

Reactions of Halogenated 1,2-Epoxypropanes and Diethylaminoethyl Cotton*

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Synopsis

Diethylaminoethyl (DEAE)-cotton has been reacted with epichlorohydrin (1,2-epoxy-3-chloropropane) neat, in alcoholic solvents, and in aprotic solvents at temperatures ranging from 25 to 95°C. Fabric properties and electron micrographs of fibers removed from these chemically treated DEAE cottons have been compared with those obtained when DEAE-cottons were treated under similar conditions with other halogenated 1,2-epoxypropanes, and with 1,2-epoxy-4,4,4-trichlorobutane. For comparative purposes, epichlorohydrin was reacted with an aminized cotton containing primary amine groups, with cotton containing quaternary ammonium groups, and with DEAE-cottons in which the tertiary amine groups had been quaternized. For reaction at 95°C with neat epichlorohydrin, greatest increase in conditioned wrinkle recovery was observed with DEAE-cottons. Only with DEAE-cottons were the add-ons and recovery angles imparted by epichlorohydrin affected by the anion associated with the amine groups. None of the halogenated 1,2-epoxypropanes reacted with unmodified cotton in the absence of a basic catalyst. Those that reacted with unmodified cotton in the presence of an external base catalyst did not improve conditioned recovery angles. The mono-, di-, and trichloro-1,2-epoxypropanes all increased the conditioned and wet wrinkle recovery of DEAE-cotton when reacted neat at 95°C. The type of oxirane ring opening of epoxypropanes was shown to be influenced by the degree of chlorination of the carbon alpha to the ring. Both primary amine groups and quaternary amine groups catalyzed the epichlorohydrin-cellulose reaction. Dilution of epichlorohydrin with alcohols or decreasing reaction temperature lowered add-ons and improvements in wrinkle recovery properties. Use of aprotic solvents for the DEAE-cotton-epichlorohydrin reaction gave finished cotton fabrics having only high wet wrinkle recovery properties.

INTRODUCTION

Previously, diethylaminoethyl (DEAE)-cottons were modified with various epoxides without additional catalyst to give fabrics with high wrinkle recovery or increased resistance to abrasion.¹ The difunctional reagent, 1,2-epoxy-3-chloropropane, (epichlorohydrin), when reacted with DEAE-

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cotton at 95°C, produced a fabric with dry and wet wrinkle recovery angles of 300 and 270(W + F)°, respectively. This report is concerned with the effect of solvents and temperature on the DEAE-cotton-epichlorohydrin reaction, and the use of other halogenated 1,2-epoxypropanes as finishing reagents for cotton containing built-in amino groups.

EXPERIMENTAL

Materials

Reagents. Reagent-grade chemicals were used without further purification. The β -chloroethyldiethylamine hydrochloride was obtained from Matheson, Coleman and Bell; epichlorohydrin and glycidyltrimethylammonium chloride from Shell Chemical Corp.; 1,2-epoxy-2,3-dichloropropane and 1,2-epoxy-3,3,3-trichloropropane from Wyandotte Chemical Co.; 1,2-epoxy-4,4,4-trichlorobutane from Olin Chemical Division; 1,2-epoxyhexafluoropropane from Peninsular Chemresearch, Inc.; and epibromohydrin from Aldrich Chemical Co., Inc.

Cotton Control. An 80 × 80 cotton print cloth weighing 3.12 oz/yd² was desized, scoured, and then processed in commercial peroxide bleaching equipment. This fabric was subsequently chemically modified to introduce various types of amino groups.

DEAE-Cottons. The DEAE-cellulose was prepared by a recently reported modification² of the Hartmann process.³ Fabrics were padded twice to 100% wet pickup with a 20% aqueous solution of β -chloroethyldiethylamine hydrochloride, immersed in 8% NaOH for 10 min at 95°C, washed in dilute acetic acid, and then washed in tap water. Fabric was air-equilibrated at least 24 hr prior to being tested or subsequently chemically modified.

Cottons with Quaternary Ammonium Groups. DEAE-cotton was quaternized under anhydrous conditions with a 20% ethanolic solution of redistilled methyl iodide.⁴ These fabrics were washed in deionized water, ironed dry, and allowed to air-equilibrate for at least 24 hr.

Quaternary groups were also introduced by reacting unmodified cotton with glycidyltrimethylammonium chloride. In this method, fabric was padded with 15% aqueous NaOH, immersed in a 10% aqueous solution of the chloride for 17 hr, washed in deionized H₂O, and allowed to air-equilibrate for at least 24 hr.

Aminized Cotton. Fabric was padded with an aqueous solution containing 10% 2-aminoethylsulfuric acid and 25% NaOH,⁵ cured 15 min at 120°C., washed in dilute acetic acid, washed in tap water, air-equilibrated for 24 hr, and then tested.

Cottons with Specific Anions. To exchange anions of the DEAE-cottons and the quaternary ammonium cottons, fabrics were soaked in 0.05N NaOH for 24 hr, washed free of excess hydroxyl ion with deionized H₂O, dried, then soaked for 24 hr in a solution which was 0.05N with respect to the desired anion and washed in deionized H₂O.

Application of Epoxides to Cotton and Modified Cottons

Fabrics were immersed in epoxides, either neat or in solutions, at temperatures ranging from 25 to 95°C. for the specified period. All fabrics were washed in solvent used in the reaction, absolute methanol, and distilled water before being ironed dry and air-equilibrated.

Textile Testing

Breaking strengths were determined by the strip method (80-thread count width) on a Scott tester,⁶ conditioned (dry) wrinkle recovery angles by the Monsanto method⁷ with a 500-g weight, and wet wrinkle recovery angles as described previously.⁸

Microscopical Examinations

Methods of optical microscopy were applied to observe the amount of swelling and dissolution of the epoxide-treated fabrics in 0.5*M* cupriethylenediamine hydroxide (cuene). More detailed information concerning the sites of crosslinking was obtained from electron micrographs of ultrathin cross sections of fibers removed from finished fabrics.⁹

RESULTS AND DISCUSSION

When epichlorohydrin reacts with DEAE-cotton at 95°C in the absence of external catalyst, some reaction occurs at the amino groups as well as at unreacted cellulosic hydroxyls since anion exchange properties are altered. Reaction at the hydroxyls was catalyzed by Lewis base amino groups or the anion associated with the amine since epichlorohydrin does not react with the cotton control without a catalyst under similar conditions. A large part of the reaction of epichlorohydrin occurred at the unreacted cellulose hydroxyls, as only a fraction of the weak-base tertiary amino groups of DEAE-cotton was converted to quaternary base groups.¹

The effects of alcoholic solvents on the epichlorohydrin-DEAE-cotton reaction are shown in bar graphs in Figure 1. Weight gains of epichlorohydrin from 20% solutions in each of the alcohols to DEAE-cotton at reflux temperatures and resultant recovery angles are compared with those obtained with epichlorohydrin alone at 95°C. There was no correlation between weight gain and wrinkle recovery, or between weight gain and ease of formation of byproduct with alcohol solvent. The most hindered, tertiary butanol, resulted in the lowest, and *n*-octanol and ethanol in the highest add-ons of epichlorohydrin to DEAE-cotton. Highest dry wrinkle recovery was obtained with neat epichlorohydrin. With the exception of methanolic and ethanolic solutions, dry recovery exceeded wet recovery. Since differences in recovery with the various solvents might be attributed to differences in fiber penetration or swelling, electron micrographs of the ultrathin cross sections of fibers subjected to layer expansion in methacry-

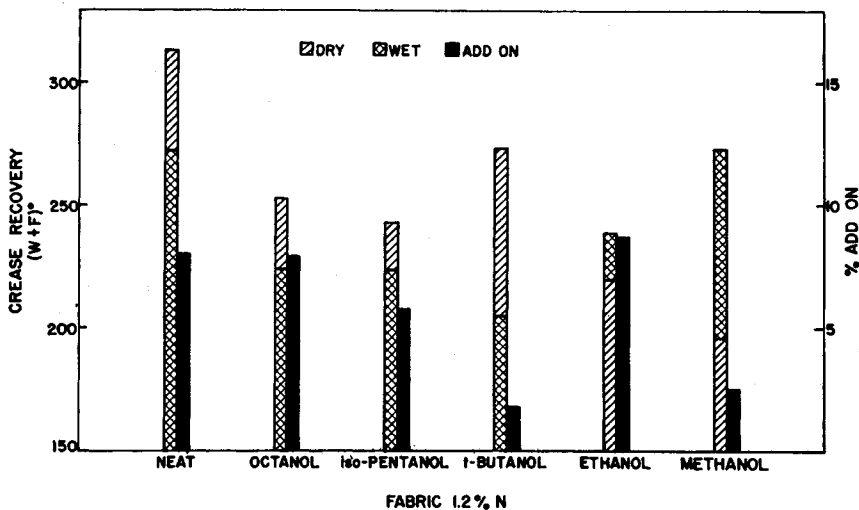


Fig. 1. Effect of alcoholic solvents on the wrinkle recovery and add-on of DEAE-cotton treated with a 20% solution of epichlorohydrin.

late were examined. DEAE-cottons treated with neat epichlorohydrin, or in methanol or ethanol, did not layer; those treated in tertiary butanol, isopentanol, and *n*-octanol showed some fibers partially expanded and others completely expanded. Those that expanded completely were greatly swollen as compared to those of the unmodified DEAE fabric. There was no correlation between dry or wet recovery and behavior of fiber cross sections subjected to layer expansion techniques.

DEAE-cottons were treated under reflux or at 75°C for 3 hr in 20% solutions of epichlorohydrin in several aprotic solvents covering a wide range of dielectric constants. Fabric properties are shown in Table I.

Increase in wet wrinkle recovery only with aprotic solvents is similar to previously reported results obtained with unmodified cottons and epichlorohydrin with external base catalysis.¹⁰ In all but one case, the per cent weight gain is greater for reactions in solvent with a lower dielectric constant. Although properties could not be correlated with dielectric constants of solvents, some differences in cross sections of fibers subjected to layer expansion techniques were observed in electron micrographs. Those reacted in diethyl ether, which showed least increase in wet recovery, swelled and were completely expanded. Those reacted in dioxane were partially expanded, and the only other showing the slightest tendency to expand was that reacted in nitromethane. All other fiber cross sections were solid, and the only one showing a great degree of swelling was that treated in CCl₄.

Cottons modified to contain from 0.5 to 0.8% *N* in the form of primary, tertiary, and quaternary ammonium groups were reacted with neat epichlorohydrin at 95°C for 3 hr. Weight gains, recovery angles, and increase in recovery angles over the control amino-cotton fabrics are shown in Table II.

TABLE I
Effects of Aprotic Solvents on the DEAE-Cotton-Epichlorohydrin Reaction^a

Solvent	Dielectric constant	Add-on wt-%	Wrinkle recovery angle (W + F) ^o		Breaking strength, lb	Flex-abrasion, cycles
			Wet	Cond.		
Dimethyl sulfoxide	48.9	2.2	282	174	35	314
Dimethylformamide	37.6	3.0	309	183	36	225
Nitromethane	37.5	4.0	290	182	39	418
Nitrobenzene	34.8	4.4	264	218	31	248
Chloroform	4.8	6.0	287	231	—	—
Diethyl ether ^b	4.3	8.3	249	166	59	980
Carbon tetrachloride	2.2	5.3	309	200	25	200
Dioxane	2.2	2.0	258	209	34	554
<i>n</i> -Hexane ^b	1.9	4.8	302	193	34	512
DEAE control (1.20% <i>N</i>)	—	—	220	228	73	521

^a DEAE-cotton of 1.20% *N* reacted at 75°C for 3 hr in a 20% solution of epichlorohydrin.

^b Reacted at reflux temperature for 3 hr in a 20% solution of epichlorohydrin.

TABLE II
Recovery Angles of Amino-Cottons Modified with Epichlorohydrin^a

Amino groups	Nitrogen, wt-%	Epichlorohydrin add-on, wt-%	Wrinkle recovery angles			
			(W + F) ^o		$\Delta(W + F)$ ^o '	
			Wet	Cond.	Wet	Cond.
Primary ^b	0.80	2.6	275	133	55	29
Tertiary ^c	0.82	11.1	213	267	22	116
Quaternary ^d	0.80	—	232	251	39	74
Quaternary ^e	0.54	3.1	266	207	67	45

^a 80 × 80 cotton print cloths chemically modified to contain indicated amino groups, converted to the base form and then reacted with epichlorohydrin at 95°C for 3 hr.

^b Fabric treated with a 20% solution of 2-aminoethylsulfuric acid.

^c Fabric treated with a 20% aqueous solution of 2-chloroethyldiethylamine hydrochloride.

^d DEAE-cotton quaternized with methyl iodide.

^e Cotton treated with glycidyltrimethylammonium chloride.

^f Final minus initial recovery of fabric types.

DEAE-cotton with tertiary amino groups had the largest weight gain and the greatest increase in dry recovery. Although the quaternized form of DEAE showed a negligible gain, it had the second largest increase in conditioned recovery. Analyses of products washed in deionized water showed that the hydroxide ions were exchanged by chloride ions produced in the reaction with epichlorohydrin.

Amine groups or the tightly held anions of the salt might be the effective

TABLE III
Effect of Anions on Fabric Properties of Epichlorohydrin-Treated
Cottons Containing Amino Groups^a

Fabric type	Nitrogen, wt-%	Epichloro- hydrin add-on, wt-%	Wrinkle recovery angles			
			(W + F) ^o		$\Delta(W + F)$ ^{o,d}	
			Wet	Cond.	Wet	Cond.
DEAE·H ⁺ OH ⁻	0.82	11.1	213	267	22	116
DEAE·H ⁺ Cl ⁻	0.82	5.2	248	269	68	90
DEAE·H ⁺ OAc ⁻	0.82	9.2	247	275	60	101
DEAE·CH ₃ ⁺ OH ^{-b}	0.80	0.0	232	251	48	74
DEAE·CH ₃ ⁺ Cl ⁻	0.80	1.1	208	260	24	90
DEAE·CH ₃ ⁺ I ⁻	0.80	-2.8	226	250	78	59
DEAE·CH ₃ ⁺ OAc ⁻	0.80	-0.4	194	254	10	84
Gly ⁺ Cl ^{-c}	0.54	3.9	262	222	44	71
Gly ⁺ OH ⁻	0.54	3.1	266	207	67	45
Gly ⁺ OAc ⁻	0.54	3.7	265	217	55	64

^a Fabric immersed in epichlorohydrin at 95°C for 3 hr.

^b DEAE-cotton reacted with 20% ethanolic methyl iodide at reflux for 3 hr to form quaternary ammonium group.

^c Cotton fabric treated with glycidyltrimethyl ammonium chloride with NaOH catalyst to form quaternary ammonium group.

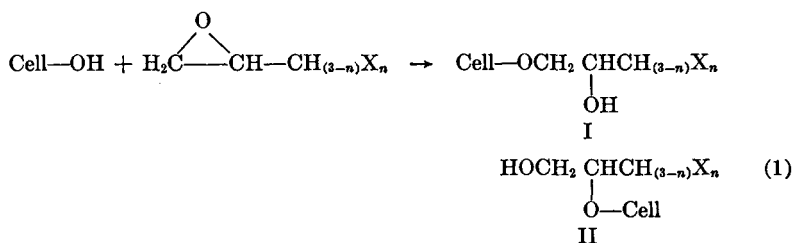
^d Final minus initial recovery of fabric types.

catalysts for the cellulose-epichlorohydrin reactions. Therefore, anions of DEAE (a weak base exchanger) and of a quaternary base cotton were exchanged with various anions. The fabrics were then reacted with epichlorohydrin at 95°C for 3 hr. Table III shows how recovery varies with type of amino group and type of anion.

Both DEAE-cotton and its quaternized form showed marked increase in dry recovery angles even though the latter showed no weight gains of epichlorohydrin. With DEAE-cotton, increase in wet recovery with the acetate or chloride forms was greater than that with the base form. Only with the quaternary base cottons prepared from the glycidyl trimethylammonium chloride were wet recoveries greater than dry recoveries for all anion forms. These latter fabrics had lowest nitrogen contents, and probably reaction with epichlorohydrin was at sites comparable to those in unmodified cottons, which results in high wet wrinkle recovery only.

In addition to epichlorohydrin, 1,2-epoxy-3,3-dichloropropane, 1,2-epoxy-3,3,3-trichloropropane, and 1,2-epoxy-4,4,4-trichlorobutane were reacted with DEAE-cottons at 95°C or at reflux temperature. None of these epoxides reacted with unmodified cottons, and none produced increased conditioned recovery when reacted with cotton in the presence of external base catalysis. After opening of the oxirane rings, all except the epoxybutane should be capable of dehydrohalogenation and thus difunctionality resulting in crosslinking of cellulose.

In (1), X represents a halogen, and I and II represent, respectively, cellulose products from normal and abnormal oxirane ring openings.



Product I can be dehydrohalogenated to form another epoxide capable of crosslinking through another cellulose hydroxyl. Product II is not easily dehydrohalogenated and should retain all covalent halogen.

Table IV contains typical data obtained with reactions between DEAE-cottons and the halogenated epoxypropanes at 95°C. and the trichlorobutane at its reflux temperature. Highest dry and wet recovery angles were obtained with epichlorohydrin, the monochloro epoxypropane. Least effective in increasing dry recovery is the epoxybutane, which should not be difunctional. Typical wrinkle recovery angles, add-ons of epoxide, and chlorine analyses given as milliequivalents per gram product are included in Table IV.

On the assumption that all chlorine resulted from formation of product II, the portion of the add-on on a dry weight basis, due to product I was calculated and recorded in Table IV as milliequivalents per gram product. Difference between add-on and product I was assumed to be product II, and these values for each halogenated epoxide are recorded in Table IV as milliequivalents per gram product. The ratio of product II to product I was calculated and taken to be the ratio of abnormal to normal ring opening.

TABLE IV
Effect of Type of Chlorinated Epoxide on DEAE-Epoxide Reaction Products^a

Reagent	Add-on, wt-%	Covalent Cl present, meq/g	Product I present, meq/g	Product II present, meq/g	Wrinkle recovery angle (W + F) ^o	
					Wet	Cond.
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{ClCH}_2\text{CHCH}_2 \end{array}$	8.21	0.101	1.29	0.101	272	313
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{Cl}_2\text{CHCHCH}_2 \end{array}$	20.40	1.04	2.47	0.520	244	267
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{Cl}_3\text{CCHCH}_2 \end{array}$	13.22	1.63	0.837	0.543	248	237
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{Cl}_2\text{CCH}_2\text{CHCH}_2^b \\ \text{DEAE control} \end{array}$	4.94 —	0.752 —	0.091 —	0.251 —	241 168	219 174

^a Fabric containing 0.85% nitrogen immersed in the epoxide and treated for 3 hr at 95°C.

^b Fabric containing 0.80% nitrogen immersed in the epoxide and treated at its reflux temperature for 3 hr.

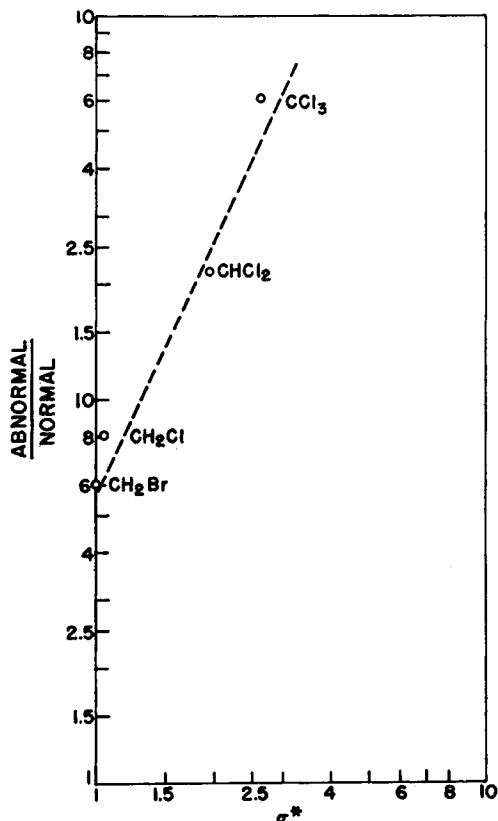


Fig. 2. Log of ratio of equivalents of products from abnormal ring opening to equivalents of products from normal ring opening vs. log of the Taft polar substituent constant, σ^* .

The ratio of II to I increases as the number of chlorines on the carbon adjacent to the epoxide increases. A logarithmic plot of the ratio of II/I versus Taft polar substituent constants,¹¹ σ^* is shown in Figure 2, which also includes a value obtained with epibromohydrin. The approximate straight line indicates that the position of nucleophilic attack of the cellulose on the epoxide is a function of the electronegativity of the carbon adjacent to the oxirane. The large ratio of II/I for 1,1,1-trichloro-3,4-epoxybutane is not due to the inductive effect of the $-\text{CH}_2\text{CCl}_3$ substituent but rather that product I cannot dehydrohalogenate. The nucleophilic attack on propylene oxide occurs primarily on the terminal carbon of the ring (normal ring opening).¹² As the terminal carbon not attached to the oxygen is substituted with more electronegative substituents, the ratio of abnormal (attack of nucleophile on central carbon) to normal ring opening increases.

Single fibers removed from fabrics etherified with the chlorinated epoxides and immersed in 0.5M cuene for 30 min gave the following order of insolu-

bility or inertness: epichlorohydrin > dichloroepoxypropane > trichloroepoxypropane > trichloroepoxybutane.

Examination of electron micrographs of ultrathin cross sections of fibers of DEAE-cotton treated with the mono-, di-, or trichloro-1,2-epoxypropanes, or with 1,2-epoxy-4,4,4-trichlorobutane, and then subjected to layer expansion in methyl methacrylate showed that all except those treated with the trichloroepoxypropane were nonexpanded. Cross sections of the latter were solid along the edges only and expanded within. In Figure 3 are shown typical electron micrographs of cross sections of fibers after layer expansion in methyl methacrylate. Electron micrographs 3a and 3b show absence of layering of those DEAE-cottons treated with 1,2-epoxy-3,3-dichloropropane and 1,2-epoxy-4,4,4-trichlorobutane, respectively. The

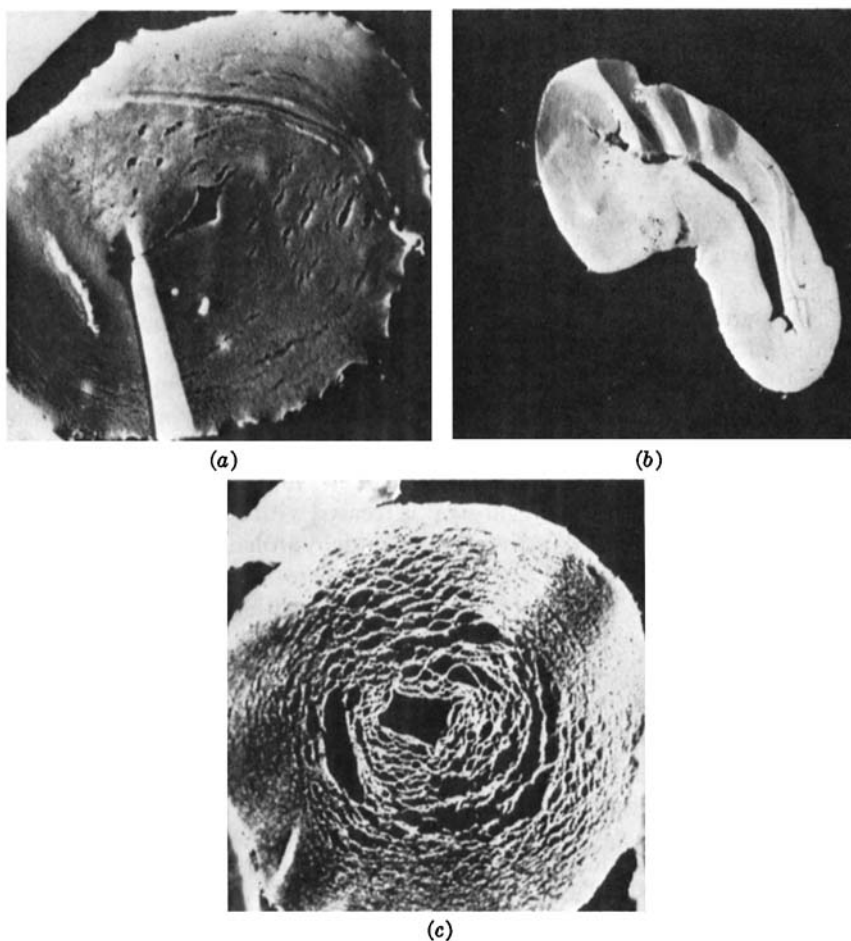


Fig. 3. Typical expansion patterns of modified DEAE-cotton fibers: (a) DEAE-cotton treated with 1,2-epoxy-3,3-dichloropropane; (b) DEAE-cotton treated with 1,2-epoxy-3,3,3-trichloropropane; (c) DEAE-cotton treated with 1,2-epoxy-4,4,4-trichlorobutane.

TABLE V
Effect of Various Halogenated Epoxypropanes on DEAE-Cotton^a

Reagent	Add-on, wt-%	Halide present, wt-%	Wrinkle recovery angle (W + F) ^o	
			Wet	Cond.
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{ClCH}_2\text{CHCH}_2 \\ \text{O} \end{array}$	8.3	0.70	272	313
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{BrCH}_2\text{CHCH}_2 \\ \text{O} \end{array}$	2.8	0.22	218	251
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CF}_3\text{CFCF}_2^b \\ \text{DEAE control} \end{array}$	4.5	3.46	162	210
	—	—	168	172

^a Fabric treated at 95°C for 3 hr.

^b Fabric treated in sealed container with gaseous material for 3 hr.

solid cross sections are similar to those obtained when DEAE-cotton is treated with epichlorohydrin.¹ Figure 3c shows typical expansion near the center of fibers after treatment of DEAE-cotton with 1,2-epoxy-3,3,3-trichloropropane.

In addition to treatment with chlorinated epoxypropanes, DEAE-cottons were treated with epibromohydrin at 95°C for 3 hr and with hexafluoroepoxypropane at room temperature under pressure developed in a sealed container at room temperature. Table V gives the results of these treatments. Results of an epichlorohydrin treatment are included for comparison. The epichlorohydrin gave the highest add-on and the highest wrinkle recovery. The fabric finished with hexafluoroepoxypropane showed only a slight increase in dry wrinkle recovery and possessed neither oil nor water repellency. There was an increase of 40° in wet recovery and 80° in dry recovery when the DEAE-fabric was treated with epibromohydrin.

Since hydrochloric acid, a by-product of dehydrohalogenation, degrades cotton fabric at elevated temperatures, an attempt was made to increase recovery of DEAE-cottons by reacting with neat epichlorohydrin for longer times at room temperature. Data in Table VI show changes in add-ons and recovery angles with times of reaction. Dry recovery angles were not as high as those realized at 95°C, but all showed increases at small weight gains in both wet and dry recovery. About 5 hr was required for angles of 250(W + F)°. This differs from reactions at 95°C where dry recovery always exceeds the wet.

Greater differences in products obtained at room temperature and 95°C were observed when alcoholic solutions of epichlorohydrin were used. As shown by data in Table VII, wet recovery always exceeds dry recovery when DEAE-cottons are treated with alcoholic solutions at room temperature; but at elevated temperatures of reaction, dry recovery was higher than wet recovery with the higher alcohols. Wet recovery produced at room temperature by epichlorohydrin in alcoholic solvent exceeds that produced in the same medium at elevated temperatures.

TABLE VI
Effect of Time on the Wrinkle Recovery of DEAE-Cotton
Treated with Epichlorohydrin^a

Reaction time, hr	Add-on wt-%	Wrinkle recovery angle (W + F) ^o	
		Wet	Cond.
1	0.0	178	195
2	1.1	202	199
3	0.9	242	238
5	1.8	253	254
7	3.1	244	254
8	—	234	247
20	3.5	258	257
22	4.2	252	259
23	4.1	258	271
24	5.9	240	233
DEAE control	—	168	174

^a DEAE-cottons immersed in epichlorohydrin at room temperature for indicated times.

TABLE VII
Effect of Alcoholic Solvents on the Wrinkle Recovery Properties of
DEAE-Cotton Treated with Epichlorohydrin^a

Solvent	Add-on, wt-%	Wrinkle recovery angle (W + F) ^o	
		Wet	Cond.
Neat	1.9	270	241
Methanol	0.3	264	233
Ethanol	1.0	253	246
<i>tert</i> -Pentanol	1.9	242	231
Iso pentanol	1.6	254	207
<i>n</i> -Octanol	2.3	258	242
DEAE control	—	168	174

^a DEAE fabrics immersed in a 20% by weight solution of epichlorohydrin in various alcohols for 24 hr at room temperature.

SUMMARY

Although halogenated 1,2-epoxypropanes do not react with unmodified cotton in the absence of catalysts and produce only increased wet wrinkle recovery in cottons reacted in the presence of external base catalysts, they can be reacted with cottons containing tertiary amino groups such as DEAE-cottons to impart conditioned and wet wrinkle recovery. Relative amounts of conditioned and wet recoveries can be changed by varying temperature or solvent medium of the DEAE-cotton epichlorohydrin reactions. Solubility in cupriethylenediamine hydroxide of DEAE-cotton modified with halogenated epoxypropanes is least with epichlorohydrin and greatest

with 1,2-epoxy-3,3,3-trichloropropane. However, differences observed with layer expansion techniques applied to DEAE cottons modified with halogenated epoxypropanes could not be correlated with differences in wrinkle recovery values.

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Trade names have been used to identify material used in the work, and such does not imply endorsement or recommendation by the U.S. Department of Agriculture over other products not mentioned.

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