

## Amine-Catalyzed Polymer Encapsulation of Cotton Fibers by Vapor Phase Application of Formaldehyde

J. C. GOSWAMI, W. BRENNER, B. RUGG, and W. LIU,  
*Department of Chemical Engineering, New York University,  
University Heights, New York, New York 10453*

### Synopsis

A process for encapsulating cotton fibers in the form of woven clothes at ambient temperatures with polyoxymethylene is described. It involves pretreatment of the cotton with a carbon tetrachloride solution of tributylamine and diphenylamine to deposit the basic catalyst on the surface of the fibers. Subsequent exposure to dry, purified vapors of monomeric formaldehyde at 25°C results in the encapsulation of individual fibers with high molecular weight polyoxymethylene. The process is relatively fast (30% fiber weight gain in approx. 20 min) with the polymer located only at the fiber surfaces. Fiber cementation does not become pronounced for weight increases below approximately 60%–65% based upon the weight of the fibers. Thickness of the polymer sheath increases with the time of the polymerization reaction. Because of the uniformity of the polymer layer deposition, the encapsulated cotton cellulose fibers can be expected to exhibit substantially different physical and chemical surface properties even at low polymer add-on. The tensile and tear strengths of the polyoxymethylene-encapsulated cotton fibers are generally improved, with some gains in abrasion resistance also noted. Differential staining techniques and polarized light microscopy have shown the location and uniformity of the polymer sheaths.

### INTRODUCTION

The treatment of cotton fibers with synthetic polymers has been extensively studied to develop composite structures which combine the advantageous properties of the polymers and the cotton cellulose and thus produce more versatile products for the consuming public. In situ polymerization of selected monomers from vapor phase application onto suitably catalyzed cotton cellulose fiber surfaces has been proposed as a practical approach for optimizing polymer coverage and contact with the cellulose substrate as well as uniformity of such coatings even at low add-ons compared to the now widely used prepolymer or polymer application methods from water, solvents, emulsions, etc. Other potential advantages for the vapor phase treatment of textile materials relate to enhanced reaction uniformity, reduction of drying costs, and water pollution problems. Also such treatments can frequently be carried out at ambient temperatures. This minimizes or avoids undesirable effects of thermal treatments which are

commonly employed for liquid phase polymer textile processing on fiber properties.

Encapsulation is defined as the complete coverage, coating, or enrobement of each individual fiber by the polymer—a process difficult if not impossible to achieve with relatively high viscosity liquid prepolymers and/or solid high molecular weight polymers. With successful encapsulation the resulting composite product should have the surface properties of the polymer and retain the shape and bulk properties of the cotton fibers. This technique should therefore offer attractive possibilities for modification of the less desirable properties of cotton, including limited durability and wash-and-wear characteristics, while maintaining the advantageous characteristics.

Encapsulation of cotton cellulose fibers with polymers is of comparatively recent interest. In 1965 Herman and co-workers<sup>9</sup> described a liquid phase process for the encapsulation of wood pulp fibers with polyethylene. Ethylene was brought in contact with precatalyzed cellulose fibers and polymerized to polyethylene which was not soluble in the reaction medium used. More recently Chanzy et al.<sup>2</sup> have discussed an ethylene encapsulation process for wood pulp fibers which was said to result in faster and more uniform polymer encapsulation. It was based on a two-component coordination catalyst system, one component of which was prepared in situ on the wood pulp fibers and completely covered their external surfaces. A similar catalyst system had previously been employed for isoprene polymerization on a surface area support.<sup>3</sup>

Vapor phase polymerization of various monomers including butadiene on surfaces has been primarily of interest for electronic insulation applications.<sup>4</sup> Specific techniques utilized include flow discharge, ultraviolet photolysis, and electron beam bombardment.<sup>5-7</sup> Also poly-*p*-xylene obtained from the pyrolysis of its dimer at about 1000°F followed by cooling the vapor below 50°C has been employed to encapsulate various materials including cellulose with a thin polymer film.<sup>8</sup>

These processes are generally carried out under quite stringent reaction conditions and require specialized and expensive equipment. They are also limited as to polymer film thickness which can be obtained within a reasonable time period. The experiments to be described below are concerned with the polymerization of gaseous formaldehyde onto suitably catalyzed cotton cellulose fibers using conventional equipment and are not subject to such limitations. The cotton fibers are physically encased with high molecular weight polyoxymethylene without the usual chemical reactions of monomeric formaldehyde or formaldehyde donors, i.e., crosslinking, with the hydroxyls of the cellulose.<sup>9</sup> Crosslinking cellulose chains with formaldehyde and/or formaldehyde donors—a technique widely used for the durable-press cotton textiles—requires elevated temperatures and strongly acidic catalysts.<sup>10</sup> The resulting serious strength and abrasion losses have at least been partially related to these reaction conditions which favor cellulose degradative processes.<sup>11</sup> The present process used alkaline

catalyst systems as proposed for the synthesis of high molecular weight polyoxymethylenes by McDonald et al.<sup>12</sup> These compositions do not deteriorate the strength of the cotton cellulose.

The thermal stability of high molecular weight polyoxymethylenes is somewhat limited because of hydroxyl endgroups which initiate depolymerization or "unzipping" reactions at elevated temperatures, with the gradual evolution of formaldehyde gas.<sup>13</sup> Improved thermal stability can be obtained by end-capping treatments which inactivate these hydroxyl groups by esterification, etherification, epoxidation, or other reactions.<sup>14</sup> Esterification with acetic anhydride is a simple yet particularly effective end-capping technique which was employed in this work to thermally stabilize the polyoxymethylene prepared in situ on the surfaces of cotton fibers. The use of difunctional anhydrides such as maleic anhydride and/or other multifunctional compounds is of interest for possible crosslinking of the cotton as well as "end capping" the polyoxymethylene polymers. Such multifunctional compounds may hopefully enhance the wrinkle recovery values with minimal deleterious effects on the physical strength properties of the polyoxymethylene-encapsulated fabrics.

## EXPERIMENTAL

### Cotton Cellulose Fabrics and Chemicals

The fabrics employed throughout this investigation were 80 × 80 de-sized, bleached, mercerized cotton print cloths (Style #400 WM) obtained from Testfabrics, Inc., New York. Fabric samples, 10 × 6 in., were cut from rolls of this cloth for use in the experiments.

Reagent-grade chemicals were employed for all the subsequently described experiments. The polymerization catalyst was prepared by dissolving 7.5 ml of tri-*n*-butylamine and 3.6 ml of diphenylamine in 1500 ml of carbon tetrachloride. The diphenylamine acted as antioxidant for this reaction. A slurry of paraformaldehyde in paraffin oil was obtained by mixing thoroughly 75 g of paraformaldehyde with 300 ml of paraffin oil in a half-liter resin kettle. Formaldehyde gas was generated by heating this slurry as described below.

### Vapor Phase Encapsulation Equipment and Process

The vapor phase encapsulation unit (Fig. 1) consisted of an 8 × 8 × 12 in. stainless steel-lined vacuum oven which acted as the polymerization chamber. This oven could be used for vacuum as well as for pressure work by using appropriate gaskets. The cloth samples were mounted on stainless steel frames which were then suspended inside the polymerization chamber from a rack, also constructed of stainless steel. A second chamber consisted of a half-liter Pyrex resin kettle which was jacketed with an electric heating mantle. This kettle contained a paraformaldehyde-paraffin oil slurry from which the formaldehyde vapors were generated by heating to 115°–120°C. The monomer was carried in dry nitrogen gas.

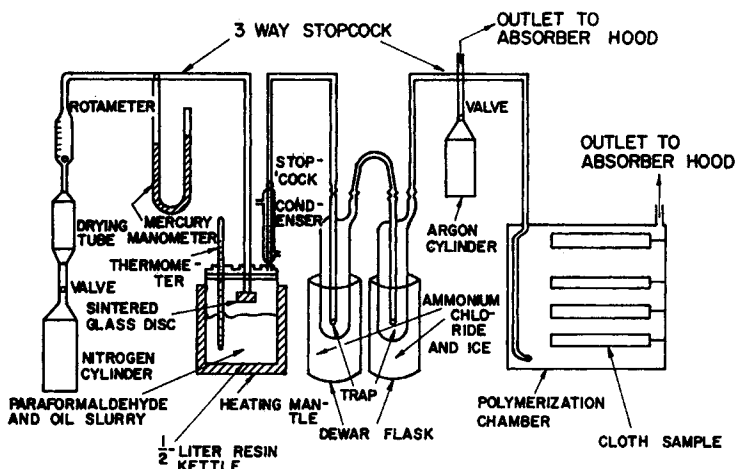


Fig. 1. Schematic diagram phase coating of cotton cloth with polyoxymethylene.

Methanol, formic acid, and water—the usual by-products from the pyrolysis of paraformaldehyde—cause undesirable premature polymerization leading to water-soluble low molecular weight polymers. Therefore, the nitrogen-formaldehyde gas stream was first passed through two traps, cooled to  $-15^{\circ}$  to  $17^{\circ}\text{C}$  by ammonium chloride and ice, to condense these by-products. Samples of  $80 \times 80$  cotton print cloth,  $10 \times 6$  in., were conditioned overnight at 65% RH and  $70^{\circ}\text{F}$  and weighed. They were then dried at  $100$ – $110^{\circ}\text{C}$  in an air-circulated oven for approximately 30 min and impregnated by immersing in the previously described catalyst solution. Next, the samples were air dried and suspended inside the polymerization chamber, which was flushed out with argon gas to displace air. The purified nitrogen-formaldehyde gas stream was directed into the chamber to cause polymerization of the formaldehyde vapor on the surfaces of the catalyst-activated cloth. The excess gaseous reagent leaving the polymerization chamber was condensed in a cold trap. A schematic drawing of the equipment is shown in Figure 1.

In this investigation, the nitrogen gas flow rate ( $0.9$  l./min), slurry temperature ( $115$ – $120^{\circ}\text{C}$ ), catalyst concentration, immersion time of the cloth samples in the catalyst solution (1 min), and polymerization chamber temperature ( $25^{\circ}\text{C}$ ) were kept constant. The exposure times of the catalyst-activated cloth samples to monomer formaldehyde vapor were varied to obtain polymer add-ons and to study the effect of the add-on on pertinent physical and chemical properties of the treated samples.

## Test Methods

### *Weight Gains and Textile Testing*

The per cent gross weight gain was determined by weighing before vapor exposure and after vapor exposure, washing for 30 min in a stream of hot

running tap water (45°–50°C), drying in a forced-air oven at 80°C for 60 min, and air-equilibrating at ambient temperature and humidity.<sup>15–18</sup> Physical strength properties of the polymer-coated cotton fabrics were measured in accordance with applicable ASTM test methods such as breaking strength, ASTM D 1682-64; Elmendorf tear strength, ASTM D 1424-63; abrasion resistance (flex), ASTM D 1175-64T; wrinkle recovery (Monsanto), ASTM D 1295-60T. For the measurement of wet wrinkle recovery values, samples were soaked with an aqueous 0.1% Triton X solution for 5 min at 150°F.

#### *Microscopical Investigations*

Microscopical studies utilized a Wild binocular light microscope (Model M-20) equipped with a built-in tungsten light source, capable of magnification of 125, 500, and 1250 $\times$ , and facilities for taking both Polaroid and 35-mm photographs. Longitudinal views of fibers were observed immersed in 2–3 drops of 1.0 *M* cupriethylenediamine solutions for 5 and 30 min under a cover glass on a microscope slide.

The absence of cellulose crosslinking or grafting in the encapsulated fibers was shown by their ready solubility in cupriethylenediamine, in which the deposited polymer was insoluble.<sup>15, 17, 18</sup>

A considerable amount of time and effort was devoted to investigations of various staining techniques to distinguish visually the polymer coating on the cotton fiber substrates. While a great number of stains were investigated, the most success was obtained with the blue dispersion dye, Setacyl Blue-2GS, conen 250%, supplied by the Geigy Chemical Co., Ardsley, New York. Staining was accomplished by placing samples of the polymer-encapsulated cloth in a water solution of this dye at pH 6.5–7.0 and heating to 200°F for approximately 1½ hr. The samples were then removed from the dye bath and washed under running water for 3–4 hr. The stained specimens were then embedded and cross-sectioned.

The embedding procedure followed was that suggested by Rohm & Haas Co., in which polymerization of *N*-butyl methacrylate monomer is catalyzed by dicumyl peroxide.<sup>19</sup> Sections 2–5 microns thick were cut with a Spencer rotary microtome equipped with a specially designed capsule holder and mounted in either glycerine or mineral oil for microscopical examination and photomicrography.

#### *Polymer Stabilization (End-Capping) and Solvent Extraction Studies*

The end-capping of the deposited polyoxymethylene was carried out by treating the polymer-coated cloth samples with acetic anhydride at 140°F for 30 min.<sup>20</sup> The anhydride-treated samples were then washed, dried, and conditioned before taking the weight measurements.

The amount of nongrafted homopolymer was determined by Soxhlet extraction of the fabric with dimethylformamide, a solvent in which the homo-

polymer but not the cellulose fiber substrate was soluble. That portion of the polymer deposit which could not be removed by repeated extractions was considered as grafted to the fiber substrate.<sup>17</sup> The following specific extraction conditions were found to be sufficient to remove homopolymer from the cloth substrates: (a) for polyoxymethylene-coated cloth samples, 2 hr; (b) for end-capped polyoxymethylene-coated cloth samples, 6 hr.

Control cloth samples were also extracted under similar conditions to determine the weight changes of the samples for comparison purposes.

### *Analysis*

Analytical studies included determination of infrared spectra, melting points, and polymer intrinsic viscosities. Polyoxymethylene and end-capped polyoxymethylene polymers were identified by taking infrared spectra of the films made of the dimethylformamide-extracted polymers. On cooling below 110°C, the extracted polymer precipitates out from the dimethylformamide solution. The precipitated polymers were filtered, washed several times with acetone and then with ether, and dried under vacuum at 50°C. Thin films were obtained by pressing a small amount of this polymer at 90°C in a laboratory press. Melting points were obtained with a Fisher-John melting point apparatus. The relative viscosity of polyoxymethylene was determined in a viscometer with a 0.5% solution of

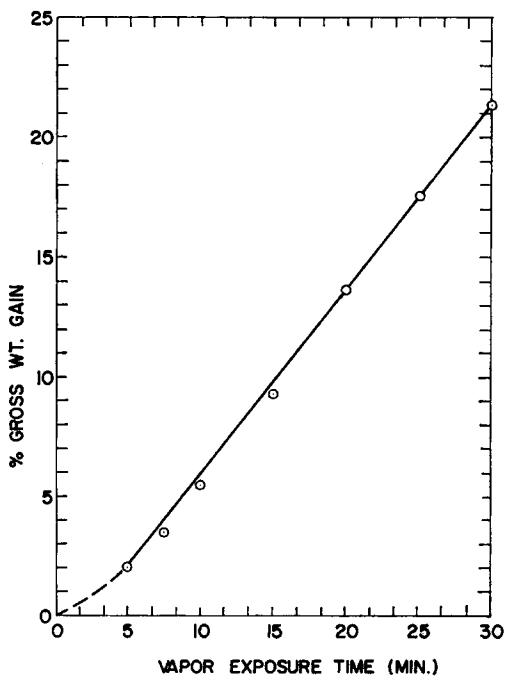


Fig. 2. Percent gross weight gain vs. vapor exposure time.

TABLE I  
Physical Properties of Polyoxymethylene-Encapsulated Cotton Cloth Samples

Sample	Weight gain, <sup>a</sup> %	Elongation, %			Breaking strength, lb <sup>b</sup>			Tearing strength, g <sup>c</sup>			Abrasion (flex) resistance, <sup>d</sup> cycles to failure	Wrinkle recovery, ° deg.			
		Warp		Fill	Warp		Fill	Warp		Fill		Dry		Wet	
		Warp	Fill	Warp	Fill	Warp	Fill	Warp	Fill	Warp		Fill	Warp	Fill	
Control	—	5.8	17.4	58.7	37.9	470	784	87	83	85	87	87	90		
#1-C <sup>f</sup>	—	8.5	20.1	63.4	34.0	578	870	74	100	100	100	97	98		
#2-C	2.0	8.0	20.8	60.6	39.9	588	908	90	89	97	89	96	91		
#3-C	5.5	7.4	20.9	60.1	39.9	590	902	119	80	94	80	70	70		
#4-C	9.3	7.4	20.3	56.6	39.0	552	904	106	97	98	97	70	66		
#5-C	14.7	7.1	19.1	61.5	38.0	540	892	153	58	70	58	66	65		
#6-C	24.0	6.3	16.3	66.2	41.1	432	850	194	27	29	27	66	71		

<sup>a</sup> Average value of 8 samples. Encapsulated samples were treated with acetic anhydride at 140°C for 30 min.

<sup>b</sup> Average value of 5 runs.

<sup>c</sup> Average value of 4 runs.

<sup>d</sup> Average value of 3 runs.

<sup>e</sup> Average value of 3 runs.

<sup>f</sup> Sample #1-C is control treated with acetic anhydride at 140°C for 30 min. Sample did not gain any weight.

polyoxymethylene at 60°C in *p*-chlorophenol containing 2% by weight alpha-pinene.<sup>12</sup> It was used to calculate the inherent viscosity in accordance with a previously developed equation.<sup>12,21</sup> The number-average molecular weight of the polyoxymethylene was then obtained from the following relationship:

$$\text{inherent viscosity} = 3.82 \times 10^{-4} \bar{M}_n^{0.83}$$

## RESULTS AND DISCUSSION

Experimental investigations of the amine-catalyzed polymer encapsulation of cotton fabrics by vapor phase application of formaldehyde ranged from the establishment of suitable experimental conditions for such polymerizations to characterization of the resulting polymer deposits and measurements of selected physical properties of polyoxymethylene-coated cotton fabrics. Typical vapor phase polymerization data are plotted in Figure 2. Selected physical test data on the polyoxymethylene-treated cotton fabrics are shown in Table I. Photomicrographs (longitudinal view) of polyoxymethylene-coated cloth samples treated with cupriethylene-diamine solvent are presented in Figures 3 and 4. Figure 5 shows photomicrographs prepared from 35-mm slides of stained and cross-sectioned samples (12%–22% weight gain) of polyoxymethylene-coated cloth. Typical infrared spectra of polyoxymethylene and end-capped polyoxymethylene polymers are given in Figures 6 and 7, respectively.

With all other variables fixed (e.g., monomer concentration, polymerization reaction temperature, catalyst concentration), the per cent gross weight gains indicative of amount of polyoxymethylene deposition increase as the vapor exposure times are lengthened. Except for the initial reaction period, the plot of per cent gross weight gain versus the vapor exposure time is a straight line. Figure 2 indicates the existence of an induction period during the initial few minutes as has previously been noted in the polymerization of aldehydes.<sup>22</sup>

The dimethylformamide extraction studies show complete removal of the polyoxymethylene from the cloth substrates within 2 hr. Similarly, the end-capped polyoxymethylene can also be removed when subjected to such dimethylformamide solvent extraction, although a longer extraction period (6 hr) is needed to completely remove it from the cloth substrates. These studies, therefore, indicate the absence of cellulose grafting or cross-linking with polyoxymethylene or end-capped polyoxymethylene.

The photomicrographs shown in Figures 3 and 4 furnish particularly useful information as to the character of the polymer deposits. The fiber samples shown in these photomicrographs were prepared by exposure of the fiber specimens to cupriethylenediamine solution for 5 min and 30 min. The immersion time of the polymer-encapsulated cloth in the cellulose solvent must be long enough to assure complete dissolution of cellulose. This required generally around 30 min at ambient temperatures. Some undissolved cellulose remains after 5–10 min immersion.



Figure 3a at 62.5 $\times$  shows polymer shells or tubes of a sample with 6.2% gross weight gain after treatment with cupriethylenediamine solvent for only 5 min. Some undissolved cellulose can be seen. In Figure 3b complete dissolution of cellulose has occurred (after 30 min immersion time in the cellulose solvent). Figures 3c and 3d at 250 $\times$  show quite uniform and transparent polymer tubes. Figure 4 can be interpreted similarly. Apparently as the per cent gross weight gain of cloth samples increases, random clumps or "dendrites" begin to form with increasing frequency, and the polymer tubes are no longer smooth as a result of this irregular growth.

Similar photomicrographs can be obtained by treating end-capped polyoxymethylene-encapsulated cloth samples with cupriethylenediamine solvent; they have been omitted here to avoid repetition. The complete solubility of cellulose after treatment with cupriethylenediamine solvent, leaving undissolved polyoxymethylene shells or tubes, as well as the dissolution of that polymer from the cloth substrates by immersion in dimethylformamide solvent show that neither cellulose grafting nor cross-linking have occurred.<sup>15, 17, 18</sup>

Figures 5a and 5b are selected photomicrographs prepared from 35-mm slides of stained and cross-sectioned samples of from 12 to 22 wt% polymer-containing polyoxymethylene-encapsulated cloth samples. The dark shaded portions locate the dye-stained polymer deposits in these pictures.

Figures 5a and 5b show two fiber cross-sections with the dye-stained polymer deposits around the fibers. Heavier coatings prevent the dye from penetrating to the inner core of the yarn. As a result, no staining of the fibers on the inner core occurs.

A study of various test data summarized in Table I shows that the physical properties such as breaking strength and elongation, tearing strength, and abrasion resistance can be enhanced by the vapor phase encapsulation of cotton cloth samples with polyoxymethylene. The dry wrinkle recovery values are relatively unaffected to a gross weight gain of about 9.3%. Thereafter, as the weight gain increases, the wrinkle recovery values begin to decrease. Similar effects are noted with the wet recovery values. Abrasion resistance increases considerably as the weight gains increase. The per cent gross weight gains do not seem to exert too much influence on the breaking and the tearing strengths, nevertheless, these values are improved compared to the control values.

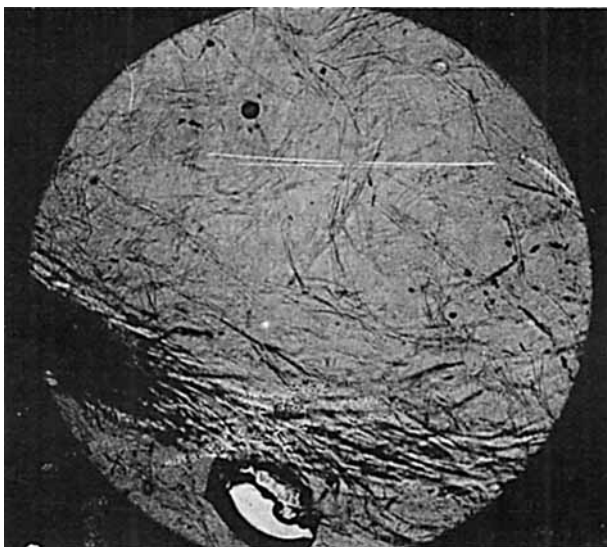
The melting points of polyoxymethylene and end-capped polyoxymethylene are the same (165°C). The molecular weight of polyoxymethylene, calculated from the inherent viscosity (0.865), is approximately 11,000.

Figure 6 shows the infrared spectrum of polyoxymethylene film. The absorption bands at 2.9 microns (characteristic of OH bond), 3.4 microns (where C—H is known to absorb), and 9.2 and 10.7 microns (where C—C bonds absorb) are characteristic of polyoxymethylene.<sup>23</sup> Figure 7 is the infrared spectrum of end-capped polyoxymethylene. The absorption band at 2.9 microns, which is attributed to OH, disappears and is replaced by an absorption band at 5.75 microns, which is due to the presence of the

C=O groups. These C=O groups are introduced into the end-capped polyoxymethylene by esterification of the terminal OH groups of polyoxymethylene with acetic anhydride. The bands on Figure 7 match those of Delrin.<sup>24</sup>

### SUMMARY AND CONCLUSIONS

A novel, reproducible, and effective method has been developed for the encapsulation of cotton fiber cloth samples with polyoxymethylene by vapor phase application. Thermal stabilization of the hydroxyl end-groups of the polyoxymethylene homopolymer has been effected by treat-

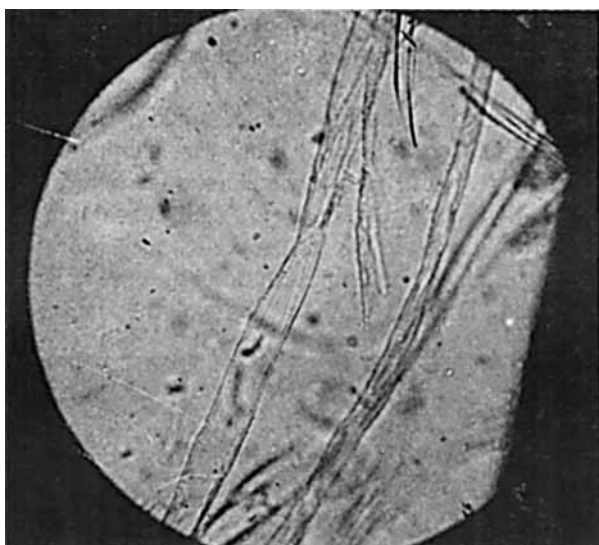


(a)

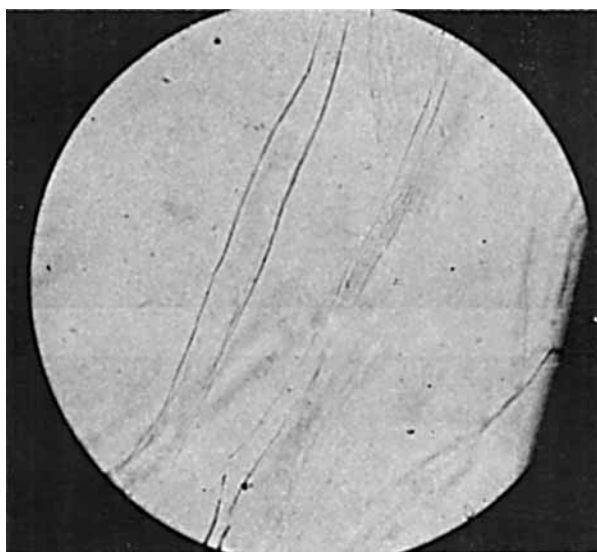


(b)

Fig. 3 (continued)



(c)



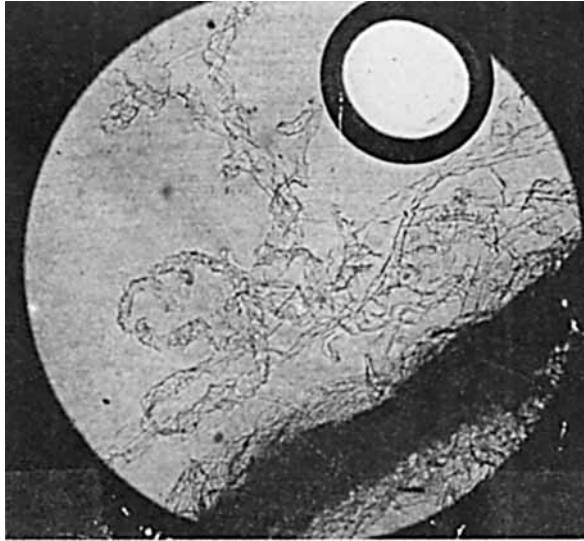
(d)

Fig. 3. Polyoxymethylene-coated cotton fibers: effect of immersion in cupriethylene-diamine solvent (longitudinal view). (a) 6.2% gross wt. gain, 62.5X; (b) 6.2% gross wt. gain, 62.5X; (c) 6.2% gross wt. gain, 250X; (d) 6.2% gross wt. gain, 250X.

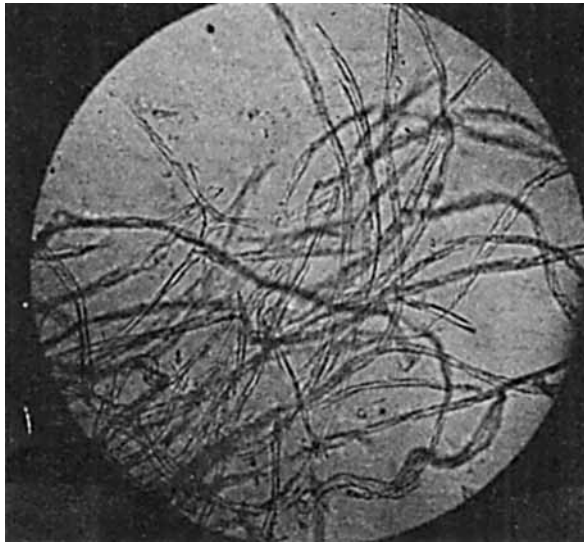
ment with acetic anhydride, a procedure previously described as "end capping." This reaction does not change the strength properties of the encapsulated fabrics. Information on growth characteristics of polymer and degree of uniformity of polymer coatings can be obtained from a study of the photomicrographs. Typically, the polymer has a melting point of 165°C and a number-average molecular weight of approximately 11,000. In sharp contrast to the acid-catalyzed formaldehyde processes<sup>18, 25-29</sup> con-

ventionally employed, the method developed in this investigation is unique in that it considerably *increases* the physical strength properties of cotton fabrics.

Acid-catalyzed reactions involving the crosslinking of cotton with formaldehyde or reactive derivatives thereof enhance shape-holding characteristics as indicated by wrinkle recovery values. However, due to the employment of strongly acid catalysts and high reaction temperatures ( $>120^{\circ}\text{C}$ ), the cotton physical strength properties such as breaking strength, elongation, tearing strength, and abrasion resistance are severely decreased. The base-catalyzed ambient-temperature polymerization process de-



(a)

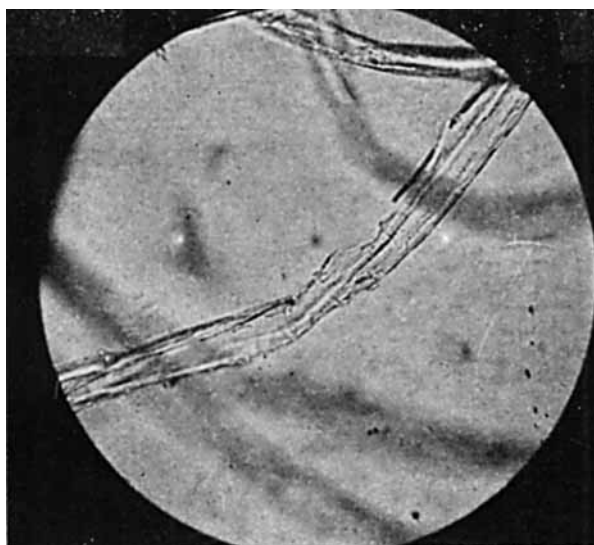


(b)

Fig. 4 (continued)



(c)



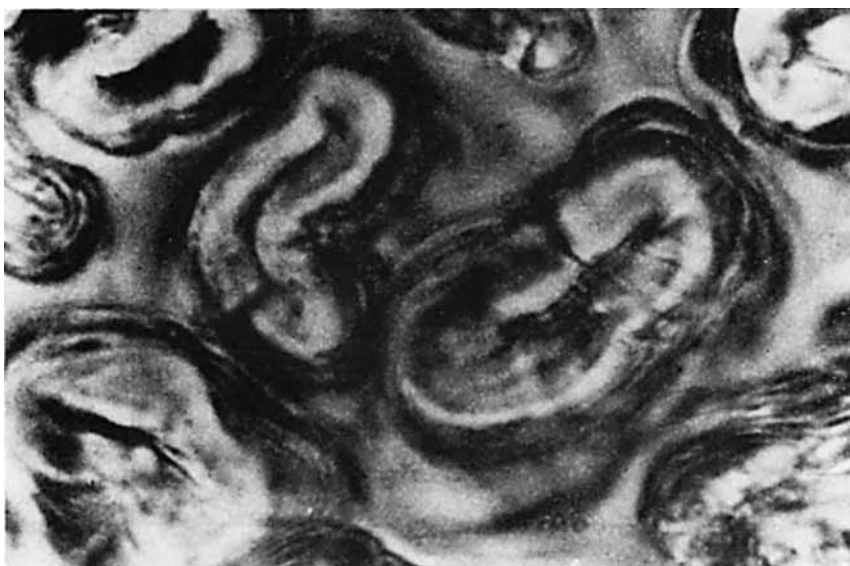
(d)

Fig. 4. Polyoxymethylene-coated cotton fibers: effect of immersion in cupriethylenediamine solvent (longitudinal view). (a) 38.3% gross wt. gain, 62.5 $\times$ ; (b) 38.3% gross wt. gain, 62.5 $\times$ ; (c) 38.3% gross wt. gain, 250 $\times$ ; (d) 38.3% gross wt. gain, 250 $\times$ .

scribed only coats the fiber surfaces and does not involve cellulose cross-linking or grafting. The retention and improvement of the physical strength properties of the encapsulated cottons are attributed to the intrinsic properties of high molecular weight polyoxymethylene in conjunction with the use of relatively mild reaction conditions which apparently do not degrade the cotton substrate. Shape-holding characteristics remain



(a)



(b)

Fig. 5. Cross sections of polyoxymethylene-coated cotton; polymer stained with Geigy dispersion dye (Setacyl Blue-2 GS, concn. 250%). (a) 12% gross wt. gain, 1900 $\times$ ; (b) 22% gross wt. gain, 1900 $\times$ .

essentially unchanged, however, as might be expected. Reaction of the polyoxymethylene-coated cotton fabrics with multifunctional anhydrides or other reagents in place of the acetic anhydride is proposed for enhancing their shape-holding properties by effecting crosslinking of the cellulose as well as end-capping of the polyoxymethylene.

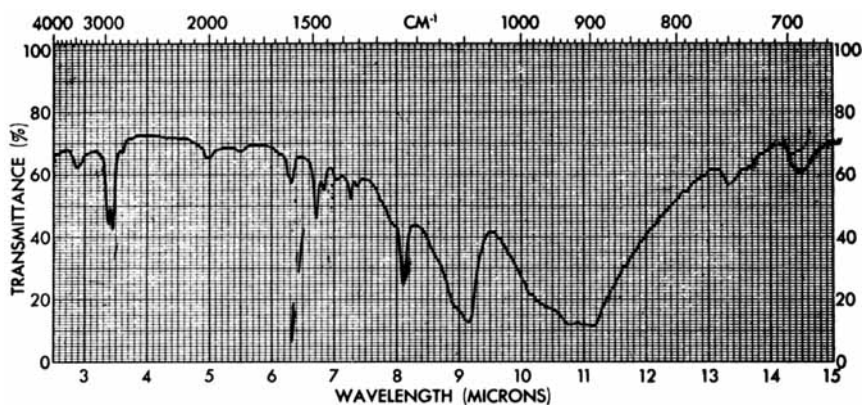


Fig. 6. Infrared spectrum of polyoxymethylene film.

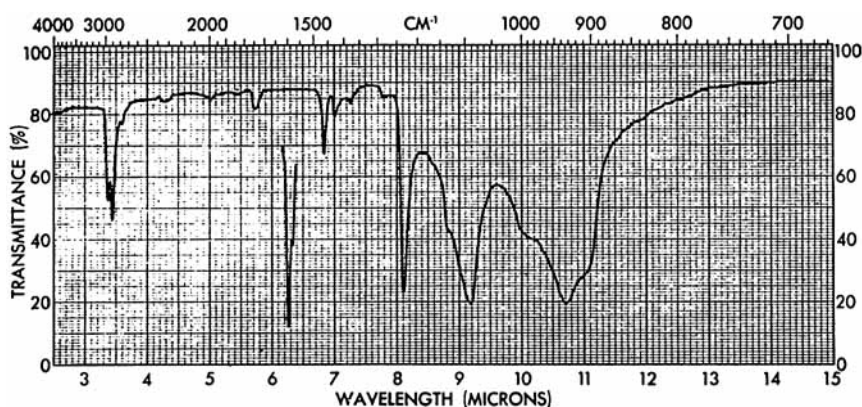


Fig. 7. Infrared spectrum of end-capped polyoxymethylene film.

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