

Diethylaminoethyl Cellulose-Anhydride Reactions*

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Synopsis

Tertiary amine groups of diethylaminoethyl cotton are internal catalysts for the reaction of cellulose hydroxyls with anhydrides to form esters. These cellulose esters are stable to mild acid steeping but hydrolyze under mild basic conditions. Anhydrides containing halogen atoms yield products with increased resistance to rot. None of the anhydrides employed produced fabrics with increased crease recovery, abrasion resistance, or breaking strength.

INTRODUCTION

Diethylaminoethylated (DEAE) cotton, which contains tertiary amine groups on the cellulose chains, has been used as the starting cellulosic material for reactions with epoxides.^{1,2} Although the amine group functioned as an additional reaction site for epoxides, its primary role was one of catalyst. Research has been extended to the use of built-in amine groups as catalysts for the reactions of cotton with other reagents. This report pertains to the reactions of DEAE-cottons with carboxylic acid anhydrides which did not react with unmodified cotton or with cotton pretreated with hot aqueous NaOH as used in preparation of DEAE-cottons.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used without further purification. The β -chloroethyldiethylamine hydrochloride and the trifluoroacetic anhydride were obtained from Matheson, Coleman and Bell. Tetrabromophthalic anhydride was purchased from Michigan Chemical Corp., pyromellitic dianhydride from Princeton Chemical Research Inc., and endic and chlor-endic anhydrides were from Velsicol Chemical Corp. The other anhydrides were purchased from Eastman Organic Chemicals Co.

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Fabrics

An 80 × 80 cotton print cloth weighing 3.12 oz/yd², desized, scoured, and then peroxide bleached, was used as the untreated control and starting fabric in preparation of DEAE-cotton and of an aminized cotton.

DEAE-cotton was prepared by a modification³ of the Hartmann⁴ process. Fabric, padded to 100% wet pickup with a 20% aqueous solution of β -chloroethyldiethylamine hydrochloride, was reacted in 8% aqueous NaOH at 95°C for 10 min. Excess sodium hydroxide was removed by washing the fabric in dilute acetic acid and then tap water. The fabric was then ironed dry. A single treatment by this process yielded a fabric of approximately 0.4% nitrogen, and higher nitrogen contents were produced by repeated treatments. To exchange anions, DEAE-cottons were soaked in 0.05M solutions of an acid, HX, for 24 hr and then washed in deionized water.

Aminized cotton was prepared by padding fabric to 100% wet pickup with an aqueous solution containing 10% 2-aminoethylsulfuric acid and 25% NaOH and curing 15 min at 120°C. The aminized fabric was washed in dilute acetic acid and in tap water before being dried.

Application of Anhydrides to Fabrics

Fabrics were treated with anhydrides or solutions of anhydrides for specified times and at temperatures indicated in the text. Fabrics were then washed in the solvent used to dilute the anhydride for reaction or in acetone or methanol in the cases of undiluted anhydrides. Initial washings were followed by washings in deionized water. Fabrics were ironed dry and allowed to air-equilibrate before being analyzed or tested for fabric properties.

Textile Testing

Breaking strengths were determined by strip method (1 in. width) on a Scott Tester,⁵ conditioned (dry) wrinkle recovery angles by the Monsanto method⁶ with a 500 g weight, wet recovery angles as described previously,⁷ and abrasion resistance by the flex method.⁹

Microscopical Examination

Ultrathin cross sections of fibers were examined after layer expansion in methyl-butyl methacrylates under the electron microscope as described previously.⁹

RESULTS AND DISCUSSION

Other workers¹⁰⁻¹³ have shown that cotton cellulose can be treated with various anhydrides under external catalytic conditions to produce cellulose esters. Preliminary results obtained when DEAE-cotton was soaked in undiluted acetic anhydride at room temperature for 24 hr showed a weight increase of 6.4% and a strong infrared absorption at 5.75 μ , the region

attributed to acid or ester carbonyl. There was no absorption in the region of 6.3μ and 6.9μ , a region associated with the carboxylate ion.

Possible reactions of DEAE-cotton in the acid (HX) salt form and acetic anhydride are illustrated in eqs. (1)–(3). Although quaternary amides, product of eq. (1), are known to exist,¹⁴ they hydrolyze rapidly in the presence of water. Our cellulose product was heated to 70°C in deionized water for 30 min and dried before analysis. The infrared spectrum still showed a characteristic carbonyl band of magnitude equal to that of the one produced originally. This indicates that the product achieved was not due to reaction 1.

If a carboxylate anion were present as illustrated by eq. (2), it should be exchangeable with anions having a stronger affinity for the weak-base cellulose exchanger than the carboxylate anion. The product from the DEAE-cotton-acetic anhydride reaction was soaked in $0.05M$ solutions of

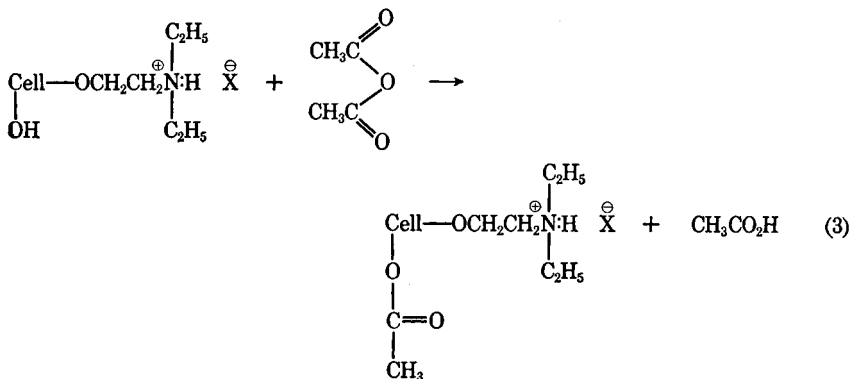
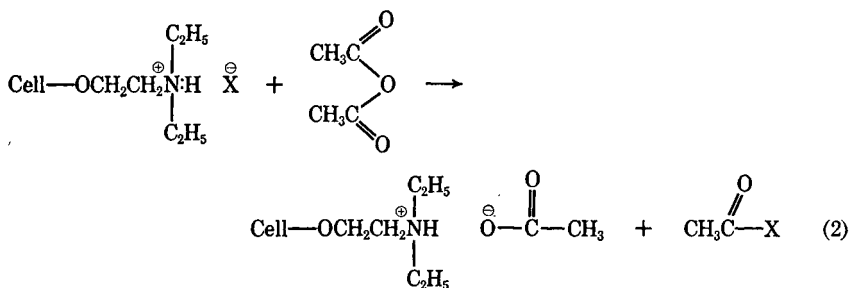
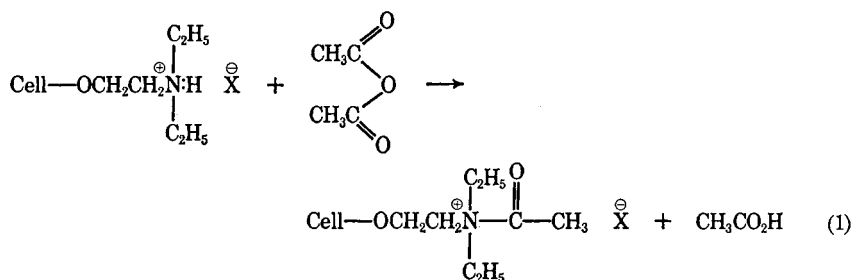


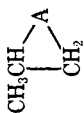
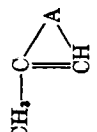
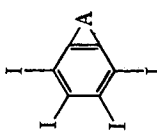

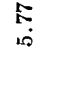




TABLE I
DEAE-Cottons Esterified with Anhydrides in Acetone^a

Name	Anhydrides	Formula ^c	Add-on, wt-%	Wrinkle recovery (W + F) ^o		Infrared absorption, μ	
				Wet	Cond.	Ester	COO ⁻
Hexanoic		$[\text{CH}_2(\text{CH}_2)_4\text{A}]_n$	2.0	187	198	5.75 (M) ^b	6.35 (M)
Glutaric			12.8	243	146	—	—
Maleic			8.4	233	169	5.80 (M)	6.30 (S)
Pyrotartaric			5.3	186	202	5.76 (S)	6.32 (S)
Citraconic			4.0	147	230	5.76 (Sh)	6.50 (S)
Tetraiodophthalic ^d			3.5	205	197	5.77 (S)	6.27 (S)

7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic ^a		3.8	166	209	5.77 (S)	6.27 (S)
4-Methyl-4-cyclohexene-1,2-dicarboxylic		5.3	182	233	5.77 (M)	6.33 (M)
Maleopimaric acid		1.6	182	228	5.76 (Sh)	6.33 (B)
5-Norbornene-2,3-dicarboxylic DEAE control		4.5	168	202	5.77 (M)	6.31 (M)
		—	168	225	—	—

^a Diethylaminoethylated cotton of 0.80% nitrogen treated at room temperature in a 20% solution of the anhydride in acetone for 24 hr and washed with acetone, then methanol, and finally deionized water.

^b (S) strong; (M) medium; (W) weak; (B) broad; (Sh) shoulder.

^c A represents a carboxylic anhydride group, .
^d Reacted at room temperature in a 20% solution of the anhydride in dimethylformamide, and then washed with dimethylformamide, methanol and finally deionized water.

HCl or NaOH, washed free of excess acid or base, dried, and then subjected to infrared analysis. Absorption at 5.75μ remained after acid treatment, but disappeared after base treatment. These results are in accord with the following order or selectivity of the anion exchanger: $\text{OH}^- > \text{CH}_3\text{COO}^- > \text{Cl}^-$. This would be an acceptable explanation, were it not for the fact that DEAE-cotton in the hydrochloride form lost no chloride ion after reaction with the anhydride. Honold¹⁵ has shown that cellulose acetates are stable and resistant to acid hydrolysis, but hydrolyze readily in the presence of base. Equation (3) is representative of the reaction of cellulose hydroxyls with the anhydride through the catalytic effect of the amine to form esters. Analyses indicate that the cellulosic hydroxyls of DEAE-cottons are esterified by acetic anhydride and that the amino groups in form of hydrosalts catalyze the esterification.

In Table I are data for partial cellulose esters obtained by reacting DEAE-cottons with various dibasic acid anhydrides in acetone at room temperature. Although groups of varied structures, including some with double bonds capable of further modification, were introduced, none of the finished fabrics showed significant increases in either wet or dry wrinkle recovery. Presence of strong absorption bands in the $6.3\text{--}6.9 \mu$ region as well as in the 5.75μ region indicates that the products are cellulose esters with carboxylate ions on one end of the ester group.

Of the anhydrides investigated, only those of chlorendic and tetrabromophthalic acids imparted rot resistance to DEAE-cottons. Treatment of a DEAE-cotton (0.8% N) for 24 hr in an acetone solution of 20% chlorendic anhydride at room temperature resulted in a fabric containing 3.30% chlorine. This fabric retained 100% of its original breaking strength after 33 days of soil burial and 43% of its original strength after 94 days of soil burial. Similar treatment of the DEAE-cotton with a dimethylformamide solution of the tetrabromophthalic anhydride yielded a fabric containing 2.43% bromine. This finished fabric retained 87% and 28% of its original breaking strength after soil burials of 35 and 94 days, respectively. Although it is possible to impart flame-resistant properties to cotton by use of tetrabromophthalic anhydride, the finished fabrics in this study were not flame resistant. Similarly, DEAE-cottons treated with trifluoroacetic anhydride resulted in fabrics with as much as 3% fluorine, but no oil- or water-repellent properties.

Pyromellitic dianhydride was employed in an effort to achieve cross-linking of the cellulose hydroxyls of DEAE-cotton. The DEAE-cotton was treated for 5 hr at reflux temperatures in a 20% by weight solution of the anhydride in dimethylformamide. With negligible weight gains, there were increases of 70 and 30 (W + F)^o in wet and conditioned wrinkle recoveries, respectively. However, when the starting material was aminized cotton, which contains primary amine groups, there was a 6% weight gain and a 65 (W + F)^o increase in both wet and conditioned recoveries. The infrared spectra of both DEAE-cotton and aminized-cotton after treatments with pyromellitic dianhydride showed strong absorption at

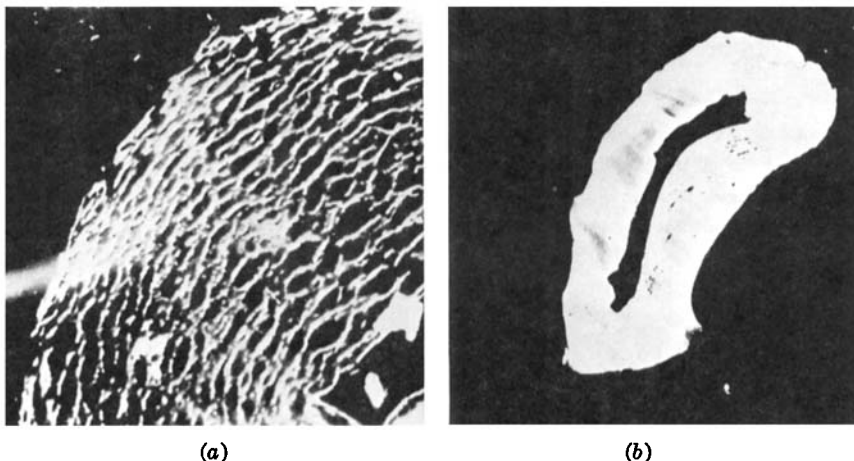


Fig. 1. Typical expansion of amino cotton fibers subsequently treated with pyromellitic dianhydride: (a) DEAE-cotton; (b) aminized cotton.

5.76 μ and no evidence of amide formation with the aminized cotton. Typical electron micrographs of cross sections of fibers removed from these finished cottons after subjection to layer expansion are shown in Figure 1. There is complete expansion of the DEAE-cotton treated with pyromellitic dianhydride as shown in Figure 1a. The solidness of the fiber in Figure 1b indicates different sites of reaction of the aminized cotton and the pyromellitic dianhydride. Since infrared analysis did not show a characteristic amide absorption for the latter product, the reaction must have occurred through cellulose hydroxyls rather than through the attached primary amine groups.

Cotton fabrics have been esterified without altering fabric properties by isatoic anhydride, in the presence of potassium acetate.^{11,16} The resultant cellulose esters contained primary aromatic amine groups which were diazotized and coupled. In this study, DEAE-cottons of 0.8% nitrogen content treated with a 20% solution of isatoic anhydride in dimethylformamide at room temperature for 18 hr showed a 4% weight gain, a total nitrogen content of 1.7%, and no change in fabric properties. The infrared spectrum resembled that of cellulose anthranilate produced with isatoic anhydride and potassium acetate catalyst.

SUMMARY

Tertiary amine groups of diethylaminoethylated cotton in their hydrosalt forms function as built-in catalysts for the reaction between the cellulose hydroxyls and carboxylic acid anhydrides to form cellulose esters. These esters show only small changes in fabric properties, but offer potentials of introducing a desired group into cotton. Resistance to rotting is imparted by chlondic anhydride or by tetrabromophthalic anhydride. As indicated by layer expansion techniques of electron microscopy, crosslinking

of cellulose by use of pyromellitic dianhydride does not occur with DEAE-cotton but does occur with aminized cotton which contains primary amine groups.

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