurs in the liquid phase at room temperature have been summarized by Pierce and Frick.² Reagents used in each treatment are listed in Table I. Since the fabric could be solvent exchanged from the rinse water, it was possible to observe fiber porosity during processing. The effects of reagents used as catalysts and/or swelling

TABLE I
Change in Surface Area of Cotton Fabric During Reaction
in Formaldehyde Crosslinking Solutions

Sample treatment ^a	Surface area, % control
<i>Form P process</i> (all at room temp. for 60 min)	
1. 77% H ₃ PO ₄	456
2. 3.7% HCl	120
3. 77% H ₃ PO ₄ + 3.7% HCl	130
4. 77% H ₃ PO ₄ + 3.7% HCl + 3.6% CH ₂ O (<i>Form P</i>) ^b	105
5. same as (4), but dried and reswollen	103
6. 75% H ₃ PO ₄ , 1 hr, transferred to Form P solution without drying	228
<i>Form D process</i> (all at room temp. for 120 min)	
1. 75% CH ₃ CO ₂ H	138
2. 75% CH ₃ CO ₂ H + 3.7% HCl	123
3. 75% CH ₃ CO ₂ H + 3.7% HCl + 3.6% CH ₂ O (<i>Form D</i>) ^b	70.3
<i>Form W process</i> (all at room temp. for 180 min)	
1. 17.5% HCl	119
2. 17.5% HCl + 3.7% CH ₂ O (<i>Form W</i>) ^b	77
<i>Form S process</i> (all at room temp. for 30 min)	
1. 47% H ₂ SO ₄	113
2. 47% H ₂ SO ₄ + 27.8% CH ₃ CO ₂ H	80.4
3. 47% H ₂ SO ₄ + 27.8% CH ₃ CO ₂ H + 7.5% CH ₂ O (<i>Form S</i>) ^b	74.1

^a Water content is 100% minus total of reagents listed.

^b Reagents in these lines comprise the crosslinking solutions.

TABLE II
Properties of Air-Dried Formaldehyde-Treated Fabrics^a

Treatment	Bound CH ₂ O, %	Moisture regain, % control	Wrinkle recovery angle (W + F), degrees	
			Wet	Dry
Form P, 1 hr	2.45	153	360	161
Form D, 2 hr	1.24	—	267	269
Form W, 3 hr	0.75	126	280	212
Form S, 30 min	1.87	117	230	258
Control	—	—	161	175

^a Data taken from Table I in publication of Pierce and Frick.²

agents were studied also. Except for one sample of Form P-treated fabric, all the samples were solvent exchanged without intermediate drying. The changes in surface area are given in Table I. Data in Table II on bound formaldehyde, moisture regain, and crease recovery angles were taken from the published data of Pierce and Frick.² When the concentration of the first phosphoric acid solutions used to study the Form P process were checked by titration, a value of 77% was obtained instead of the 75% concentration used by Pierce and Frick. However, the surface area data illustrate the effect of formaldehyde crosslinking in decreasing the porosity while the cotton is immersed in the treating solution. The fact that crease recovery is not a consistent function of the amount of formaldehyde which has been reacted with the cotton (Table II) illustrates the role of internal fiber morphology at the time of crosslinking; this is also discussed by Pierce and Frick.

A large decrease in swelling by the 77% aqueous phosphoric acid was observed when 3.7% hydrochloric acid was included in the treating solution (Table I). This finding illustrates the very critical dependence of fiber swelling on acid concentration in this range, as discussed in part I. Apparently this dependence is based on the dissociation of the phosphoric acid and is a function of the water-to-phosphoric acid ratio.³ Pertinent to the study of the Form S process are findings reported by Warwicker and Clayton,⁴ who reported no evidence of increased accessibility in cottons treated for 30 min at room temperature with aqueous solutions of sulfuric acid of less than 60% concentration. The small increase of 13% in surface area (Table I) resulting from treatment with 47% sulfuric acid for 30 min is in fair agreement with their findings. A large decrease in area is caused by adding acetic acid to the solution. The addition of the crosslinking reagent resulted in only slightly more decrease in surface area. There was visible evidence of fiber damage in the crosslinked, but not in the other two sulfuric acid-treated samples. Frick, Pierce, and Tripp⁵ reported evidence of acid degradation in fabric after this Form S treatment and of a nonuniform lateral distribution of crosslinked fibrils which was visualized in an electron micrograph of a treated fiber cross section.

In the Form D treatment, the addition of hydrochloric acid to the solution of 75% acetic acid caused much less reduction in surface area than was measured for the mixture of HCl with phosphoric acid in the Form P process. Data on the Form W process show some increase in surface area in the sample treated with 17.5% hydrochloric acid for 3 hr; however, interpretation of swelling effects in cottons treated in sulfuric and hydrochloric acid solutions is always complicated by the hydrolytic effects of these reagents which result in removal of short lengths of a fibril along its length.

It would be interesting to interpret the difference observed in area between the undried Form D sample (Table I) and the much lower areas found in Form D samples which were dried then reswollen with water (Table III). It is probable that this lower area is the result of formation of a greater number of stronger and more stable interlamellar hydrogen bonds

TABLE III
Surface Areas of Wrinkle Resistance-Treated Cottons

Treatment	Surface area, % control
<i>Formaldehyde</i>	
Dry cure (7)	
0.27% CH ₂ O	41.2
1.68% CH ₂ O	25.6
Form D (8)	
0.41% CH ₂ O	35.0
0.84% CH ₂ O	27.4
Form W (9)	
0.51% CH ₂ O	76.4
0.78% CH ₂ O	71.5
Vapor phase (10)	
0.18% CH ₂ O	11.1
0.40% CH ₂ O	7.4
<i>Butadiene diepoxide (BDO) (11, 12)</i>	
Base catalysis	
8.7% add-on	8.2
14.7% add-on	19.3
Acid catalysis	
0.7% add-on	11.6
2.5% add-on	11.7
<i>Tris(1-aziridinyl)phosphine oxide (APO) (13)</i>	
7.9% add-on	14.0
17.8% add-on	12.5
<i>Melamine formaldehyde condensates (14)</i>	
Wet fix	
cloth rolled 15 min, 82°C, 4.72% add-on	42.6
cloth flat 10 min, 82°C, 6.29% add-on	22.3
cloth flat 24 hr, room temp. 6.78% add-on	37.7
Poly-set	
3 min, 59°C, 3.5% add-on	27.9
10 min, 60°C	30.8
<i>Stearoyl chloride (15) 16.5% add-on</i>	
	6.1

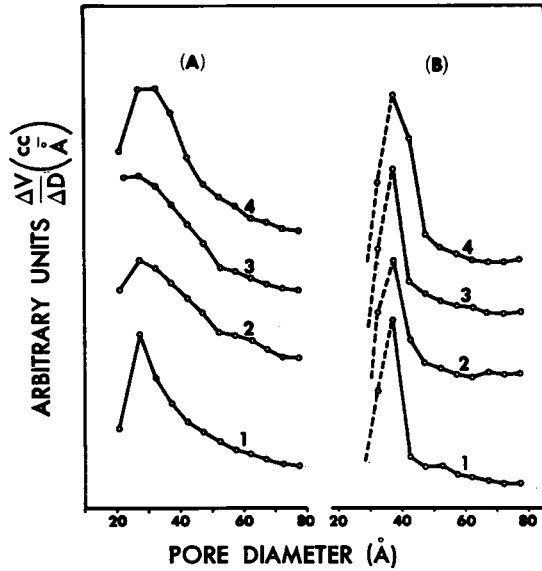


Fig. 1. Pore size distributions in fibers from cotton fabrics treated with reagents of Form P process: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) 77% H_3PO_4 + 3.7% HCl, undried; (2) Form P, undried; (3) Form P, dried; (4) swollen 75% H_3PO_4 and undried before treating with Form P process, undried after Form P process. Ordinate values scaled to permit comparison of shapes of distributions.

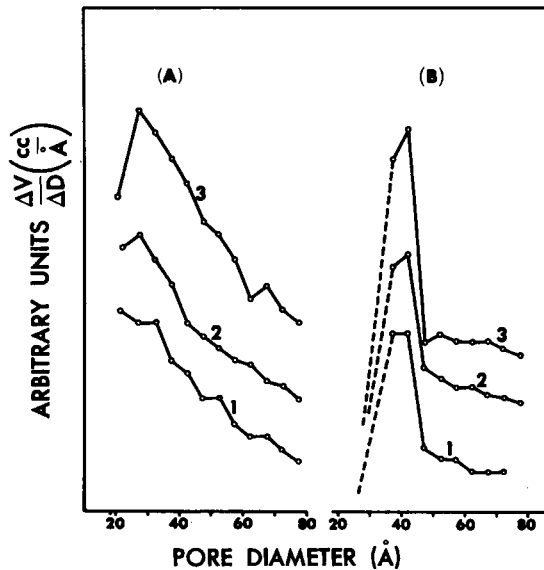


Fig. 2. Pore size distribution for fibers from fabrics treated with various formaldehyde processes: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) Form D; (2) Form S; (3) Form W. All were undried before reswelling in water for sample preparation. Ordinate values scaled to permit comparison of shapes of distributions.

when the rinse water evaporates. Also of interest is the fact that the value of surface areas of the undried Form W sample and the dried samples in Table III show little difference; the unchanged area of the Form P sample upon drying again suggests the concept of decreased interlamellar crosslinking or of longer crosslinks in samples which are reacted in the water-swollen state. Apparently crosslinking between lamellae makes the interior of individual lamellae inaccessible to liquids.

Pore size distributions were calculated from complete isotherms on each of the samples listed in Table I. There were no large differences among the uncrosslinked samples, except for those treated with reagents used in the Form P process (Figs 1 and 2). Phosphoric acid swelling was discussed previously.¹ Crosslinking with formaldehyde in the Form P process increases the peak width in the distributions obtained from the adsorption isotherms, resulting in practically equal heights at 27.5 and 32.5 Å (Fig. 1). There is little difference in the distributions for the crosslinked samples before and after drying. However, the peak appears sharper as a whole for the sample preswollen before crosslinking. This latter sample had an average pore diameter of 42 Å, compared to the former two with values of 48 Å and 46 Å for the undried and dried samples, respectively. Distributions from the desorption isotherms all have peaks at 37.5 Å.

The remaining undried, crosslinked samples show little change compared to untreated cottons in distributions calculated from the adsorption isotherms (Fig. 2a). The desorption isotherms (Fig. 2b) show peak broadening; peak heights at 42.5 Å are equal to or greater than the 37.5 Å peak heights. Average pore diameters equal to 47 Å were calculated for the Form D and Form W samples from the adsorption branch of the isotherms, and a diameter of 49 Å was found for the Form S crosslinked sample.

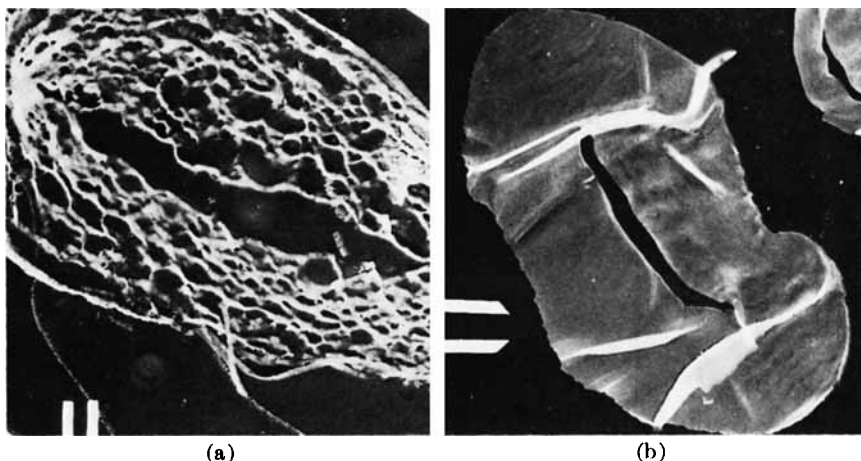


Fig. 3. Electron micrographs of cross sections of fibers treated with wrinkle resistance processes and dried before reswelling in water and embedding with methacrylate: (a) Form W, 0.47% CH_2O ; (b) BDO, base catalysis, 10.2% add-on. Distance between markers is 1 micron.

These values show a small increase over the values for untreated cottons. However, the Form D sample, discussed in the next section, which had been dried after treatment had an average pore diameter of 54 Å. These pore size distribution data indicate that reactions with bifunctional reagents in solution cause changes in porosity which, in certain cases, may be further increased upon drying the cotton.

Pierce and Frick included electron micrographs of these treated cottons in their report.² The Form D-treated cotton had a closed structure similar to that shown for a BDO-treated cotton in Figure 3b. The Form S treatment resulted in a structure composed of a closed region near the periphery of the fiber with the remainder of the cross section open as in the micrograph of a Form W sample (Fig. 3a). However, the type and degree of lamellar separation in Form D and Form S treatments has been shown to be a function of the amount of formaldehyde bound during treatment.⁶ In the form P sample, the cross section was swollen throughout by interlamellar separation as observed in untreated cotton, with perhaps slightly more swelling in some regions.

Porosity Changes Brought about by Wrinkle-Resistance and Other Chemical Treatments

Wrinkle Resistance Treatments

A variety of wrinkle resistance treatments, which have been intensively studied in recent years, was applied to portions of the control fabric by appropriate experts (Table III). All of these samples were cured, rinsed, and dried before reswelling in water, in preparation for adsorption studies. Each treatment is described in the reference given in Table III. Maximum reduction in surface area was observed in samples treated with stearyl chloride, with formaldehyde applied by the vapor phase method and with BDO at an 8.7% add-on. Except for the Form W-treated samples, all surface areas measured were less than one half the area of the control untreated fabric. As discussed in the previous section, in the Form W treatment, the reaction is completed at ambient temperatures in an aqueous medium. Electron micrographs of cross sections of Form W-treated fibers, which were swollen with water when placed in the methacrylate embedding medium, show that a moderate amount of separation of the lamellae remains, although the lamellae appear thickened and are fewer in number than observed in an untreated fiber (Fig. 3a). In contrast, there is no evidence of layer separation in the cross section of the low-area, BDO-treated sample (Fig. 3b). This lack of lamellar separation in electron micrographs of wrinkle-resistant cottons is routinely used to illustrate effectiveness of treatment and is typical for most of the remaining samples, except the wet-fix and poly-set samples. Lamellar separation intermediate to that shown in Figures 3a and 3b is found in these latter two treatments.

Complete isotherms were obtained on only three of these wrinkle resistance-treated samples because their low surface areas limited the accuracy

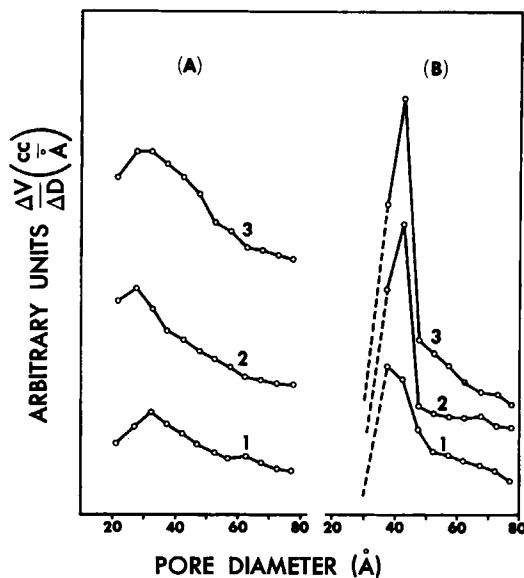


Fig. 4. Pore size distribution for fibers from wrinkle resistant treated fabrics: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) dry-cure formaldehyde, 0.3% CH_2O ; (2) melamine formaldehyde condensate, wet-fix, 4.72% add-on; (3) Form W, 0.51% CH_2O . All fabrics were dried after processing before reswelling in water for sample preparation. Ordinate values scaled to permit comparison of shapes of distributions.

of the adsorption data. Pore size distributions (Fig. 4) calculated from these isotherms show that the largest change from the distributions shown for untreated cottons in part I of this paper occurs in the sample which had a dry-cure formaldehyde treatment; the least change occurs in the sample treated with a melamine-formaldehyde condensate by a "wet-fix" treatment for 15 min at 82°C . The wet-fix and dry-cure treatments caused almost equal reductions in surface areas (Table III) which were significantly larger than the reduction produced by the Form W treatment. These findings suggest that crosslinking by the wet-fix method, using a melamine-formaldehyde condensate, results from reaction which is non-preferential in relation to pore size, whereas the other two treatments react preferentially in the smaller pores. However, more adsorption studies on these and similar samples are needed to substantiate this concept. Average pore diameters for Form W and dry-cure formaldehyde treatments were increased to 49 \AA and 54 \AA , respectively, compared to a calculated value of 44 \AA for the wet-fix sample. This latter value is not significantly different from the values for untreated cotton, 44.8 \AA to 45.7 \AA .

Protective and Other Treatments

The fibrillar structures of cotton often show marked changes when mono-functional substituent groups are attached to one or more of the 2,3- or 6-

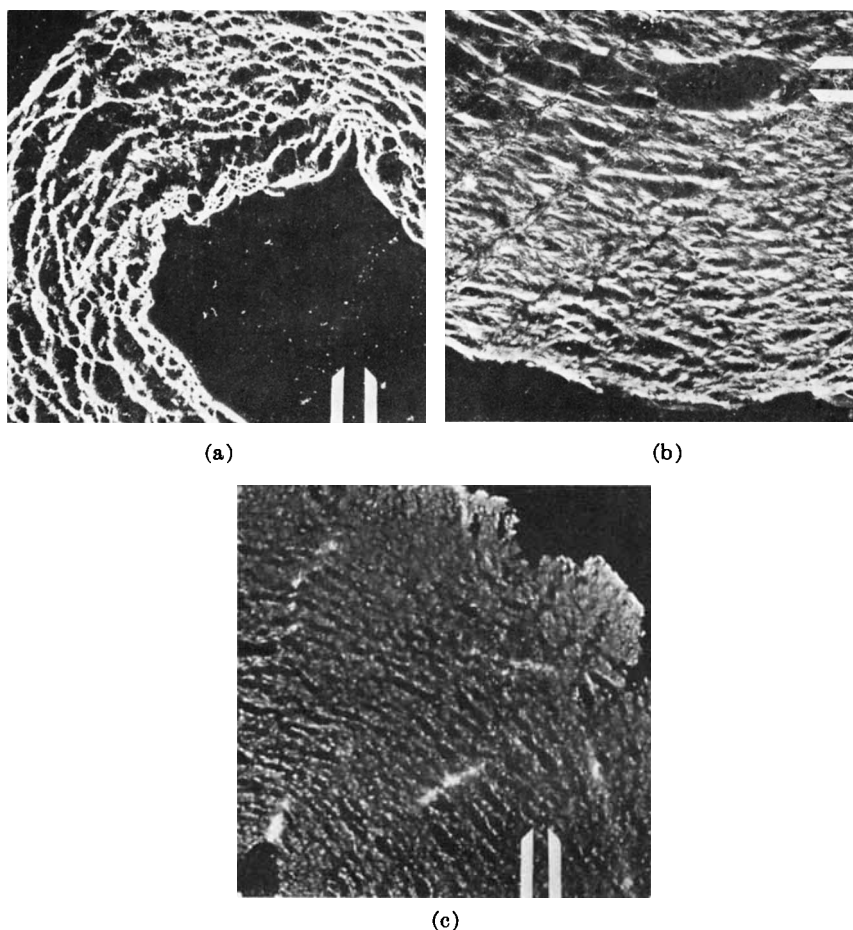


Fig. 5. Electron micrographs of cross sections of water-swollen, chemically modified cotton fibers embedded with methacrylate: (a) cyanoethylated, D.S. = 1.6; (b) acetylated, D.S. = 1.25; (c) aminized, D.S. = 1.14.

positions on the anhydroglucose units (Fig. 5). However, in these cottons the chemical nature of the substituents may be more influential in attaining the desired product properties than ensuing changes in fibrillar structure. Acetylated and cyanoethylated fabrics, which are resistant to heat, rot, and mildew, decrease in density and crystallinity with increasing degrees of substitution (D.S.), but these changes do not result in increased surface area (Table IV). In cyanoethylated cotton, Conrad¹⁶ reported a decrease in density from 1.55 g/cc for the untreated cotton to between 1.20 and 1.25 g/cc at a D.S. of 2.0, extensive decrystallization, and evidence of increase of fiber cross-sectional area. Tripp, Giuffria, and deGruy,¹⁷ in studies of acetylated cottons, reported changes in density from 1.55 g/cc to 1.435 and 1.407 g/cc and increases in fiber cross-sectional area of 30% and 52%, at a D.S. of 1.09 and 1.42, respectively.

TABLE IV
Surface Areas of Cottons Treated with Protective and Other Processes

Treatment	Surface area, % control	Crystallinity, % ^a		
		Cell I	Cell II	Amorphous
Phosphonomethylated, Cell—O—CH ₂ — P(O)(ONa) ₂				
D.S. = 0.08	327	0	25	75
D.S. = 0.14	103	0	12	88
Acetylated Cell—O—C(=O)—CH ₃ , D.S. = 1.25	25	—	—	—
Aminized Cell—O—CH ₂ —CH ₂ —NH ₂ , D.S. = 0.06	5.6	—	—	—
Cyanoethylated Cell—O—CH ₂ —CH ₂ —C≡N, D.S. = 1.6	4.7	—	—	—
Control scoured fabric	100	73	0	27

^a X-ray diffraction measurements were made on portions of samples which were used in adsorption tests, then rinsed to remove solvents, and dried at 60°C.

Although the electron micrographs of fiber cross sections of the cyanoethylated and acetylated samples each show the swelling of the fiber cross section observed by other methods, the cell wall of the acetylated fiber appears more highly swollen than that of the cyanoethylated fibers (Fig. 5). In the latter, the lamellae appear fused and fewer in number than observed in untreated cotton; much of the swelling appears to result from expansion of the lumen space. Previous studies of cyanoethylated fibers which had been fragmented in water showed evidence of fibrillar swelling and fusion across the sheets of microfibrils. The electron micrograph of the acetylated fiber cross section shows swelling of the individual lamellae but with retention of much of their interior fibrillate texture. The increase in fiber cross-sectional area in this cotton appears to result from swelling throughout the cell wall. Both micrographs were made of cross sections from fibers which were water swollen before being embedded in methacrylate. However, it has been shown that when these cottons are embedded dry, lamellae separation will occur to some extent, but the cross sections are not quite as swollen as the ones pictured here.

Although aminized cottons are almost water soluble during treatment when the D.S. is 0.157 or more,¹⁸ the surface area measured on the sample of fabric having a D.S. of 0.06 is only 5% of the area of the untreated sample. In the electron micrograph of an aminized fiber (D.S. = 0.14) cross section (Fig. 5c), the cell wall appears highly swollen and has lost the lamellar and fibrillar structures found in untreated fibers. This appears to be due to fusion of the microfibrils within the lamellae and extensive fusion of lamellae. The two tears through the outer walls of the fiber, seen in the lower left corner, show the embrittlement of the cellulosic structures which has occurred. Since the surface area at D.S. = 0.06 is only 5% of the

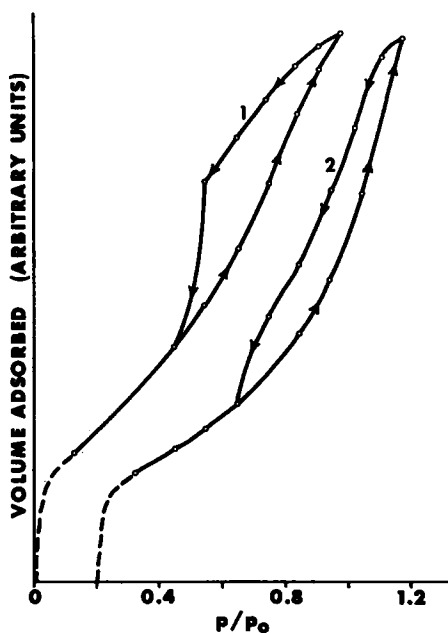


Fig. 6. Adsorption isotherms of phosphonomethylated cotton fabrics: (1) D.S. = 0.08; (2) D.S. = 0.14. Values on ordinate scaled to permit comparison of isotherm shapes. Values on abscissa moved $0.2 p/p_0$ to right for second isotherm.

area of the control sample, the micrograph of the more highly substituted sample is probably typical of aminized cottons.

In contrast to the losses in surface area measured for the three modifications discussed above, phosphonomethylation¹⁹ to D.S. = 0.08 results in a surface area equal to 327% of the control. At D.S. = 0.14, the surface area decreased to a value approximately equal that of the control cotton sateen sample used to prepare this modification. These phosphonomethylations were accomplished in the presence of a solution of mercerizing-strength sodium hydroxide. The substituent group at D.S. = 0.08 appears to result in reswelling approximately equal to values for undried mercerized cotton, although the samples were cured, washed, and dried before being rewet for preparation for gas adsorption studies. Values of $(p/p_0)_{ads}^2$ $(p/p_0)_{des}$ calculated from the isotherm (Fig. 6) range from 0.99 to 1.01. These are less than the values of 1.00 to 1.26 found for the undried mercerized cotton, but are significantly higher than the values for mercerized samples that were dried before reswelling in water. However, the x-ray diffractograms (Fig. 7 and Table IV) indicate extensive decrystallization in this sample and even more loss of crystallinity in the sample with a D.S. = 0.14. There is a distinct change in shape of the isotherm of the more highly substituted sample (Fig. 6). This sample had shown visible evidence of dissolution after swelling in water. Preliminary electron-microscopic studies of these cottons²⁰ show marked swelling of the microfibrils,

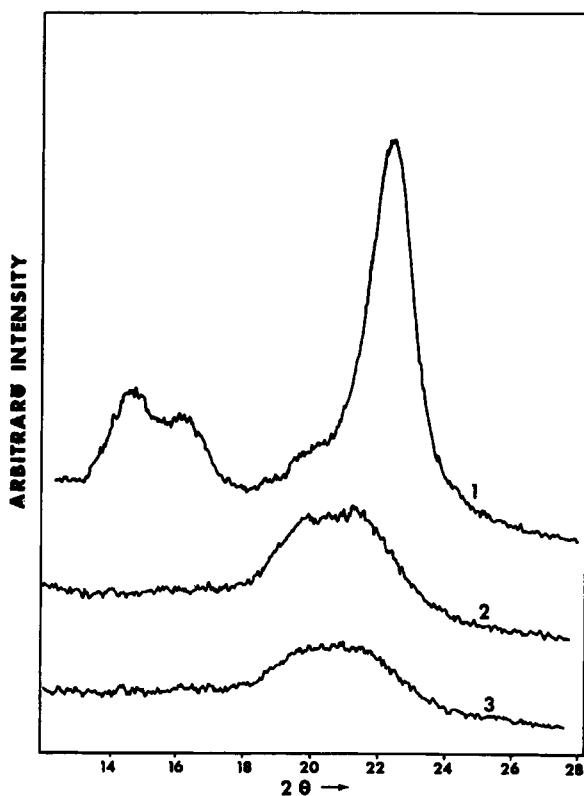


Fig. 7. X-Ray diffractograms of phosphonomethylated and control fabrics. Ordinate values moved up for successive diffractograms to permit comparison of peak heights: (1) control untreated fabric; (2) D.S. = 0.08; (3) D.S. = 0.14.

but this swelling apparently did not result in significant fibrillar fusion at a D.S. \approx 0.08.

Complete isotherms were obtained only for the acetylated and phosphonomethylated samples because of the low surface areas of the other two modifications. The pore size distributions from each branch show definite evidence of a shift to larger pore sizes (Fig. 8). Average pore diameters of 57, 54, and 68 Å were calculated from the adsorption branches of the isotherms for the acetylated cotton and for phosphonomethylated cotton of D.S. = 0.08 and D.S. = 0.14, respectively. With the exception of the sample treated with 85% phosphoric acid, these were the largest average pore diameters found in any of the samples studied.

DISCUSSION AND CONCLUSIONS

Interpretation of Nitrogen Adsorption Isotherms

The BET method of measuring surface areas, used for comparing treated and untreated cottons, appears to yield results which are in agreement with

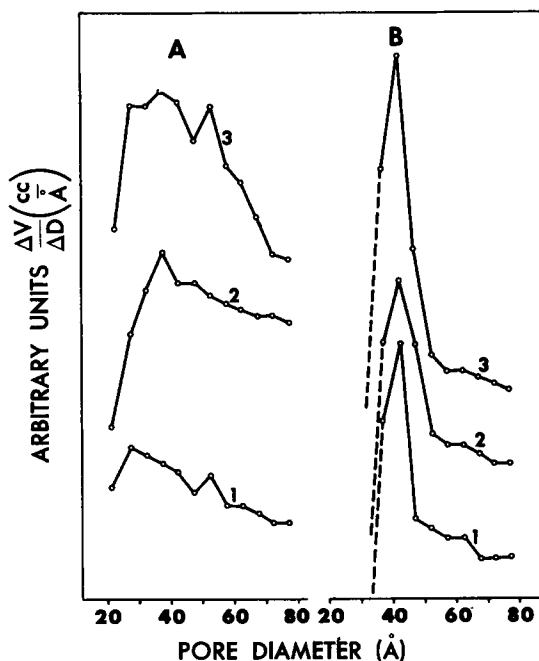


Fig. 8. Pore size distribution in fibers from acetylated and phosphonomethylated cotton fabrics: (a) from adsorption branch of isotherm; (b) from desorption branch; (1) acetylated, D.S. = 1.25; (2) phosphonomethylated, D.S. = 0.14; (3) D.S. = 0.08. Values on ordinate scaled to permit comparison of shapes of distributions.

comparisons by other techniques. Although no adsorption studies at low relative pressures were made to determine the adsorptive potentials of cotton for nitrogen, calculations of the differential heats of adsorption from data above 0.1 relative pressure were made by the method outlined by Bering, Dubinin, and Serpinsky.²¹ Only the stearyl chloride-treated cotton and a sample treated with BDO of a high add-on fell outside the curve for all the other samples. Thus, even though nitrogen adsorption sites may be heterogeneously distributed as found for argon on the cottons studied by Barber,²² a "monolayer," used to evaluate the surface area by the BET method, should represent similar amounts of adsorbed nitrogen in the samples compared in these tests.

The complete adsorption-desorption isotherms obtained for many of the samples reported are most nearly described by the type B or type D models proposed by Everett.²³ The adsorption branch resembles that described by Brunauer as type II.²⁴ None of the isotherms fits with any degree of certainty the models proposed by deBoer, which are based on adsorbents having uniform pore sizes and shapes.²⁵ It was not possible under the conditions of our experiments to determine the closure or nonclosure of the desorption branches of the isotherms. In most instances, too few measurements were made below relative pressures of approximately 0.5 during desorption to

establish conclusive evidence of closure or nonclosure. Also, for most isotherms, the long intervals required to complete the isotherms resulted in some drift in calibration of the thermal conductivity cell detectors. Recalibration did not give consistent corrections, but nonclosure frequently

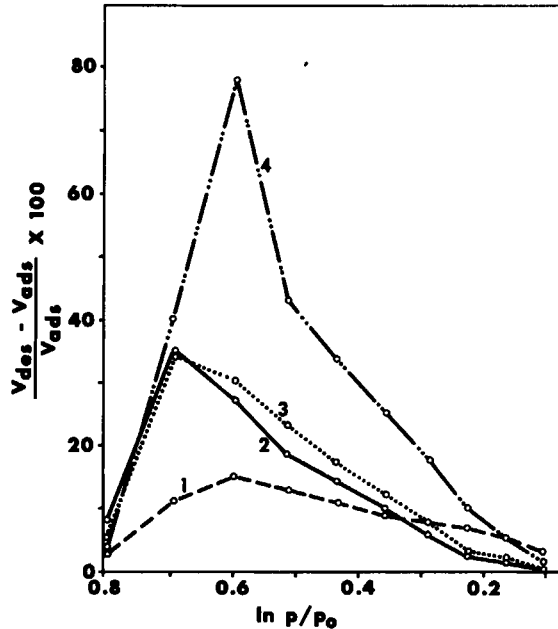


Fig. 9. Height of hysteresis loops in isotherms of cottons swollen with 5.0M NaOH: (1) control, untreated fabric; (2) treated slack, dried; (3) treated with tension, dried; (4) treated slack, undried.

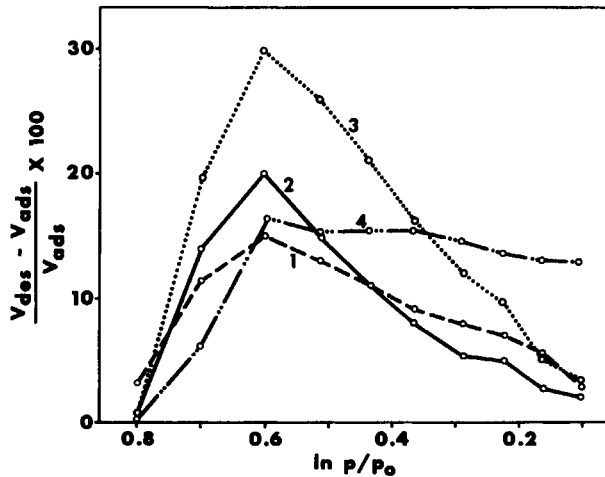


Fig. 10. Height of hysteresis loops in isotherms of cottons treated with various concentrations of phosphoric acid: (1) control untreated fabric; (2) 77% acid; (3) 81% acid; (4) 85% acid. All treated samples undried before sample preparation.

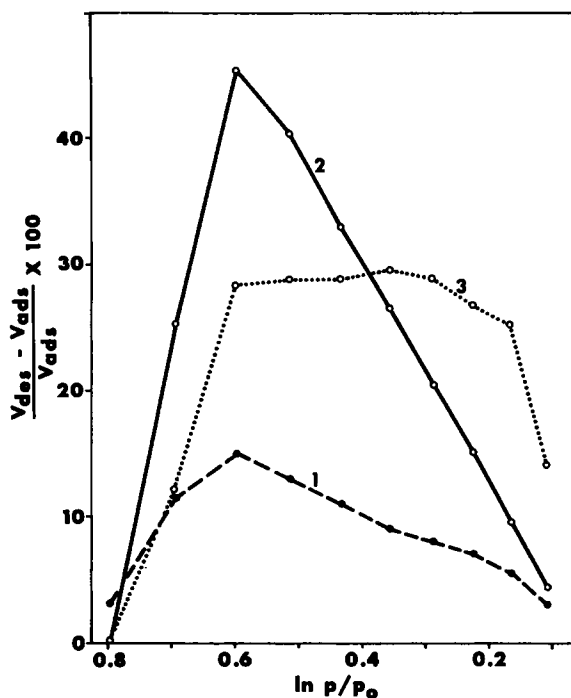


Fig. 11. Height of hysteresis loops in isotherms of phosphonomethylated fabrics: (1) control, untreated fabric; (2) D.S. = 0.08; (3) D.S. = 0.14. Samples dried before reswelling for sample preparation.

appeared; however, the differences in values of adsorbed nitrogen between the adsorption and desorption branches below a relative pressure of approximately 0.35 were very small compared to the differences in values above this pressure.

Comparison of the shapes of the hysteresis loops is facilitated by plotting the vertical height of the hysteresis portion of the isotherm as a function of the logarithm of relative pressure, as described by Everett.²³ Graphs for treated cottons showing the largest deviations from hysteresis observed for untreated cotton are shown in Figures 9, 10, and 11. The three treatments showing the maximum differences in height of their hysteresis curves also showed maximum increases in surface areas.

Cranston and Inkley suggested that the branch of the isotherm selected for calculation of pore size distribution should be the one which showed best agreement between the accumulated surface area calculated by their analysis and the area calculated by the BET method.²⁶ They also suggest that the comparison of cumulative and measured values of adsorbed volumes could be used in this selection. The data in Table V summarize these comparisons for a number of cotton samples. The differences in BET areas and areas calculated from the desorption branches of the isotherms is maximum in the samples shown in the footnote in Table V. These same

TABLE V
Comparison of Values of BET Areas and Measured Volumes of
Adsorbed N₂ with Cumulative Values from Cranston-Inkley Analyses

Parameter	Number of samples	
	Adsorption branch	Desorption branch
Surface area		
agreement 0-5%	26	25
5-10%	19	14
10-15%	5	3
15-20%	0	3 ^a
above 20%	0	5 ^a
Volume		
agreement 0-3%	44	24
3-5%	3	13
5-10%	3	8
above 10%	0	5 ^b

^a 81% H₃PO₄, 22.6%; 5.0M NaOH, 36.3 and 35.6%; and phosphonomethylated D.S. 0.08 and 0.14, 29% and 30.6%, respectively.

^b 81% H₃PO₄, 11%; 5.0M NaOH, 12.8 and 12.2%; and phosphonomethylated D.S. 0.08 and 0.14, 13.7% and 10.0%, respectively.

samples also showed maximum variations in height of the hysteresis curves shown in Figures 9, 10, and 11. Of the untreated cottons, all the three varieties of cottons showed best agreement between BET areas and the areas calculated from desorption isotherms. The ratio of the difference in cumulative and BET areas to the BET area for the adsorption branch was approximately 5% greater than the ratio for the desorption branch. The dewaxed fibers grown at constant temperature showed best agreement in areas with the adsorption, but best with the desorption branch after scouring. For the most part, samples treated in solutions containing acids showed best agreement with the areas from adsorption branches, as did treatments with basic solutions. Although these comparisons suggest changes in pore shapes, they do not seem to justify definite conclusions about the shapes of the pores without more confirmatory evidence.

Changes in Porosity of Chemically Modified Cottons

Surface areas were reduced in all the chemically modified cottons studied, with two exceptions: (1) samples crosslinked with formaldehyde in the Form P process, in which reaction occurs in swollen fibers in the presence of water; (2) samples phosphonomethylated to a D.S. of 0.08 or 0.14 in aqueous solutions containing mercerizing-strength sodium hydroxide, which swell the fibers. These comparisons were made with the control untreated fabric which was swollen in water only. Since both treated samples were preswollen before or during reaction with the modifying reagent, it appears that preswelling before modification is necessary to prevent loss of accessibility to water in the modified cottons used in these experiments. De-

creases in surface areas fell into two groups: (1) areas which were only 43% or less of the area of the control sample and (2) areas which were 70% or more of the control. The latter group was composed of (a) the two formaldehyde-crosslinked samples which were crosslinked while in formaldehyde solutions containing only water and hydrochloric acid (Form W) or water and phosphoric acid (Form P) and were dried before preparation for adsorption study; and (b) of all the samples crosslinked while in solution but not dried before sample preparation.

In the limited number of pore size distributions obtained on chemically modified samples, it appears that reaction with the cellulose results in some broadening of the pore size distribution peaks, and this is most evident in the acetylated and phosphonomethylated samples. Samples reacted with formaldehyde while in solution and not dried before sample preparation, and the sample cured by a wet-fix process showed the smallest changes in pore size distributions. Maximum change in distribution was observed in the sample which was phosphonomethylated to a D.S. of 0.14. The shape of the hysteresis curve for this sample was quite distinct from that of all the samples reported, except the sample treated with 85% phosphoric acid,¹ as shown more concisely by the graphs of the heights of the hysteresis curves given in Figures 9, 10, and 11.

Significant changes in pore size distributions were accompanied by changes in crystallinity in the phosphonomethylated and mercerized samples; however, the sample treated with 81% phosphoric acid, which had maximum increase in surface area among all samples studied and a significant broadening of the pore size distribution, showed no change in crystallinity.

Although the changes observed in electron micrographs of the cottons may be distorted by the expansion which results from the method of methacrylate embedding of the fibers, the relative patterns of the fibrillar aggregates appears to parallel findings from gas adsorption studies. Decreases in surface areas apparently result from decreased separation of the lamellae and less comminution of individual lamellae, in samples treated with polyfunctional reagents. Treatments with monofunctional reagents yield more complex fibrillar patterns. The principal pattern is one of swelling and fusion of the microfibrils within the lamellae, although disposition of lamellae is not greatly altered, in the three cottons showing decreased areas. Preliminary observations of the phosphonomethylated cotton which showed increased area shows a fibrillar structure which in part is similar to that observed in mercerized cottons. However, there was evidence of some fusion of microfibrils. This fusion was most evident in the sample with a higher degree of substitution and a decreased area.

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