

Reactions of Cotton or Diethylaminoethyl Cotton with 1-Chloro-2,3-Epithiopropene*

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Synopsis

Sulphydryl groups have been introduced into cotton and into diethylaminoethyl (DEAE)-cotton by reaction with neat 1-chloro-2,3-epithiopropene or alcoholic solutions of the thiirane. Reactions at room temperature have been compared with those at higher temperatures, and fabric properties obtained with various S/Cl ratios have been compared. The effects of additional external base catalysis on these reactions have been studied. Fabric properties resulting from cotton-1-chloro-2,3-epithiopropene or DEAE-cotton-1-chloro-2,3-epithiopropene reactions have been compared with properties obtained with the corresponding reactions of cotton or DEAE-cotton with epichlorohydrin. Sulphydryl groups have also been introduced into cotton and DEAE-cotton by the *in situ* formation of 1-chloro-2,3-epithiopropene in the fabric as a result of the reaction of the oxygen analog with a thiourea or a thiocyanate. These *in situ* reactions have been carried out in the absence and presence of solvent and external base catalysts. Attempts to vary the wet and conditioned (dry) recovery angles by oxidation of sulphydryl groups and by reduction of disulfide groups met with little success. Smaller improvement in wrinkle recovery properties imparted by the thiirane than by epichlorohydrin at a given add-on has been explained on the basis of greater tendency of the thiirane to open abnormally in neutral or slightly acidic conditions and thus the greater tendency of the thiirane to form polymers rather than to crosslink cotton. Tendency of the oxirane to open normally and therefore act difunctionally results in finished fabrics with low chlorine contents, a high degree of crosslinking, and little polymer formation.

INTRODUCTION

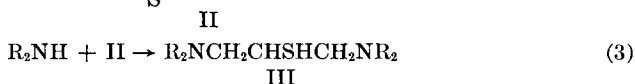
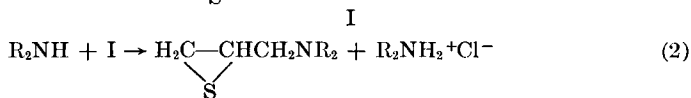
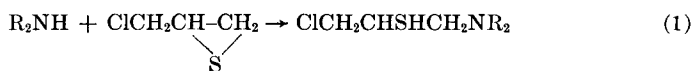
Cotton attains various degrees of wet wrinkle recovery by base-catalyzed reactions with 1-chloro-2,3-epoxypropane (epichlorohydrin) or its halo-hydrin precursors.¹⁻³ It is only under controlled basicity^{4,5} that cotton can be treated with epichlorohydrin to produce cottons with improved conditioned recovery and high wet wrinkle recovery. External base catalysis results in higher wet than conditioned recovery. Cotton does not react with epichlorohydrin, either neat or in solvents, in the absence of a catalyst, or with the usual acid catalysts. However, a built-in nucleophilic catalyst,

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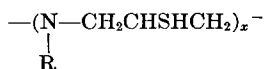
as is present in diethylaminoethyl cotton (DEAE-cotton), rather than an external base catalyst for the cellulose-epichlorohydrin reaction results in cottons with high dry as well as high wet wrinkle recovery.⁶

Stewart,⁷ in his study of reactions of 1-chloro-2,3-epithiopropene with primary or secondary amines, noted close analogy of reactions of oxiranes and thiiranes with these nucleophilic reagents. Polymers were formed with primary amines; *N*-substituted epithiopropanes were formed with secondary amines; but reactions with tertiary amines were not investigated. Since the preparation of 1-chloro-2,3-epithiopropene in relatively good yield had been reported,^{7,8} and the literature pertaining to cottons modified with sulfhydryl groups⁹⁻¹² indicates little improvements in dry wrinkle recovery, it was of interest to study reactions of cotton with this compound.

This report deals with an investigation of the reactions of cotton and DEAE-cotton with the sulfur analog of epichlorohydrin, 1-chloro-2,3-epithiopropene, under experimental conditions very similar to those used with epichlorohydrin. It also deals with the *in situ* preparation of the sulfur analog in cotton as a result of application of epichlorohydrin in the presence of a thiocyanate or a thiourea. Such data were needed to detect differences in fabric properties imparted by sulfhydryl groups as compared to hydroxyl groups. It is assumed that the respective heterocyclic rings open and add to cotton in the presence of the tertiary amino nucleophiles to form hydroxy or sulfhydryl ethers of cellulose. In addition, there is the possibility of quaternization of the amino groups in cotton as occurred in the DEAE-cotton-epichlorohydrin reaction.⁶ According to Stewart,⁷ the sequence of reactions with a secondary amine nucleophile is as shown in eqs. (1)–(3).



Although the oxygen analogs of I, II, and III have been isolated, only II and III have been isolated as reaction products of the thiopropane. With the thiopropane, step (2) is faster than step (1). Compound II is formed as a result of steps (1) and (2) rather than of direct nucleophilic displacement of chlorine by amine, as such a reaction is too slow in comparison to opening of a thiirane. Stewart also demonstrated cleavage of the primary C—S bond or normal ring opening for steps (1) and (3) of the thiirane and tendency for the formation of polymers of the type



A steric hindrance factor was also demonstrated when a hindered RNH_2 was used, as III was never isolated regardless of the amount of di-*n*-butylamine

in excess. Schwenker⁹ introduced sulfhydryl groups by a different procedure and concluded that crosslinking cotton in the swollen state through disulfide bonds results in high wet recovery but relatively low dry recovery. Hobart¹⁰ formed disulfide crosslinks in the cellulose matrix of dialdehyde or dialcohol cottons, and Benesch¹¹ formed disulfide bonds in aminized cottons by reactions with *N*-acetylhomocysteinethiolactone. More recently, Tesoro¹² reported on reversible crosslinks in cotton modified with *N*-hydroxymethylacetylthioacetamide ($\text{HOCH}_2\text{NHCOCH}_2\text{SCOCH}_3$). The acetylthioacetamidomethylcellulose was saponified under mild conditions to the thiol derivative, mercaptoacetamidomethylcellulose, which provided a model for the investigation of changes in recovery with formation and reduction of disulfide links. In all of the cottons containing disulfide links, the degree of wrinkle recovery in both wet and dry states was not as high as one might expect from the sulfur contents.

EXPERIMENTAL

Materials

Reagents. Reagent-grade chemicals were used without further purification. Epichlorohydrin was obtained from the Shell Development Corporation. The 1-chloro-2,3-epithiopropene was prepared from epichlorohydrin and thiourea by the method of Culvenor⁸ except for substitution of dioxane for methanol as the reaction solvent and the substitution of diethyl ether for chloroform in the washing step. The changes were made to improve solvation during reaction and to aid stripping of the solvent after washing. Use of 0.1% concentrated sulfuric acid in the dioxane was found to slightly increase the purity over that of an otherwise identical preparation in which no acid was used. The yield of distilled product was 20%. The 1-chloro-2,3-epithiopropene reacted with fabric was prepared by the modified procedure with the use of the acid catalyst and analyzed as follows: Cl, 32.4%; S, 28.6%; n_D^{25} , 1.5250; bp, 73–75°C/80 mm. The theoretical values are Cl, 32.6%; S, 29.5%. The data of Culvenor show Cl, 32.9%; S, 29.8%; n_D^{25} , 1.5280; bp 79–81°C/114 mm.

Fabrics. An 80 × 80 cotton print cloth weighing approximately 3.12 oz/yd² which had been desized, scoured, and peroxide-bleached was used. Most experiments were with samples measuring 12 × 12 in. and weighing approximately 10 g.

Diethylaminoethyl (DEAE) cotton was prepared from the same cotton fabric by a modification¹³ of the method of Hartmann.¹⁴

Modification of Fabrics

With 1-Chloro-2,3-epithiopropene. All reactions with fabrics were at atmospheric pressure, and reactions at reflux temperatures were in an all-glass standard laboratory reflux system heated by an electric mantle. Other reactions at elevated temperatures were carried out in a power ventilated oven. Fabric samples loosely coiled inside 250-ml graduated

cylinders containing 1-chloro-2,3-epithiopropene neat or in solvent were agitated periodically. All containers for an experiment were heated simultaneously, and time of reaction was taken as actual time at the elevated temperature. After reactions, fabric samples were washed, dried, and equilibrated for 24 hr before being tested.

With 1-Chloro-2,3-epithiopropene Prepared *in Situ*. A simplified procedure of reacting cotton or DEAE-cotton with epichlorohydrin in the presence of thioureas or thiocyanates in attempts to prepare the thiirane *in situ* was followed. Reactants were mixed and applied to fabrics by methods followed for the application of pure 1-chloro-2,3-epithiopropene. The mole ratios of thio compounds and epichlorohydrin and the various solvents are indicated in the tables.

Determination of Anion-Exchange Properties. DEAE-cottons before and after treatment with thiirane were ground to pass a 20-mesh screen, regenerated to the base form with 0.05M NaOH, and dried over P₂O₅ under vacuum to constant weight before elemental analyses and anion exchange capacities were determined as described previously.¹⁵ All pH measurements were with a Beckman Model GS pH meter to ± 0.05 pH units on samples containing approximately 0.8 meq of replaceable anion in 1M NaCl in nitrogen atmospheres in specially designed titration flasks.

Textile Testing

Conditioned (dry) wrinkle recovery angles were determined by the Monsanto method,¹⁶ and wet wrinkle recovery angles as previously described.¹⁷ Nitrogen was determined by the Kjeldahl method. Sulfur and chlorine contents were determined by chemical analyses and x-ray fluorescence techniques. The two methods gave similar analyses for sulfur and chlorine percentages with similar reproducibility. The percentages used in tables and figures were obtained by x-ray fluorescence.

Microscopical Examinations

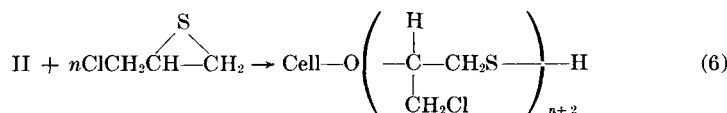
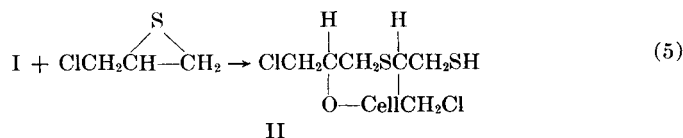
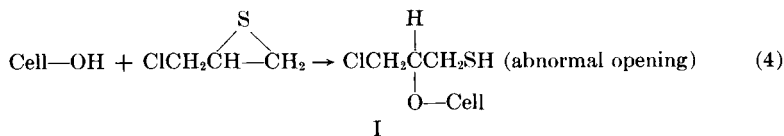
Methods of optical microscopy were used to observe behavior of whole fibers removed from finished fabrics and immersed for 30 min in 0.5M cupriethylenediamine hydroxide (cuene). To derive more information, electron micrographs of ultrathin cross sections of fibers were made after application of layer expansion techniques described previously.¹⁸

RESULTS AND DISCUSSION

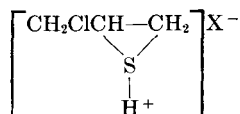
Use of polar solvents and base catalysts favor opening of thiiranes analogous to the opening of the corresponding oxiranes. It is only in presence of acids that abnormal ring opening, that is cleavage of the bond between S and the secondary carbon atom, is favored.¹⁹ In presence of slightly basic conditions, the RS⁻ ion is a weaker base than the corresponding RO⁻ ion, but the greater nucleophilicity of RS⁻ as compared to RO⁻ results in a nucleophilic attack of RS⁻ on unopened thiirane to form polymers. Usu-

ally with the corresponding epoxide, termination by ROH rather than polymerization occurs.

Equation sequence (4)–(6) is illustrative of the reaction between cellulosic hydroxyls and 1-chloro-2,3-epithiopropene.



Equation sequence (4)–(6) is favored by neutral or acidic conditions. With acid catalysis, the oxygen analog has less tendency than the thirane to form an “onium” ion. The initial step in the acid catalyzed reaction is the formation of the sulfonium ion,



With such abnormal ring openings, the chlorine atoms should not be lost through a dehydrohalogenation step because the chlorine and sulfhydryl groups are not adjacent. With base catalysis, which favors normal ring opening followed by dehydrohalogenation,²⁰ the chlorine content should be very low compared to the sulfur content of the finished fabric.

Reactions of 1-Chloro-2,3-epithiopropene with Cotton and DEAE-Cotton in Absence of Added Catalyst

Results of reactions of neat 1-chloro-2,3-epithiopropene with cotton and DEAE-cottons for 8 hr at 26 and 55°C are summarized in Table I. As nitrogen content of fabric increased, add-ons and corresponding percentages of sulfur and chlorine decreased, thus indicating reaction at sites other than at tertiary amine groups. Unlike epichlorohydrin, the thio compound reacted with unmodified cottons without addition of catalyst. There is the possibility of traces of acid catalyst (H₂SO₄) present from synthesis of this compound, but this acid did not cause epichlorohydrin to add to cotton. However, 1-chloro-2,3-epithiopropene has been shown to open abnormally in presence of aqueous HCl.¹⁹ Largest increases in wet recovery angles were obtained at lowest add-on in the DEAE fabric of least sulfur content.

Largest increases in dry wrinkle recovery were obtained with DEAE-cotton of highest nitrogen content and with unmodified cotton. In spite of the large add-ons in some instances, wet recoveries were never as high as those obtained with comparable add-ons of epichlorohydrin. With comparable add-ons of epichlorohydrin to DEAE-cottons,⁶ dry recovery angles are larger and always greater than wet recovery angles. The molar ratio of S/Cl varied somewhat with fabric and with temperature but was approximately $4/1$ for all.

TABLE I
Effect of Temperature on Reaction of 1-Chloro-2,3-epithiopropene
with Cottons (8 Hr^a)

Fabric	Temp, °C	Add-on, wt-%	Sulfur, %	Chlorine, %	Wrinkle recovery (W+F) ^o		Moisture %	
					Dry	Wet	Content	Regain
Control	—	—	—	—	150	160	—	—
Unmodified	26	9.03	3.45	1.63	188	175	—	—
Unmodified	55	17.60	4.55	2.12	190	202	—	—
Control DEAE	—	—	—	—	224	182	5.96	6.34
DEAE(0.44% N)	26	3.60	1.66	0.56	209	196	—	—
DEAE(0.44% N)	55	5.06	3.14	0.98	201	196	—	—
Control DEAE	—	—	—	—	181	182	11.5	13.0
DEAE(0.85% N)	26	1.25	0.29	0.08	218	261	7.94	8.63
DEAE(0.85% N)	55	0.17	0.94	0.24	233	230	8.15	8.88

^a 80 × 80 cotton or DEAE-cotton immersed in pure 1-chloro-2,3-epithiopropene for 8 hr, washed, dried, and air-equilibrated before analyses.

In Figure 1 are shown electron micrographs of ultrathin cross sections prepared by layer expansion techniques with methacrylate. The expanded cross section of a fiber removed from the DEAE-cotton of 0.44% N which had been treated with 1-chloro-2,3-epithiopropene up to a 3.14% S content (Fig. 1a) is very similar to that of the original DEAE-cotton fiber shown in Figure 1b. DEAE-cotton which had been similarly treated to a like add-on with the oxygen analog, epichlorohydrin yielded solid cross sections as shown in Figure 1c. Figure 1d is representative of the unmodified cotton treated with 1-chloro-2,3-epithiopropene neat to a 4.55% S content. There is some evidence in Figure 1d of reaction at fiber edges.

Reaction of 1-Chloro-2,3-epithiopropene at pH 8.

In another series of experiments, the epithiirane was adjusted to pH 8 with NaOH and then used to treat cotton and DEAE-cotton (0.85% N). If normal opening of the 1-chloro-2,3-epithiopropene to form a 1-chloro-2-thiolpropane occurred,^{20,21} dehydrohalogenation would occur immediately in the pH range 7.5–9.5, and finished products should have negligible chlorine contents. With DEAE-cotton, the S/Cl molar ratio was still 4, and the only effect of increase in pH was to lower the dry recovery angles

from 233 to 193(W + F)^o. With the unmodified cotton, the add-ons of S and Cl were reduced to 1.36 and 1.33%, respectively, and the S/Cl molar ratio to 1; but there were no changes in wrinkle recoveries.

DEAE-Cotton Reactions in Alcoholic Solutions of 1-Chloro-2,3-epithiopropene

Results of refluxing DEAE-cotton (0.85% N) in a 10% solution of 1-chloro-2,3-epithiopropene in either *n*-octyl or *tert*-pentyl alcohol are given in Table II. The most unexpected result was the sulfur to chlorine ratio of 0.5:1 as compared to 4:1 when the reagent was used neat. Although wet recovery angles of 260(W + F)^o were obtained at approximately 3% add-ons of the thiirane to DEAE-cotton, conditioned recovery angles were not improved over the control values. This is in contrast to results of DEAE-cottons with epichlorohydrin reacted out of these two alcohols,⁶ where higher dry than wet recoveries are obtained and finished fabrics had negligible chlorine contents.

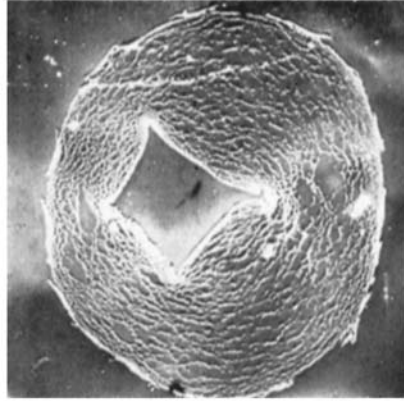
TABLE II
Reaction of 10% 1-Chloro-2,3-epithiopropene at Reflux
in Alcohols with DEAE-Cotton (0.85% N)

Time, hr	Alcohol	Sulfur, %	Chlorine, %	Wrinkle recovery (W+F) ^o	
				Dry	Wet
4	Octyl	0.58	1.14	159	226
	<i>tert</i> -Pentyl	0.64	1.23	158	223
8	<i>tert</i> -Pentyl	0.89	1.79	165	259
	(DEAE-cotton control)	—	—	181	182

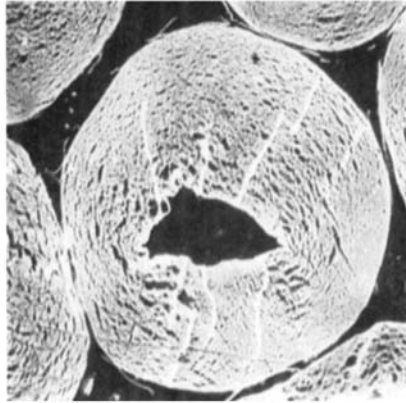
Potentiometric titration curves of a DEAE-cotton modified with 1-chloro-2,3-epithiopropene, the original DEAE-cotton, the DEAE-cotton converted to a quaternary base cellulose exchanger, and a DEAE-cotton finished with epichlorohydrin were compared. All modifications were performed in *tert*-pentanol. Typical curves in Figure 2 show conversion of the DEAE-cotton reacted with epichlorohydrin to a quaternary-base strong anion exchanger. DEAE-cottons modified with the sulfur analog were still weak-base exchangers like the original DEAE-cottons. Weak-base titration curves indicate DEAE-cotton reacted with the thiirane at cellulosic hydroxyl groups rather than quaternizing at tertiary amine groups as occurs with the oxygen analog and DEAE-cotton.

Reactions of 1-Chloro-2,3-epithiopropene and Fabrics Prepadded with Base

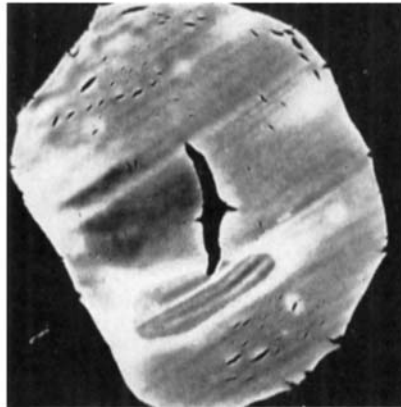
Typical data for cotton or DEAE-cotton (0.85% N) prepadded with 15% NaOH to 100% pickup and then reacted at 100°C for 1 hr with neat 1-chloro-2,3-epithiopropene or in *n*-octanol solution of 10% thiirane are



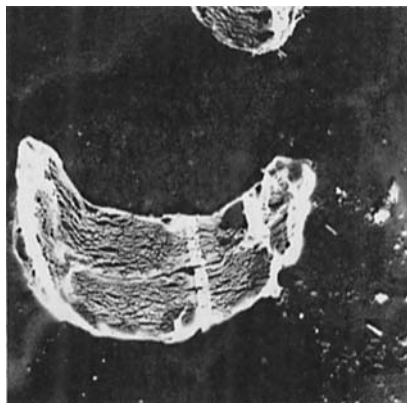
(a)



(b)



(c)



(d)

Fig. 1. Typical expansion patterns of modified cottons: (a) DEAE-cotton subsequently modified with 1-chloro-2,3-epithiopropane to give 3.14% S, low wet and low dry recovery angles; (b) DEAE-cotton control; (c) DEAE-cotton subsequently modified with oxygen analog, epichlorohydrin, to give fabric with high wet and high dry recovery; (d) unmodified cotton reacted with 1-chloro-2,3-epithiopropane to give 4.55% S, low wet and low dry recovery angles.

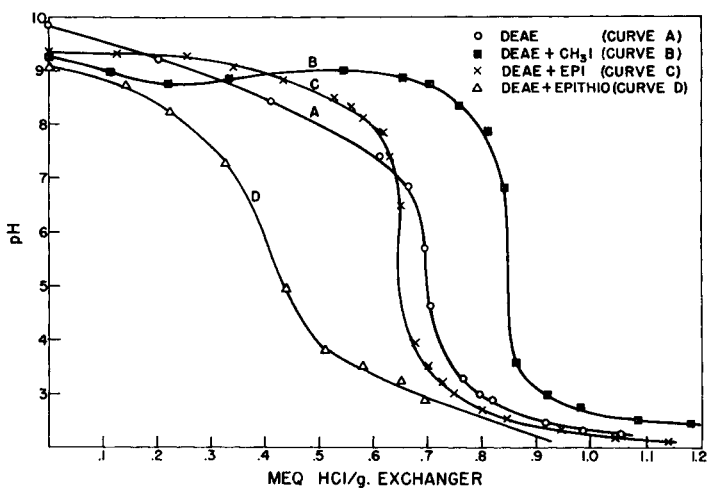


Fig. 2. Potentiometric titration curves for (A) the reaction product of DEAE-cotton and epichlorohydrin; (B) the weak base anion exchangers DEAE-cotton; (C) the quaternary base anion exchanger prepared from cotton and glycidyltrimethylammonium chloride; (D) the reaction product of DEAE-cotton and 1-chloro-2,3-epithiopropane.

recorded in Table III. Increase in wet wrinkle recovery with add-on or sulfur content resulted with both cotton and DEAE-cotton. With DEAE-cottons, add-on was greater with octanol solution than with thiirane used neat, and the S/Cl mole ratio was the same (9/1). The sulfur content of approximately 4% for the DEAE-cotton was much higher than that ob-

tained with thiirane used neat or in the absence of base when an octanolic solution of the thiirane was used. With base pretreatments, the thio analog imparted recoveries very similar to those imparted by epichlorohydrin. Only wet recovery angles were improved, but the improvement with the thiirane at a given add-on was less than observed with epichlorohydrin.

TABLE III
Effect of Prepadding Fabric with Alkali on Reaction
with 1-Chloro-2,3-epithiopropene^a

Fabric	Sulfur, %	Chlorine, %	Wrinkle recovery (W+F) ^o	
			Dry	Wet
Unmodified	1.31	0.17	195	239
DEAE (0.85% N)	1.46	0.18	143	263
Unmodified ^{2/b}	1.55	0.07	146	255
DEAE (0.85% N) ^{2/}	3.84	0.48	196	289
Cotton control	—	—	150	160
DEAE-cotton control	—	—	181	182

^a Fabric padded with 15% aqueous NaOH to 100% pickup and reacted at 100°C for 1 hr either neat or in octanol containing 10% 1-chloro-2,3-epithiopropene.

^b In *n*-octanol.

In Figure 3a is shown the electron micrograph of an ultrathin cross section of a fiber from a DEAE-cotton of 0.80% N which had been padded with 15% aqueous NaOH to 100% pickup and treated with 1-chloro-2,3-epithiopropene at 100°C to 2.80% S content. The fabric had high wet, 258(W+F)^o, and low dry, 157(W+F)^o, recovery angles. The expanded cross section is similar to that of the original DEAE-cotton fiber shown in Figure 3b. The DEAE-cotton similarly prepadding with base and treated with the oxygen analog, epichlorohydrin, and then subjected to layer expansion shows solid cross sections as shown in Figure 3d. Figure 3c is the cross section of a fiber from the same DEAE-cotton treated similarly to the others except for the use of a 10% solution of the thiirane in *n*-octanol. This sample, with 3.84% S, exhibits a solid cross section with ragged edges which have swollen and ruptured. The high wet, 289(W+F)^o, low dry, 196(W + F)^o, recovery angles and solid cross section are similar to results obtained with epichlorohydrin in octanol.

Reactions of DEAE-Cottons and Cotton with Thiiranes Prepared *in Situ*

1-Chloro-2,3-epoxypropane, 1,1-dichloro-2,3-epoxypropane, or 1,1,1-trichloro-2,3-epoxypropane was reacted with thiourea (in the ratio of 9 parts oxirane to 1 part thiourea) to produce the corresponding thiirane *in situ* within the fabric in excess oxirane as solvent. Results of reactions carried out at 26°C for 3 hr, 50°C for 1 hr, or 100°C for 5 min are presented in Table IV. Data for samples reacted with the dichloro compound are lacking due to the formation of a sticky brown polymeric material which,

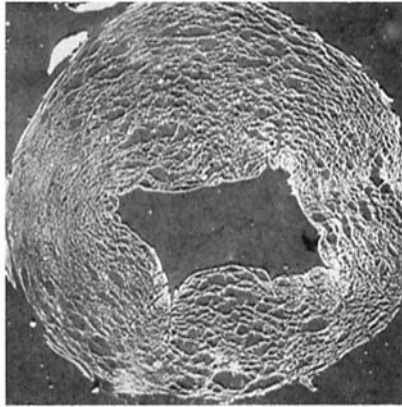
though somewhat soluble in benzene, could not be completely extracted. At 26°C, there was no reaction with epichlorohydrin and slight reaction with the trichloro compound. At 100°C, the trichloro compound was so reactive that samples were carbonized. The odor of all polymeric materials was skunklike and persistent. The 1-chloro-2,3-epoxypropane reaction was easiest to control and gave S:Cl ratios about 3:1 compared to about 1:3 for *in situ* reactions with the trichloro compound. Dry and wet wrinkle recovery angles of approximately 250(W+F)° resulted when DEAE-cotton was reacted with the monochloro compound at both 50 and 100°C. At 100°C, even unmodified cottons showed an add-on and improvement in wet and dry recovery with the monochloro compound. There was no improvement in wrinkle recovery with even higher add-ons of the trichloro compound. In addition to reaction with thiiranes formed *in situ*, the DEAE-cottons can react with oxiranes. However, in the absence of thiourea, DEAE-cottons reacted with epichlorohydrin at 95°C have higher wrinkle recovery and acquire higher dry, 300(W+F)°, than wet recovery, 270(W+F)°, angles. Also, when DEAE-cottons react with epichlorohydrin alone, there is only a negligible chlorine content in finished fabrics.⁶

TABLE IV
In Situ Production of Thiiranes by Reaction of Fabrics
with Chlorinated Epoxypropanes and Thiourea^a

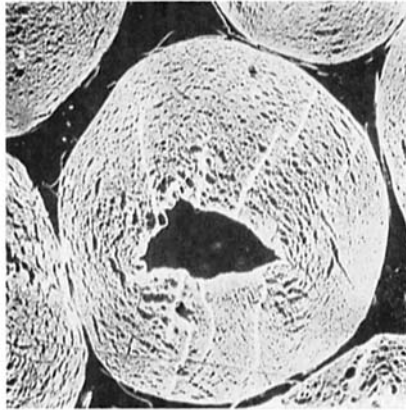
Fabric	2,3-Epoxypropane	Temp, °C	Time, hr	Sulfur, %	Chlorine, %	Wrinkle recovery	
						Dry	Wet
Unmodified	1,1,1-Trichloro	26	3	0	0.05	185	180
DEAE-cotton	1,1,1-Trichloro			0.10	0.32	195	219
Unmodified	1-Chloro	50	1	0.14	0.04	178	185
DEAE-cotton	1-Chloro			0.54	0.07	246	243
Unmodified	1,1,1-Trichloro			2.41	4.02	152	173
DEAE-cotton	1,1,1-Trichloro			1.27	10.61	175	198
Unmodified	1-Chloro	100	0.08	0.69	0.31	226	218
DEAE-cotton	1-Chloro			1.86	0.36	244	238
Unmodified control						150	160
DEAE-cotton control						181	182

^a Cotton or DEAE-cotton reacted in epoxypropane-thiourea (9:1).

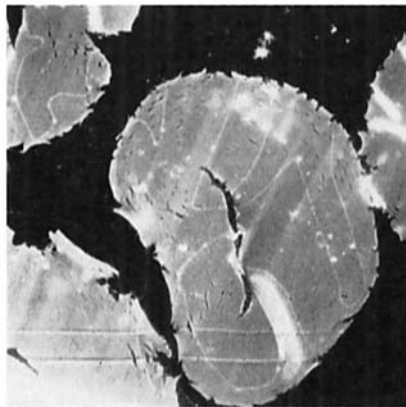
In Figures 4a and 4b are the expansion patterns for the DEAE-cotton and modified cotton treated with thiirane prepared *in situ* at 100°C, respectively. The solid cross section in 4a shows partially fused or dissolved areas with some swelling, and ragged edge indicative of a ruptured primary wall which has been noticed in other DEAE-cottons. The layering pattern in Figure 4b is similar to that of a mercerized cotton showing some incipient layering but with some fibrils fused nonuniformly.



(a)



(b)



(c)

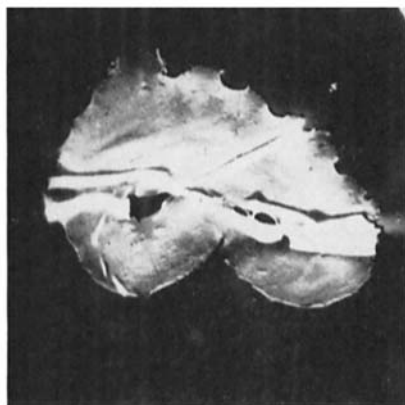


(d)

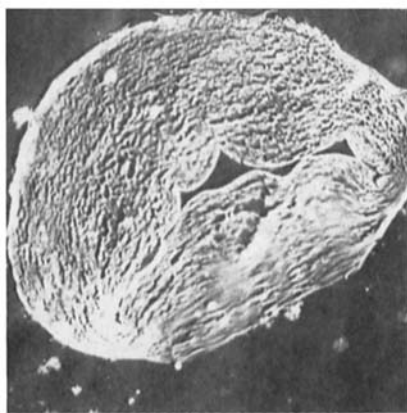
Fig. 3. Typical expansion patterns of modified cottons: (a) DEAE-cotton prepadded with 15% aqueous NaOH and reacted with 1-chloro-2,3-epithiopropene at 100°C to give fabric of 2.8% S, high wet and low dry recovery; (b) original DEAE-cotton of low dry and low wet recovery; (c) DEAE-cotton prepadded with 15% NaOH and reacted with octanolic solution of 10% 1-chloro-2,3-epithiopropene to give fabric of 3.8% S, high wet and low dry recovery; (d) DEAE-cotton prepadded with 15% aqueous NaOH and reacted with epichlorohydrin at 95°C to give high wet and low dry recovery.

Reaction of Cotton and DEAE-Cotton with 1-Chloro-2,3-epithiopropene Prepared *in Situ* in *n*-Octanol

Cotton or DEAE-cotton (0.85% N) was reacted at 100°C. for 1 hr with an equimolar mixture of epichlorohydrin and either thiourea or KSCN diluted to a 20 wt-% solution in *n*-octanol. As shown in Table V, the S content was higher with thiourea than with KSCN, and DEAE-cottons had greater S content than cotton. Prepadding with 15% aqueous NaOH increased S content of cotton more than that of DEAE-cotton. The slight change in sulfur add-on in the case of DEAE-cotton indicates that the basic character of the amino group in DEAE-cotton can catalyze the reaction. In the absence of base pretreatment, both dry and wet wrinkle recoveries of the DEAE-cottons were increased by *in situ* formation and reaction with the thiopropene, but there was little change in recovery properties of the unmodified cottons. Use of aqueous NaOH pretreatments resulted in only wet wrinkle recovery properties with the DEAE-cottons but high dry as well as high wet wrinkle recovery angles for the finished cottons. In Figure 5 are shown layer expansion patterns of a DEAE-cotton treated with a mixture of epichlorohydrin and thiourea in *n*-octanol at 100°C to an 0.8% S content (Fig. 5a) and of an unmodified cotton prepadded with base and then similarly treated to an 0.80% S content (Fig. 5b). Both of the finished fabrics had dry recovery angles of approximately $255(W+F)^{\circ}$ and slightly higher wet recovery angles. The solid cross sections depicted in Figure 5b show no evidence of layering; in Figure 5a there was no layering at the edges but some evidence of attempted layering



(a)



(b)

Fig. 4. Typical expansion patterns of modified cottons: (a) DEAE-cotton reacted with 1-chloro-2,3-epithiopropene produced *in situ*, fabric had 1.9% S, high dry and wet recovery angles; (b) unmodified cotton treated as above (a) to 0.7% S and moderate dry and wet recovery angles.

near the center. This tendency toward layering near the center contrasted to layering at edges only when DEAE-cotton was treated with epichlorohydrin in *n*-octanol in the absence of thiourea.⁶ Also, in the absence of thiourea, DEAE-cottons finished with epichlorohydrin had higher dry than wet wrinkle recovery angles. Both high dry and high wet wrinkle recovery angles in the case of unmodified cotton prepped with base may be attributed to S-S crosslinks. Unmodified cottons, reacted similarly with epichlorohydrin, acquire high wet recovery only. Unmodified cottons had negligible chlorine contents compared to those of the finished DEAE-cottons. The S/Cl mole ratios of products prepared from these *in situ* reactions were similar to those of products prepared with thirane in *n*-octanol.

TABLE V
In Situ Production and Reaction of 1-Chloro-2,3-epithiopropene (Epi)
 in *n*-Octanol^a

Reactants	Sulfur, %		Chlorine, %		Wrinkle recovery (W+F) ^o			
	Un- modi- fied	DEAE	Un- modi- fied	DEAE	Dry		Wet	
					Un- modi- fied	DEA	Un- modi- fied	DEAE
Epi + thiourea	0.25	0.82	0.09	0.20	188	254	217	265
Epi + KSCN	0.12	0.43	0.01	0.82	189	212	210	263
NaOH, Epi + thiourea ^b	0.80	0.93	0.03	0.15	259	160	281	245

^a Unmodified cotton or DEAE-cotton reacted at 100°C. for 1 hr in equimolar mixture of epichlorohydrin (Epi) and sulfur compound diluted to 20 wt-% solution in *n*-octanol.

^b Fabric prepped with 15% aqueous NaOH and reacted as above.

Effects of tetramethylurea, 1-cyclohexyl-1,3(2-morpholinoethyl) thiourea, and KSCN as compared to that of thiourea used in preparation of 1-chloro-2,3-epoxypropane *in situ* in octanol are shown in Table VI. Fabric samples, either plain or prepped in 15% aqueous NaOH, were immersed in octanolic solutions which were 0.1M with respect to both epichlorohydrin and the thio compound. Reactions were for 8 hr at 55°C. With prepped fabrics, add-ons of sulfur were higher than obtained with other methods of application and, with the exception of the cyclic thiourea, sulfur contents of finished cottons were less than those of finished DEAE-cottons. In samples not pretreated with base, the sulfur contents of the finished DEAE-cottons were lower than those of the finished cottons. In spite of high sulfur contents in fabrics prepped with base, dry recovery was not improved. Greatest improvement in wet recovery was after pretreatments with base; and only DEAE-cottons showed improvement in wet recovery angles in absence of base pretreatments.

Data in Table VII compare fabric properties obtained when cotton and DEAE-cottons were reacted with 0.1M solutions of epichlorohydrin in *n*-octanol which was also 0.1M with respect to the urea, tetramethylurea, or the respective thio analogs. With both thioureas and their oxygen analogs, epichlorohydrin imparted only wet wrinkle recovery to DEAE-cotton in the absence of other base. With aqueous base pretreatments epichlorohydrin imparted to both cotton and DEAE-cottons high wet wrinkle recovery with all ureas, and some dry recovery to cotton. Large sulfur contents did not contribute to improved dry recovery.

Oxidation and Reduction of Sulfur Attached to Cellulosic Fabrics

Because of the ease of oxidation of sulfhydryl groups, an equilibrated fabric sample being tested for wrinkle recovery would be expected to have

TABLE VI
In Situ Production of 1-Chloro-2,3-epithiopropane in *n*-Octanol
 by Reaction of Epichlorohydrin with Different Thio Compounds^a

This compound	Cotton fabric	Sulfur, %		Chlorine, %		Wrinkle recovery (W+F) ^c			
		Plain	Prepad ^b	Plain	Prepad ^b	Dry		Wet	
						Plain	Prepad ^b	Plain	Prepad ^b
Thiourea	Unmodified	0.65	3.42	0.10	0.11	195	180	190	287
	DEAE(0.85% N)	0.35	8.18	0.14	0.14	143	113	266	274
Tetramethyl thiourea	Unmodified	0.15	5.34	0.03	0.15	169	215	129	231
	DEAE(0.85% N)	0.18	9.47	0.07	0.30	193	151	261	273
Cyclic thiourea ^c	Unmodified	1.09	1.62	0.08	0.12	195	215	166	301
	DEAE(0.85% N)	0.14	0.94	0.13	0.28	205	177	225	306
KSCN	Unmodified	0.78	3.51	0.04	0.02	195	192	133	202
	DEAE(0.85% N)	0.28	7.90	0.10	0.18	192	153	231	253
	Unmodified cotton							150	160
	DEAE control					181		182	

^a Reaction conditions: 0.1 mole each of epichlorohydrin and thio compound, 100 ml octanol, 55°C, 8 hr.

^b 1-Cyclohexyl 1-3(2 morpholinoethyl) thiourea.

^c Prepped with 15% aqueous NaOH to 100% takeup before reaction as indicated in footnote a.

TABLE VII
Comparison of Ureas and Thioureas Reacting *in Situ* with
Epichlorohydrin and Fabric^a

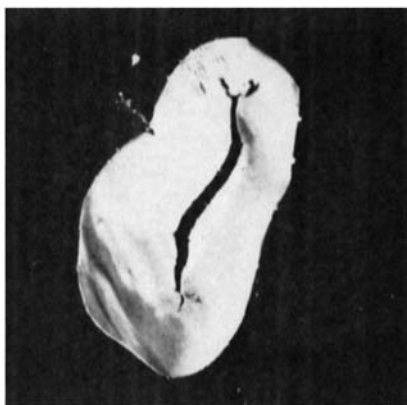
Urea or thiourea	Fabric	Sulfur, %				Chlorine, %				Wrinkle recovery (W+F) ^o			
		Urea		Thiourea		Urea		Thiourea		Dry		Wet	
		Urea	Thiourea	Urea	Thiourea	Urea	Thiourea	Urea	Thiourea	Urea	Thiourea	Urea	Thiourea
Urea	Unmodified	—	0.65	0.03	0.10	169	195	169	190	169	190		
	DEAE(0.85% N)	—	.35	.06	.14	198	143	258	266	258	266		
Tetramethyl- urea	Unmodified	—	.15	.01	.03	176	169	176	129	176	129		
	DEAE(0.85% N)	—	.18	.06	.07	218	193	247	261	247	261		
Urea	Unmodified ^b	—	3.42	.02	.11	229	180	318	287	318	287		
	DEAE(0.85% N) ^b	—	8.18	.38	.14	Stiff	113	Stiff	274	Stiff	274		
Tetramethyl- urea	Unmodified ^b	—	5.34	.03	.15	207	215	302	231	302	231		
	DEAE(0.85% N) ^b	—	9.47	.38	.30	Stiff	151	Stiff	273	Stiff	273		
	Unmodified control						(150)		(160)		(160)		
	DEAE-cotton control						(181)		(182)		(182)		

^a Unmodified cotton or DEAE-cotton reacted at 55°C for 8 hr in octanolic solution 0.1M with respect to epichlorohydrin and 0.1M with respect to urea or thiourea.

^b Fabrics prepadded with aqueous 15% NaOH and then reacted as above.



(a)



(b)

Fig. 5. Typical expansion patterns of modified cottons: (a) DEAE-cotton reacted with 1-chloro-2,3-epithiopropene produced *in situ* in *n*-octanol at 100°C, fabric had 0.8% S, high dry and wet recovery angles; (b) unmodified cotton treated as (a) except pre-padded with base, fabric had 0.8% S, high dry and wet recovery angles.

disulfide bands. Nevertheless, to assure complete oxidation of sulfhydryl groups, all finished fabrics were oxidized in a 0.5% aqueous solution of KBrO_3 for 24 hr. The disulfide bonds were subsequently reduced by a 54% aqueous solution of ammonium thioglycolate. Effects on wrinkle recoveries are presented in Table VIII.

Oxidation generally raised the dry recovery by 20° for DEAE-cottons and approximately 30° for cottons having high sulfur content. Reduction lowered the dry recovery again in every case except the cotton which had a very low sulfur content. Changes in wet recoveries followed the same general pattern although they were less consistent. The general implication is that sulfhydryl groups have been added as pendant groups, and that

TABLE VIII
Effects of Oxidation and Reduction on Wrinkle Recovery angles of
Cellulose Fabrics Modified with 1-Chloro-2,3-epithiopropene^a

Starting fabric	Sulfur, %	Chlorine, %	Wrinkle recovery (W + F) ^o					
			Dry			Wet		
			Start	Oxi- dized	Re- duced	Start	Oxi- dized	Re- duced
DEAE-cotton (0.85% N)	0.64	1.23	159	183	170	223	260	265
	0.89	1.79	157	187	165	228	253	230
	5.70	0.22	156	173	148	250	270	256
	8.29	0.14	183	206	191	311	304	272
Unmodified cotton	0.15	0.03	169	178	179	129	159	143
	0.78	0.04	195	202	193	173	178	179
	3.42	0.11	180	214	187	287	289	278
	7.90	0.02	192	222	188	202	309	256

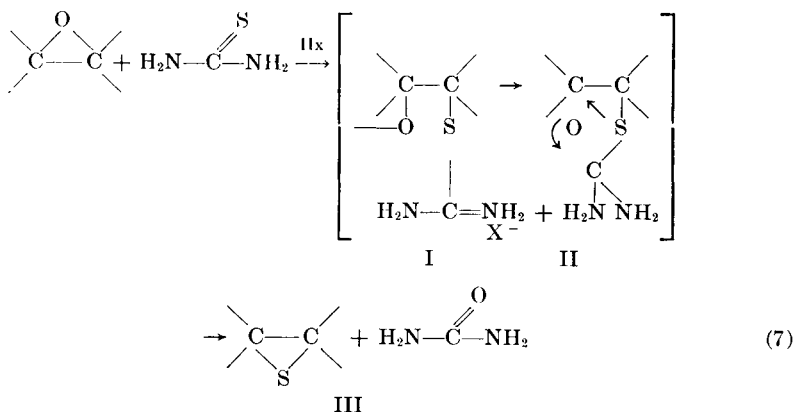
^a 0.5% Aqueous KBrO₃, 24 hr, 26°C for oxidation of SH groups; 54% aqueous ammonium thioglycolate, 24 hr, 26°C for reduction of S-S groups.

these groups can be crosslinked by mild oxidation and the crosslinks broken by mild reduction.

SUMMATION

Obviously, different mechanisms were followed in the instances of epichlorohydrin and its sulfur analog whether used neat or in alcoholic solutions. Whereas epichlorohydrin did not react with unmodified cotton in the absence of a catalyst, the thio analog was acidic enough to react with cotton. With DEAE-cotton, which contains basic or nucleophilic groups, epichlorohydrin reacted to impart high wet and high dry recovery angles; it quaternized some of the tertiary amino groups, and the absence of covalent chlorine indicated normal opening of the oxirane ring followed by dehydrohalogenation. The cross sections of the fibers showed no expansion into layers; the fibers were insoluble in cuene. With the thio analog, the finished DEAE-cottons had covalent chlorine, low dry and low wet recovery angles, no quaternary-base groups, and the fiber cross sections were expanded. It appears as if normal ring opening, resulting in loss of covalent chlorine and difunctionality of the oxirane or thiirane; favors improvement in wet and dry recovery. With excess base catalysis, 1-chloro-2,3-epithiopropene reacted with both DEAE-cotton and with unmodified cotton to give high wet recovery only and negligible chlorine contents, indicating more normal than abnormal ring openings.

The mechanism²² for the formation of a thiirane from the reaction of an oxirane with either a thiocyanate or a thiourea is illustrated with thiourea in eq. (7).



In the presence of aqueous base, the thiirane is not isolated, but a 2-hydroxyethanethiol is formed. Both dry and wet recovery angles of approximately $250(W+F)^\circ$ were imparted to DEAE-cottons by reaction with epichlorohydrin in the presence of thiourea in the temperature range from $50\text{--}100^\circ\text{C}$. These fabrics had relatively low chlorine contents and electron micrographs showed no layering in cross sections prepared by the expansion techniques. Even unmodified cottons showed some improvement in wet and dry recovery by the use of the *in situ* formation of 1-chloro-2,3-epithiopropene. Use of external aqueous NaOH to prepad unmodified cotton before its reaction with 1-chloro-2,3-epithiopropene prepared *in situ* resulted in greatest improvement in both dry and wet recovery angles. This finished cotton with high recovery angles had negligible chlorine contents and showed no evidence of layering when subjected to layer expansion techniques.

In spite of large sulfur contents given to both cotton and DEAE-cottons by 1-chloro-2,3-epithiopropene used neat or prepared *in situ* in the presence or absence of external base catalysts, the dry and wet recovery angles of finished fabrics could not be dramatically lowered by reduction or raised by oxidation of the sulfhydryl groups to disulfide bonds. Whereas larger add-ons of the thio analog than of epichlorohydrin could be added to DEAE-cotton in absence of a base or to cotton or DEAE-cotton in the presence of a base, the improvements in wet recovery angles were greater with epichlorohydrin than with the thio analog. In particular, it was easier to impart high dry recovery to DEAE-cotton with epichlorohydrin than with 1-chloro-2,3-epithiopropene.

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