

Grafting of Cyclic Carbonates onto Cotton and Modified Cottons

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Synopsis

Cyclic carbonates react with amines to form carbamates, with alcohols to form hydroxyalkylated products, and with dibasic acids or dibasic acids plus a glycol to form polyesters. These types of reactions between ethylene, propylene, or glycerine carbonate and cotton, either unmodified or modified to contain amine or carboxyl groups, were investigated. Effects of method of application, temperature, time of reaction, and pressure were studied. Temperature in excess of 100°C and reduced pressures were satisfactory for removing the water formed. Reaction between cyclic carbonates, dibasic acids, a glycol, and nonaqueously prepared carboxymethylated cotton in a vacuum oven yielded a fabric with conditioned and wet wrinkle recovery of approximately 300(W + F)%. Infrared spectra, wrinkle recovery, and weight gain indicated that crosslinks formed in reactions between unmodified or carboxymethylated cotton and the cyclic carbonate. Reactions with aminized or diethylaminoethylated cotton formed terminal grafts.

INTRODUCTION

Selected cyclic carbonates react with alcohols and polyols to form hydroxyethylated or hydroxypropylated ethers,¹⁻³ with amines to form hydroxyethyl or hydroxypropyl carbamates,⁴⁻¹⁰ with dibasic acids to form polyesters,¹¹⁻¹³ and with a combination of dibasic acid and glycol to form copolyesters.¹³ This is a report of the use of cotton cellulose in its unmodified form as the alcohol or glycol and its use as the amine or acid reactant after its modification to an aminized or carboxymethylated cotton. The objectives were to improve fabric properties of cotton by either grafting linear polymers to cellulose chains or crosslinking the cellulose chains by reactions of the cyclic carbonates with hydroxyl, amine, or carboxyl groups within the cellulose matrix.

EXPERIMENTAL

Materials

Reagents. The colorless, noncorrosive, and nontoxic ethylene carbonate, propylene carbonate, and glycerine carbonate were used as obtained commercially from the Jefferson Chemical Company, Inc. Propylene and glycerine carbonates are liquid at room temperature, but ethylene carbonate melts at 36°C. Propylene and ethylene carbonates boil at about 240°C, whereas glycerine car-

bonate decomposes at temperatures above 125°C. Diethylene glycol was technical grade. Malonic acid was reagent grade.

Fabrics. 80 × 80 Cotton printcloth, approximately 3.12 oz/yd², that had been desized, scoured, and peroxide bleached was used. This fabric was used either unmodified or was converted into carboxymethyl (CM), aminoethyl (AM), or diethylaminoethyl (DEAE) cotton. Most experiments were conducted with samples measuring 6 × 12 in. and weighing approximately 5 g. Details of the preparation of CM cotton by aqueous¹⁴ and nonaqueous¹⁵ methods and of the preparation of DEAE cotton by a modification¹⁶ of the Hartmann method¹⁷ have been reported. AM cotton was prepared by the method of Guthrie.¹⁸

Modification of Fabrics with Cyclic Carbonates

Reaction between fabric and reagent took place in an oven operated at either atmospheric or reduced pressure. Reagent mixtures were prepared immediately prior to contact with the fabrics which were then immersed in reagent or padded to 100% take-up of reagent. Reactions in solution took place with fabric immersed flat in solution. Padded fabric samples were suspended vertically in the oven for reaction. In each case, the oven was preheated and the reaction was timed, beginning when the sample was placed in the oven. At the conclusion of the reaction, samples were immediately removed from the oven and thoroughly washed with water. Samples were dried and equilibrated for 24 hr before testing.

Analyses of Fabrics

The carboxyl contents of CM cottons were determined by a back-titration method,¹⁹ and the average number of substituents per anhydroglucose unit (D.S.) was calculated.

Nitrogen contents of cottons modified to contain amine groups were determined by the Kjeldahl method and reported as meq N/g of fabric. D.S. values based on nitrogen analyses were calculated.

Conditioned (dry) wrinkle recovery angles were determined by an ASTM standard test,²⁰ and wet recovery angles were determined as described previously.²¹ Infrared (IR) spectra were made by the KBr disc method²² on a Perkin-Elmer 21 infrared spectrophotometer.

Information concerning crosslinks was obtained from ultrathin cross sections of fibers removed from the finished fabrics and subjected to layer expansion in polymerized methyl methacrylate.²³ Scanning electron microscopy techniques used are described in the literature.²⁴

RESULTS AND DISCUSSION

Figure 1 is a summation of our proposed scheme of possible reactions between cellulose and ethylene carbonate (A), ethylene glycol (B), and/or a dibasic acid (C). Under conditions of our reaction, cellulose acts as the nucleophile, and the other reagent, after loss of CO₂ or H₂O, acts as the electrophile. After the initial reaction, either A, B, or C can act as nucleophile or electrophile. The product varies depending on which materials are present, the extent to which they react, and whether or not glycol is a byproduct.

TABLE I
Wrinkle Recovery of Cotton Reacted with Propylene Carbonate Solutions^a

Carbonate	Composition of solution, g			Wrinkle recovery, (W+F) ^o	
	Diethylene glycol	Malonic acid	K ₂ CO ₃	Conditioned	Wet
Control	—	—	—	181	182
100	—	—	—	180	172
100	—	—	0.5	170	176
50	50	—	0.5	185	173
50	50	1	—	215	200
50	50	5	—	210	198
100	—	1	—	200	205

^a 80 × 80 Printcloth padded with a solution of indicated composition, heated in an oven at atmospheric pressure at 180°C for 60 min.

Results from reactions between unmodified cotton and propylene carbonate, diethylene glycol, and dibasic acid at atmospheric pressure are summarized in Table I. Propylene carbonate, either alone, with K₂CO₃, or with diethylene glycol, had little effect on conditioned wrinkle recovery. There was some increase when dibasic acid was present, but there was no advantage in using 5% dibasic acid. Malonic acid was used because it was found to be the most soluble of those tried. Best results were obtained when the glycol, dibasic acid, and propylene carbonate were all present. A 3-hr reaction in solution produced about the same effect as did 1 hr of heating a fabric that had been padded with the solution. Weight gains for reactions with unmodified cotton were very low (0% to 0.2%) in every case.

High temperatures discolored the fabric, and considerable water generated by heating of the glycol and dibasic acid was removed with vacuum. Data in Table II show that 35 mm vacuum was effective for all three carbonates.

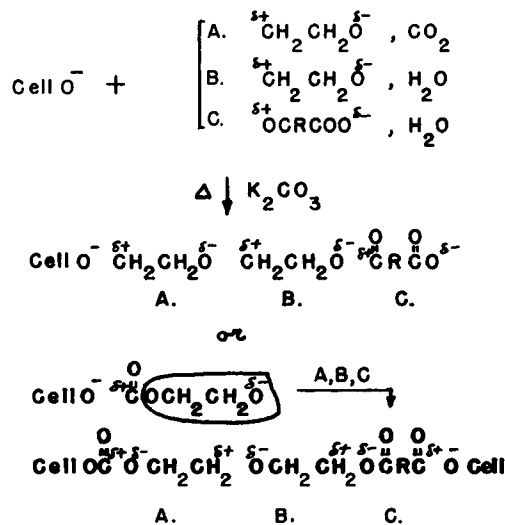


Fig. 1. Schematic of reactions between cotton cellulose and (A) ethylene carbonate, (B) ethylene glycol, and/or (C) dibasic acid.

TABLE II
Wrinkle Recovery of Cottons Treated with Cyclic Carbonates Under Vacuum^a

Cyclic carbonate	Time of cure, min	Wrinkle recovery, (W+F) ^o	
		Conditioned	Wet
Control	—	181	182
Propylene	60	241	201
Propylene ^b	60	220	200
Propylene	30	215	195
Propylene	120	238	210
Ethylene	60	235	210
Glycerol	60	231	218

^a 80 × 80 Cotton printcloth padded to 100% wet pickup with solution of a cyclic carbonate, diethylene glycol, and malonic acid at a 50/50/1 ratio (weight) and dried at 180°C for indicated time in an oven at 35 mm Hg pressure.

^b 160°C Cure.

Figure 2 compares IR spectra of unmodified cotton and cotton modified under vacuum with a mixture of propylene carbonate, diethylene glycol, and malonic acid. The band at 5.8 μ is typical of ester groups and is expected whenever crosslinks or terminated chains are formed. However, the increased dry recovery with negligible weight gain indicates crosslinks. Between cellulose chains, crosslinks, even at very low add-ons, increase the conditioned wrinkle recovery values. Grafted, terminated straight chains can also increase wrinkle recovery, but the effect is not so pronounced as with crosslinking and usually is associated with rather large add-ons.²⁵

Figure 3 outlines our proposed scheme of reactions between CM cellulose and a mixture of ethylene carbonate (A), ethylene glycol (B), and/or a dibasic acid (C). As with unmodified cotton cellulose (Fig. 1), CM cotton can react to form either terminated linear grafts or crosslinks. The CM cotton was prepared by either an aqueous or by a nonaqueous procedure. The material prepared by the aqueous process was treated with mineral acid to obtain the acid form, whereas that prepared by the nonaqueous process was already in the acid form.

Various combinations of propylene carbonate and the other reactants improved the dry wrinkle recovery of CM cotton, with the mixture of the carbonate,

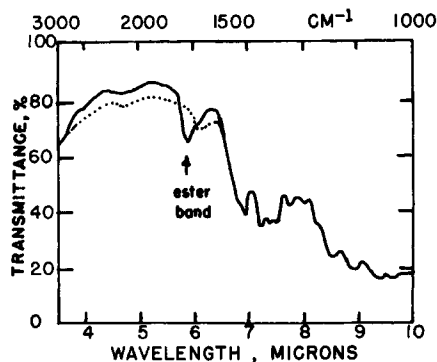


Fig. 2. IR spectrum of cotton treated with a solution of propylene carbonate, diethylene glycol, and malonic acid and cured *in vacuo* (dotted line is spectrum of unmodified cotton control).

TABLE III
Effect of Propylene Carbonate Solutions on Wrinkle Recovery
of Carboxymethylated Cotton^a

Carbonate	Composition of solution, g			Wrinkle recovery, (W+F) ^o	
	Diethylene glycol	Malonic acid	K ₂ CO ₃	Conditioned	Wet
Control	—	—	—	181	175
100	—	—	—	204	190
100	—	—	0.5	232	213
50	50	—	0.5	236	220
50	50	1	—	242	237
50	50	5	—	248	229
100	—	1	—	230	222

^a Carboxymethylated cotton (prepared in aqueous solution from 80 × 80 printcloth reacted to a D.S. of 0.03) padded to 100% wet pickup with a solution of indicated composition and then cured at atmospheric pressure at 180°C for 1 hr.

glycol, and dibasic acid (Table III) having a slight advantage. Reaction in solution did not work as well as the padding method and resulted in lower wrinkle recoveries in the conditioned state.

The reaction of CM cotton proceeded better in an evacuated oven than at atmospheric pressure (Table IV). A higher temperature for a longer period increased the wrinkle recovery, but yielded a tan rather than a white product. Neither glycerine nor ethylene carbonate was as effective as propylene carbonate. A relatively short time at 200°C produced high conditioned recovery, but the product was brown. Although only slightly better, a mixture containing carbonate, glycol, and dibasic acid is preferable for reaction with aqueous CM cotton, and a cure temperature of 180°C is about as high as can be used without discoloration of the cellulose.

Table V presents the results of reactions at atmospheric conditions with nonaqueously prepared CM cotton. With the nonaqueous CM cotton, propylene

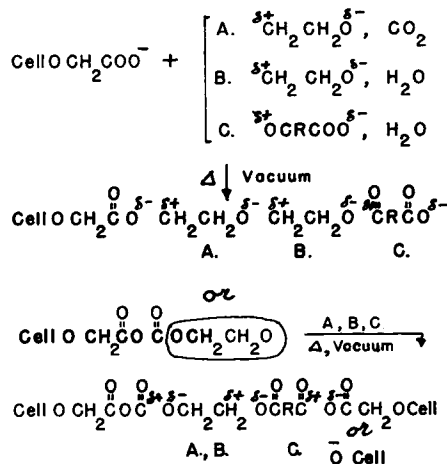


Fig. 3. Schematic of reactions between carboxymethylated cotton and (A) a cyclic carbonate, (B) glycol, and/or (C) dibasic acid.

TABLE IV
Effect of Cyclic Carbonates on Wrinkle Recoveries of Carboxymethylated
Cottons Cured Under Vacuum^a

Cyclic carbonate	Temp., °C	Cure time, min	Wrinkle recovery, (W+F) ^o	
			Conditioned	Wet
Control	—	—	181	175
Propylene	160	60	246	210
Propylene	180	60	251	235
Propylene	200	60	280	214
Propylene	180	30	225	195
Propylene	180	120	260	231
Ethylene	180	60	216	200
Glycerol	180	60	212	208

^a Carboxymethylated cotton (prepared in aqueous solution from 80 × 80 cotton printcloth to a D.S. of 0.03) padded to 100% wet pickup with a solution of 50/50/1 ratio of cyclic carbonate/diethylene glycol/malonic acid and then cured under 35 mm Hg pressure.

carbonate alone produces excellent wrinkle recovery even at atmospheric pressure. Dry recoveries were about the same as for the aqueous CM cotton. The wet recoveries were all high because nonaqueously prepared CM cotton has a high wet recovery that is not altered by the reaction with the cyclic carbonate. Under vacuum, the mixture of propylene carbonate, glycol, and dibasic acid reacted with the nonaqueously prepared CM cotton to produce a white fabric with both high dry (291) and high wet (285) recovery instead of the tan or brown colors obtained with the aqueously prepared CM cottons.

Figure 4 compares IR spectra of CM cotton before and after its reaction with a mixture of propylene carbonate, diethylene glycol, and malonic acid. Reaction decreased the absorption band at 5.8 μ ascribed to the carboxyl group and increased the band at 6.2 μ . Soignet et al.²⁶ found that CM cotton reacted with other materials showed this effect. It seems, then, that improvement in dry

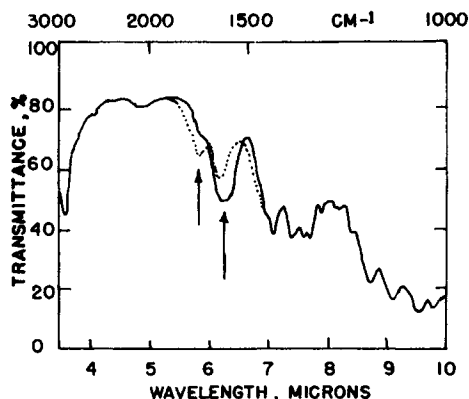


Fig. 4. IR spectrum of carboxymethylated (CM) cotton treated with a solution of malonic acid in propylene carbonate and diethylene glycol and cured *in vacuo* (dotted line is spectrum of control CM cotton).

TABLE V
Effect of Propylene Carbonate Solutions on Nonaqueous Carboxymethylated Cotton^a

Carbonate	Composition of solution, g		Wrinkle recovery, (W+F) ^o	
	Diethylene glycol	Malonic acid	Conditioned	Wet
		D.S. = 0.3		
Control	—	—	202	281
100	—	—	248	288
50	50	—	237	288
50	50	1	241	285
100	—	1	229	278
		D.S. = 0.1		
Control	—	—	213	252
100	—	—	246	261
50	50	—	239	264
50	50	1	233	270
100	—	1	214	261

^a Carboxymethylated cottons of indicated D.S. padded with solutions of indicated compositions to 100% pickup and heated in an oven at 160°C for 30 min at atmospheric pressure.

wrinkle recovery with only 0.2% weight gain is due to crosslinks, and IR spectra indicate addition at the carboxyl group.

Figure 5 shows how AM cotton, which is structurally a primary amine, may react with cyclic carbonates to form a hydroxyethyl carbamate which may lose ethylene glycol, leaving it free to react with either another amine group or a cellulosic hydroxyl group. Two products are shown, depending on whether the hydroxyethyl carbamate intermediate crosslinks to another amine group or to a cellulosic hydroxyl group. Either would produce crosslinks and improve dry wrinkle recovery, but the urethane IR spectra should show an amide band, whereas the urea structure would not.

Table VI gives results of reacting AM cotton with propylene carbonate under different conditions. AM cotton showed more tendency to turn yellow, so lower temperatures were used. With weight gains of 1.3% to 1.8%, dry wrinkle recoveries increased considerably, indicating crosslinks. These large increases, ob-

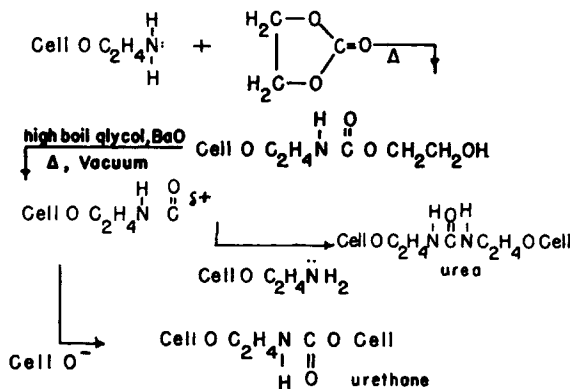


Fig. 5. Schematic of reactions between aminoethylated cotton and a cyclic carbonate.

TABLE VI
Wrinkle Recovery of Aminoethylated Cotton Treated with
Propylene Carbonate Under Vacuum^a

Reaction conditions	Cure time, min	Wrinkle recovery, (W+F) ^o	
		Conditioned	Wet
Control	—	95	264
Neat propylene carbonate	60	118	267
Neat propylene carbonate	180	157	266
2% K ₂ CO ₃ in propylene carbonate	180	170	281
Prepadded 2% K ₂ CO ₃ in H ₂ O, dried	180	165	266

^a Aminoethylated cotton of D.S. = 0.06 padded to 100% wet pickup with propylene carbonate, cured at 140°C and 35 mm Hg pressure.

served with only the cyclic carbonate, indicate crosslinking. The hydroxyethylated carbamate, however, would be the expected product. When this cyclic carbonate-treated aminoethylated fabric was allowed to react in the presence of barium oxide or zinc borate, dry wrinkle recoveries of 115(W + F)^o and 106(W + F)^o, respectively, were obtained. Wrinkle recovery was lower with barium oxide, which was expected to result in crosslinks and higher dry wrinkle recovery, than when the carbonate was catalyzed by the amine group only.

The IR spectra for the AM cotton, before and after its treatment with the propylene carbonate and with propylene carbonate and barium oxide, are compared in Figure 6. Use of barium oxide broadened the band around 6.2 μ , indicating an amide structure. Such a structure is possible with the crosslinked urethane and also with the terminated hydroxyethylated carbamate. The small increase in wrinkle recovery suggests the latter product. The IR curve of reaction product formed without barium oxide shows a change in absorbance where the amide band (6.1) and the urethane band (5.95) are located, which indicates a mixture of urethane crosslinks and hydroxyethyl carbamate linear groups. A

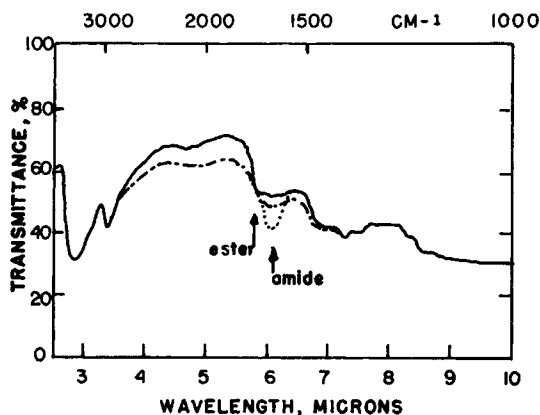


Fig. 6. IR spectra of aminized cotton before (—) and after its modification with propylene carbonate in the absence (····) and presence (- - - - -) of barium oxide.

TABLE VII
Wrinkle Recovery of Diethylaminoethylated Cotton Treated
with Propylene Carbonate^a

Cure temp., °C	Cure time, min	Pressure, mm Hg	Wrinkle recovery, (W+F) ^o	
			Conditioned	Wet
Control	—	—	181	182
140	30	760	193	199
140	60	760	198	187
160	30	760	215	242
160	120	35	217	265

^a Diethylaminoethylated cotton of 0.85% nitrogen padded to 100% wet pickup with propylene carbonate.

mixture of products would explain the large weight gain with moderate increase in wrinkle recovery.

DEAE cotton and AM cotton would be expected to react similarly to produce two possible crosslinked products and the carbamate intermediate (Fig. 7). As with AM cotton, both the intermediate and the product with urethane crosslinks have amide groups.

Table VII presents results of these reactions with DEAE cotton. At atmospheric pressure and 140°C, there was little, if any, reaction with propylene carbonate as indicated by wrinkle recovery. Reaction increased somewhat at 160°C. Use of vacuum improved only wet recovery. Reactivity with the tertiary amine groups of DEAE cotton was less vigorous than it was with AM cotton. When the barium oxide was used as catalyst, there was some increased reaction; dry recovery went from 217 to 228. Zinc borate does not work as well as barium oxide. Weight gains for DEAE cotton treated with propylene carbonate ranged from 0.5% to 0.9%, but averaged about 0.8%.

The IR spectra for DEAE cotton exhibited a small shift toward a lower wavelength in the area of an amide (6.1) or urethane (5.95), just as it did with

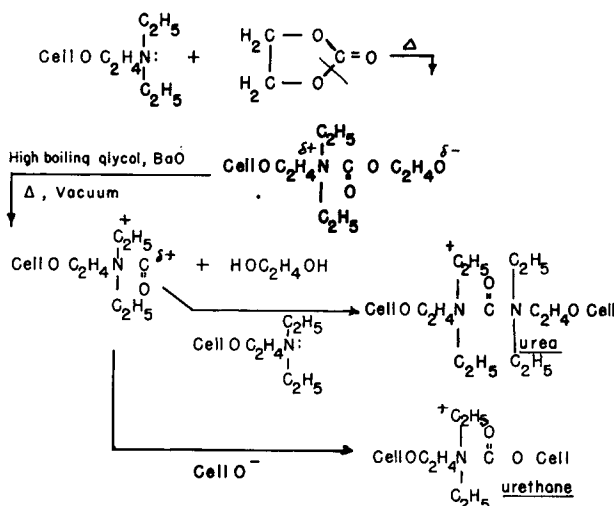
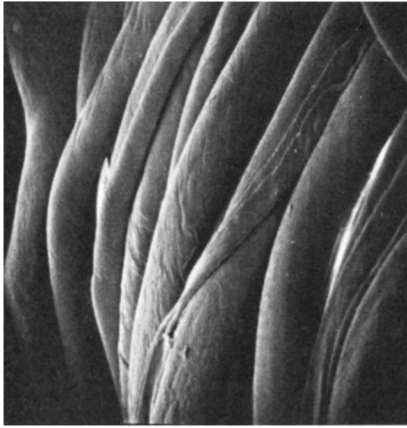


Fig. 7. Schematics of reactions between diethylaminoethylated cotton and a cyclic carbonate.



COTTON



CARBOXYMETHYL-COTTON

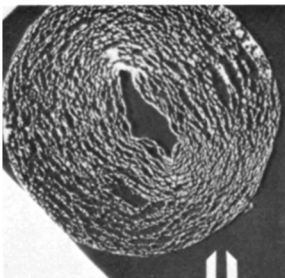


AMINOETHYL-COTTON

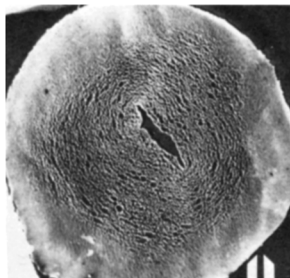


DEAE - COTTON

Fig. 8. Scanning electron micrographs (1000X) of cotton and chemically modified cotton fabrics after treatments with propylene carbonate.



A



B



C

Fig. 9. Electron micrographs of methyl methacrylate expansion patterns of ultrathin cross sections of fibers removed from (A) CM cotton; (B) CM cotton reacted in vacuum with propylene carbonate, glycol, malonic acid; and (C) CM cotton reacted as in (B) and dissolved in 0.5M cupriethylenediamine.

AM cotton reacted with propylene carbonate. The increase in wrinkle recovery was not large enough to indicate crosslinks; this observation, together with the weight gain, suggests that the intermediates are hydroxyethylated carbamates.

The scanning electron photomicrographs in Figure 8 show that both unmodified cotton and CM cotton, after treatments with the cyclic propylene carbonate, exhibit essentially smooth surfaces with no coating or particles indicative of polymer formation. These smooth surfaces, small weight gains, and increased wrinkle recoveries indicate crosslinking. After reaction, DEAE and AM cottons appeared dull and had particles adhering to them. The larger weight gains, deposits on surfaces, and modest improvement in wrinkle recoveries indicate terminated linear chains coating fibers of the DEAE cottons.

Differences in solubility in cupriethylenediamine (cuene) of fibers removed from the various treated fabrics were studied. Ultrathin cross sections of fibers were also examined by the layer expansion technique to detect extent of crosslinking, if any. In Figure 9A, the photomicrograph showing layering of the CM cotton is not unlike that of an untreated cotton, which also undergoes layer expansion throughout the cross section. Photomicrograph 9B, typical of a CM cotton after its reaction with the cyclic carbonates, shows layering at the core and no layering toward the periphery of the fiber. After immersion in cuene, the inner part dissolves and the outermost part of the fiber is insoluble as shown in photomicrograph 9C. From such observations, it was concluded that crosslinking of cellulose chains in CM cottons by cyclic carbonates occurred on outermost surfaces of the fibers and prevented their layering in methyl methacrylate and solubility in cuene. In contrast, all fibers removed from DEAE, AM, or unmodified cottons reacted with cyclic carbonate layered throughout the cross sections and all were soluble in cuene, indicating little or no crosslinking of cellulose chains.

Other means of promoting reaction and removing the water at atmospheric pressure were tried. Reaction in vapor, reaction between glass plates, dipping in a boiling reagent, use of nitrogen as a sweep gas, and ironing were less satisfactory than the vacuum oven procedure.

SUMMARY

Cyclic carbonates reacted with unmodified, carboxymethylated, aminized, and diethylaminoethylated cottons. Reaction occurred within 1 hr at 180°C, and reduced pressure favored reactivity. The small weight gains, accompanied by large increases in wrinkle recovery, smooth surfaces, and ester bands in the IR spectra, indicate crosslinks in unmodified and CM cottons after treatment with cyclic carbonates.

In contrast, aminized and DEAE cottons showed large weight gains, variable gains in wrinkle recovery, dull surfaces with irregular deposits, and IR amide group bands. Such data indicate chiefly terminated linear grafts that coated fabric surfaces rather than crosslinks.

Excellent conditioned and wet wrinkle recoveries were obtained by reacting nonaqueously prepared CM cotton with propylene carbonate, diethylene glycol, and malonic acid at 180°C for 60 min at 35 mm Hg in a vacuum oven.

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