

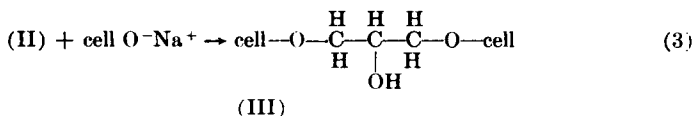
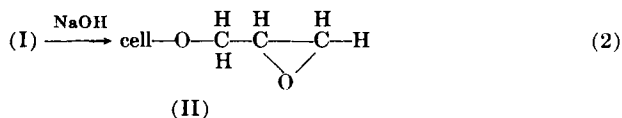
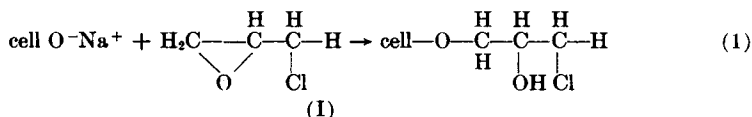
The Action of Epichlorohydrin in the Presence of Alkalies and Various Salts on the Crease Recovery of Cotton*

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INTRODUCTION

Cellulose-Epichlorohydrin Reaction

Chemical reaction between alkali cellulose and epichlorohydrin was first observed in 1921 by Dreyfus¹ who visualized reaction at the chloro group with the resultant formation of cellulose ethers and sodium chloride.²⁻⁴ Later⁵ he claimed that reaction occurred at the oxirane oxygen only under neutral or acidic conditions and reported the formation of chlorohydroxy-cellulose ethers in the absence of alkali.³ In 1929 Lilienfeld⁶ patented the process, as it increased fiber luster and elastic feel. Brown and Steger⁷ in 1953 claimed that dimensional stability and insolubility in cuprammonium hydroxide resulted from treatment of cellulosic fabrics with epichlorohydrin or its glycerol halohydrin precursors in the presence of strong alkali. Imparting of crease resistance, and of the wet variety only, was first mentioned in the Deering-Milliken patents.⁸⁻¹⁰ Others¹¹⁻¹³ have discussed the reaction in regard to improvement in wet crease recovery, and some^{7,12,13} have postulated that cellulose was crosslinked according to the following steps.



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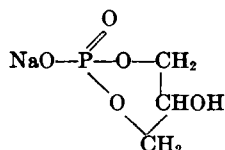
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From recent work in this laboratory¹⁴ it appears that dry as well as wet crease recovery would result if such a proposed mechanism were followed when the cellulosic fibers were swollen to only a very limited extent. The idea of dietherification of cellulose with epichlorohydrin probably stems from the experiments of Fairbourne et al.¹⁵ He demonstrated the formation of epichlorohydrin as a reaction product when either 1,2-dichloro-3-propanol or 1,3-dichloro-2-propanol was treated with 1 equiv. of caustic in ethyl alcohol, and the formation of the monoethyl ether and the diethyl ether of glycerol when an excess of 1 equiv. of NaOH was used. It should be noted that Fairbourne did not investigate the use of polyols or cellulose, and that investigations in this laboratory indicate that epichlorohydrin does not add to alkali cellulose in ethanol. Indication of the difunctionality of epichlorohydrin is given in the Maxwell patent,¹⁶ which deals with its use in conjunction with other etherifying agents such as dimethyl sulfate and offers as evidence only viscosity increases in the resultant soluble cellulose ethers.

Effect of Anions on Epichlorohydrin Reactions

Recently McEwen,¹⁷ Van der Werf,¹⁸ and Ingham¹⁹ and their associates reported that bimolecular nucleophilic reactions between azide ions and epoxides in aqueous dioxane solutions of sodium azide resulted in the formation of azido alcohols. A 55% yield of 1,3-diazido-2-propanol was obtained from epichlorohydrin. Ingham proved that the azide ion first opens the epoxide ring and generates alkali in so doing. By removing the alkali, he isolated the 1-azido-3-chloro-2-propanol. Dehydrohalogenation of the monoazide gave glycidyl azide, which reacted with azide ions to form the 1,3-diazido-2-propanol. In contrast, the reaction of epichlorohydrin with sodium hydroxide results in replacement of both chloro and epoxide groups. Hill and Fischer²⁰ reported a 60% yield of epichlorohydrin from 1,3-dichloro-2-propanol in concentrated (33%) solution of sodium hydroxide at 12°C., and only an 11% yield at 25°C. where the main product is glycerol.

A cyclic compound



said to be analogous to the isopropylidene glycerol of Fischer and Pfähler,²¹ was isolated from the reaction mixture of trisodium phosphate and epichlorohydrin by Bailly²² in 1922, but little use has been made of this reaction. Potassium cyanate also causes epichlorohydrin to undergo a cyclization reaction.^{23,24} Use of sodium bisulfite or sodium sulfite causes the formation of sodium salts of glycerol mono- and disulfonic acid esters.²⁵ Sodium cyanide results in the cyano derivative, if the alkali is removed;

otherwise, cyano derivatives of *p*-dioxane form.²⁶ Although the use of certain silicates as dehydrohalogenating agents has been published,²⁷⁻²⁹ the effects of many of the common alkalies, such as soap builders and detergents, on epoxides, have not been investigated. According to Swain and Scott³⁰ and Petty and Nichols,³¹ the effects of all anions on epoxide ring openings are not very dissimilar.

Earlier work in this laboratory indicated that no reaction between cotton and epichlorohydrin occurred in the absence of a catalyst, or in the presence of hydrogen ions or zinc fluoborate catalysts.^{11,32} Sodium hydroxide far outranked other alkalies or salts in promoting the cellulose-epichlorohydrin reaction, but only wet crease resistance was imparted to the cotton cellulose. Therefore, it was thought that use of sodium azide or other salts capable of causing cyclization reactions of epichlorohydrin might result in a type of cellulose-epichlorohydrin reaction capable of yielding dry crease-resistant as well as wet crease-resistant cottons.

EXPERIMENTAL

Materials

All chemicals were of reagent grade and used without further purification. Epichlorohydrin was obtained from the Shell Development Corporation, and the soluble silicates from the Philadelphia Quartz Company. (Trade names have been used to identify materials used in this work, and such use does not imply endorsement or recommendation by the U.S. Department of Agriculture over other products not mentioned.)

Fabric Treatments

Desized and bleached 80 × 80 cotton printcloth was used throughout. A 5 g. swatch was padded through the desired aqueous salt or alkali solution to an approximate 100% wet pickup. The loosely rolled swatch was then dropped into a graduated cylinder containing approximately 80 ml. of epichlorohydrin or a solution of epichlorohydrin in CCl₄; this was stoppered and held at the desired temperature. When larger pieces of cloth were used, glass netting was wrapped with the swatch. The reaction vessels at 25°C. were agitated on a wrist-action shaker. At the higher temperatures, vessels were placed in a forced-draft oven or oil bath at the desired temperature and occasionally shaken during the reaction time.

At the end of the reaction, the swatches were unrolled, acidified with dilute acetic acid, and washed well in tap water. Epichlorohydrin in the fabric is quickly replaced by the water alone, and could be recovered. Those samples which were reacted in presence of silicates were given a 15 min. soaking in dilute HF followed by copious water washing. The swatches were ironed dry and equilibrated 24 hrs. before tests were made.

Samples were tested by the following ASTM or Federal Specifications Standard Methods: breaking strengths by the strip method (80 thread

count width) on a Scott Tester,^{33a} tearing strengths by the Elmendorf method,^{33b} crease recovery angles by the Monsanto method^{33c} with a 500 g. weight. Total chlorine analyses were determined analytically by the method described by Cheng.³⁴

Yarn Treatments

Skeins of mercerized yarns were immersed in 13% aqueous NaOH, degassed under a bell-jar for 0.5 hr., and centrifugally extracted to a 200% wet pickup before being immersed in either pure epichlorohydrin or a 20% by volume (15.4 wt.-%) solution of epichlorohydrin in CCl₄. After the desired reaction times had elapsed, the yarns were washed with CCl₄, acidified, washed with water, dried at 105°C., and equilibrated before being weighed.

RESULTS AND DISCUSSION

NaN₃ Pretreatments

Preliminary experiments indicated that the Van der Werf reaction,

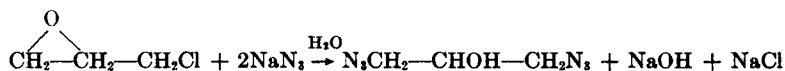


TABLE I
Effect of Concentration of Sodium Azide Solutions on Addition of Epichlorohydrin to Cellulose^a

NaN ₃ , wt.-%	React. time, hr.	Add-on, wt.-%	Temp., °C.	Monsanto crease angles ^c (W + F), deg.	
				Wet	Dry
5	0.5	loss	80	—	—
10	0.5	1.0	80	202	200
10	0.5	1.4	80	242	230
15	0.5	1.2	80	211	190
20	0.5	2.3	80	255	215
20	0.5	3.6	80	278	225
24	0.5	3.8	80	287	220
24	1.0	4.5	80	243	206
24	24.0	2.5	25	270	228
20	20.0	3.1	25	292	220
20	46.0	4.2	25	255	250
10 ^b	24.0	0.2	25	219	174
10 ^b	70.0	1.7	25	217	193
20 ^b	24.0	1.7	25	230	188
20 ^b	70.0	2.6	25	230	183

^a 80² fabric padded twice to 100% wet pickup with NaN₃ solution and then made to react with 100% epichlorohydrin.

^b 20% epichlorohydrin in CCl₄ after pretreatment.

^c Control fabric 166° wet, 196° dry.

proceeds at room temperature, without the use of dioxane, in water alone in 24 hrs. Within a few minutes, the pH rose from an initial value of 8 to 11. Pretreatments of fabric with aqueous NaN_3 solution up to saturation (24%) resulted in only small weight gains from 100% epichlorohydrin at 25 and 80°C. Data in Table I show weight gains of epichlorohydrin and crease angles obtained at 80 and 25°C. after various pretreatments with NaN_3 . Improvements in dry crease resistance at 25°C. were significant only after pretreatments with high concentrations (20–24%) of the azide. Greatest improvement in dry crease resistance resulted after approximately 4% weight gain from 100% epichlorohydrin after a slow reaction (2 days) at 25°C. Faster reactions at 80°C. resulted in weight gains of 1–4% as

TABLE II
Effect of Concentration of NaOH on Addition of Epichlorohydrin to Cellulose^a

NaOH solutions, wt.-%	24 hrs. at 25°C.			0.5 hr. at 80°C.		
	Add-on, wt.-%	Monsanto crease angles ^b (W + F), deg.		Add-on, wt.-%	Monsanto crease angles ^b (W + F), deg.	
		Wet	Dry		Wet	Dry
0.5	—	—	—	loss	186	192
1.0	0.0	173	208	loss	—	—
2.0	0.5	210	204	loss	165	201
3.0	—	—	—	1.7	242	201
4.0	1.4	261	207	1.7	281	209
6.0	4.8	258	193	4.0	281	217
8.0	6.6	261	201	7.5	313	209
10.0	10.1	323	218	10.1	323	218
12.0	—	—	—	14.9	294	218
15.0	29.8	319	231	—	—	—
20.0	52.8	(Sample disintegrated)		—	—	—

^a 80° fabric pretreated by padding twice to 100% wet pickup with aqueous NaOH and then reacting against 100% epichlorohydrin as indicated.

^b Control fabric 166° wet, 196° dry.

compared with the larger weight gains of 4–6% at temperatures above 80°C. However, at the latter temperatures, a gas was evolved throughout a 30 min. reaction interval. At 80°C., use of concentrations of NaN_3 as low as 10% resulted in some improvement of dry crease resistance even at low add-ons of epichlorohydrin. Use of 20% epichlorohydrin in CCl_4 at 25°C. lessened the rate of add-on and gave no improvement in dry crease recovery. In contrast to add-ons after aqueous NaOH pretreatments (Table II), the weight gains from 100% epichlorohydrin after NaN_3 pretreatments are much smaller at 25 and 80°C. Increase in rate of add-on by elevation of 80–90°C. did not improve dry crease resistance as much as did the slower process at 25°C.

NaOH Pretreatments

After a comparison of the effects of NaN_3 pretreatments with those obtained with NaOH, it was decided to alter the caustic concentrations to obtain weight gains similar to the low add-ons obtained with NaN_3 pretreatments. In the case of yarns, the rate of reaction is given by the following equation:

$$d(\text{add-on})/dt = k(\text{OH}^-)(\text{epichlorohydrin})(\text{cellulose})$$

Under the experimental conditions of this investigation, the volume of the organic phase is large compared with the volume of the aqueous phase, and the concentration of the epichlorohydrin can be considered approximately constant. For a given concentration of hydroxyl ions used in the pretreatment, the weight gains on cellulose, y (grams), from either 100% epichlorohydrin or from 20% by volume of epichlorohydrin in CCl_4 , varied linearly with the time of reaction, x (minutes), up to approximately 25% weight gain. The equations of the lines (as determined by the method of least squares) for pretreatments with 13% aqueous NaOH followed by reactions in 20% by volume solutions of epichlorohydrin in CCl_4 at 25, 50, and 65°C., respectively, are as follows:

$$y = 0.036x$$

$$y = 0.222x$$

$$y = 0.508x$$

Similar equations obtained with 100% epichlorohydrin at 25 and 50°C., respectively, are as follows:

$$y = 0.047x$$

$$y = 0.429x$$

At add-ons in excess of 25%, the rates are no longer pseudo zero-order reactions.

In contrast to the slow, mild action with NaN_3 solutions, which are quite alkaline after reaction, it will be noted that with NaOH the reaction is exceedingly vigorous, as judged by fabric weight gains recorded in Table II. Again, epichlorohydrin does not produce dry crease recovery even with dilute base pretreatments and may be acting as a monoepoxide. The data in Tables I and II show that the most interesting differences are the effects on dry crease recovery at approximately equal weight gains, irrespective of time or temperature of reaction. While NaN_3 solutions do not appreciably swell cotton cellulose, the effects of caustic soda are well known. In addition, the solubility of water in epichlorohydrin increases with temperature,³⁵ thus accounting for the extraction of some water and occasionally some salt as observed after reactions at 80°C. Data in Table II show that dry crease angles of only approximately 200° (W + F) were obtained at low weight gains. At add-ons in excess of 15% the dry crease angles were about 230°, but the fabrics were stiff or boardlike and unsuitable for

TABLE III
Fabric Properties Obtained by Partial Removal of Water from Caustic Pretreated Fabric before Application of Epichlorohydrin^a

Treatment	Reaction time, hr.	Weight gain, %		Crease angles (W + F), deg.		Breaking strength, % retained		Tearing strength, % retained		Elongation at break, %	
		Wet	Dry	Wet	Dry	Warp	Fill	Warp	Fill	Warp	Fill
20% epichlorohydrin in CCl ₄ at 25°C.	4	1.7	249	190	102	87	87	87	84	—	—
“	16	3.7	291	225	73	50	59	54	54	6.6	18.3
“	24	3.7	276	209	82	59	52	49	49	—	—
100% epichlorohydrin, at 25°C.	7	1.1	218	187	101	97	75	85	85	8.7	23.1
100% epichlorohydrin, at 80°C.	0.25	1.2	205	191	100	87	74	75	75	8.9	22.3
“	1.0	3.5	286	214	—	—	—	—	—	—	—
Control	—	—	140	192	(46.36 lbs.)	(36.72 lbs.)	(1113 g.)	(773 g.)	(773 g.)	9.3	—

^a 80° fabric twice padded with 2% aqueous NaOH, solvent extracted with acetone and then ether before application of epichlorohydrin.

clothing. Use of dilute NaOH and 100% epichlorohydrin resulted in the desired low weight gains, but there was no improvement in dry crease resistance. Only wet crease resistance was improved, and this could be obtained with only small add-ons. The highest dry crease angle obtained under any of the conditions giving practical add-ons was 218° , and such values have been shown previously to be caused by heating cotton fabric with caustic solutions alone,³⁶ possibly by producing a better rearrangement of the normal hydrogen bonding. In general, slow reaction at 25°C . resulted in weight gains and crease recovery properties comparable to those obtained by the faster reaction at 80°C . Reaction times as long as 4 hrs. at 80°C . after pretreatments with 3% aqueous NaOH resulted in add-ons of 3%, wet crease angles of approximately 300° (W + F), but no improvement in dry crease resistance.

Effect of Water Content on the Epichlorohydrin-Soda Cellulose Reaction

Previous work and experiments presently under investigation in this laboratory^{14,37} have shown the importance of the moisture content of the fabric at the time of the cellulose-diepoxide reaction. Apparently, some water is required to make diepoxides react with soda cellulose, as cotton soda cellulose dried over P_2O_5 for 24 hrs. does not react. Removal of less water from soda-cellulose by shorter exposures to P_2O_5 , by use of less effective dehydrating agents, or by solvent extraction resulted in dry as well as wet recovery in fabrics at low add-ons of butadiene diepoxide. Typical data, recorded in Table III, show that extraction of water after dilute caustic pretreatments before application of epichlorohydrin failed to produce the desired dry crease recovery of cotton. Under similar techniques, dry and wet crease angles of 300° (W + F) were obtained with add-ons of approximately 4% of butadiene diepoxide.³⁷ Similar application of epichlorohydrin from 20% CCl_4 solutions without the extraction of excess water from fabrics pretreated with 2% aqueous NaOH resulted in 2% weight gains after a 16 hr. reaction time, dry crease angles of 200° , and wet crease angles of only 220° . Data in Table III show that removal of water before treatment with epichlorohydrin resulted in an increase of the wet angle to approximately 300° , but of the dry crease angle to only 225° . It was also of interest to note that pretreatment of fabric with methanolic solutions containing 2% NaOH before immersion in 20% epichlorohydrin in CCl_4 for periods up to 8 hrs. resulted in negligible weight gains and no improvements in wet or dry crease resistance. Again, similar experiments with butadiene diepoxide resulted in dry and wet crease-resistant fabrics.

Salts as Catalysts

A number of salts in aqueous solutions varying from 15 to 25% by weight were used as pretreatments to catalyze the cellulose-epichlorohydrin reactions at 25 and 80°C . Salts such as NaCl, CaCl_2 , KI, and $\text{Na}_2\text{S}_2\text{O}_3$ caused small weight gains (2%) but little improvement in wet or dry crease

resistance. The reaction is apparently too slow. The only improvement noted in wet crease resistance ($250^{\circ} \text{W} + \text{F}$) was with saturated NaCl solution used as pretreatment at 25°C . The use of a 25% solution of KCNS with epichlorohydrin at 80°C . resulted in 4% weight gains, but no improvement in crease resistance properties. Other salts, such as NH_4Cl , KCNO , Na_2CO_3 , NaCN , $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, and $\text{Zn}(\text{BF}_4)_2$ produced negligible weight gains in the cellulose-epichlorohydrin reaction. Acid salts such as NH_4Cl , $\text{Zn}(\text{BF}_4)_2$, NaH_2PO_4 , and NaHSO_3 do not catalyze the reaction between cellulose and epichlorohydrin although they may react with epichlorohydrin. Alkaline Na_2SO_3 catalyzed the reaction at both 25 and 80°C .; the weight gain at 80°C . was much greater, but was not accompanied by improvements in either wet or dry crease resistance. Slower reaction at 25°C . catalyzed with Na_2SO_3 imparted both wet and dry crease resistance to the fabric (approximately $250^{\circ} \text{W} + \text{F}$) at only 1% add-on. The more alkaline Na_2S effected a weight gain accompanied by improvement in wet crease recovery only. In general, alkaline salts such as the sulfite, sulfide, cyanide, and carbonate of sodium, disodium phosphate, trisodium phosphate, sodium tetrapyrophosphate, sodium metasilicate, borax, and commercial sodium orthosilicate differ considerably in alkalinity and also in catalytic ability. Some of these salts are used as soap "builders" and for detergent purposes by the alkali industry, but as a class are not useful in the cellulose-epichlorohydrin reaction. In fact, the effects of most would remain unknown had not concentrated solutions of them been examined. Sodium carbonate, borax, and sodium tetrapyrophosphate are without action up to saturation. The same may be said of the dodecahydrate of trisodium phosphate, but if a solution of the latter heated to $60\text{--}70^{\circ}\text{C}$. is used in padding, small weight gains and dry crease recovery occur. Such solutions require hot padding to prevent crystallization. The silicates, however—either the *meta* or commercial *ortho*—show weight gains when less concentrated solutions are employed. This is especially true of orthosilicate which is scarcely "less alkaline" in dilute solutions than is caustic soda itself.

Fabric samples selected to cover the range of experimental conditions and types of salts used in pretreatments were analyzed for total chlorine. These fabrics, varying from 2 to 10% in weight gains after treatment with epichlorohydrin, contained only 0.03 to 0.04% chlorine, as did the original untreated cotton.

Pretreatments Resulting in Dry and Wet Crease-Resistant Cottons

From a study of twenty salts, in a wide pH range, it was concluded that only trisodium phosphate dodecahydrate, commercial sodium orthosilicate, and sodium metasilicate are of interest because of their catalytic action and economic considerations. In Figure 1, dry crease angles obtained with 100% epichlorohydrin for 30 min. at 80°C . after various pretreatments with each of these salts or NaOH are plotted against concentrations of solute used in pretreatment solutions. Data for all solutes except tri-

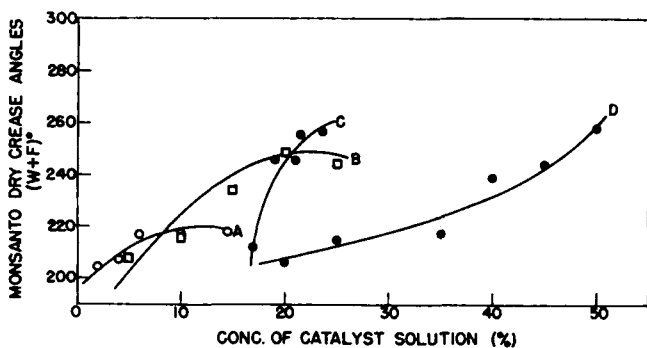


Fig. 1. Variation of dry crease angles with weight percentage of solute used in pretreatment of fabric finished with epichlorohydrin at 80°C. Pretreatments: (A) NaOH; (B) Na_4SiO_4 ; (C) Na_2SiO_3 ; (D) $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

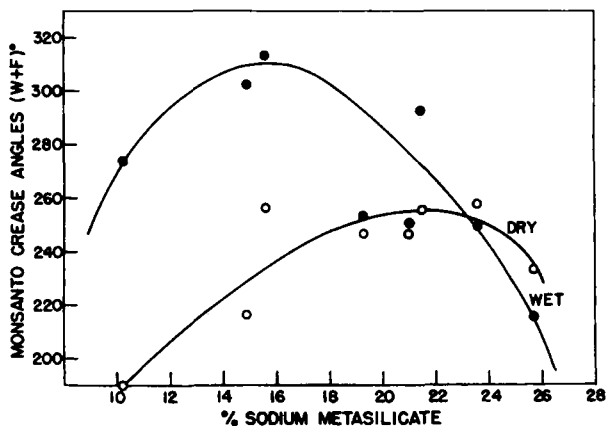


Fig. 2. Variation of wet and dry crease angles with weight percentage of Na_2SiO_3 used in pretreatment of fabric finished with epichlorohydrin at 80°C. for 30 min.: (O) dry angles; (●) wet angles.

sodium phosphate dodecahydrate are plotted as per cent active ingredient; the latter is in terms of per cent hydrate (per cent active ingredient = $0.458 \times$ per cent hydrate). It can be noted that dry angles above 220° are imparted to the fabric only when the salts are fairly concentrated. In fact, trisodium phosphate causes little or no add-ons at 30% concentration (13.7% active ingredient). However, fabrics pretreated with higher concentrations of phosphates or silicates possess high dry and wet crease resistance and good luster and color. They retain approximately 50% of the original breaking strength, 40% of tearing strength, and about 60% of the original elongation value. These findings are similar to those obtained with fabrics treated with butadiene diepoxide.¹⁴ In comparison, caustic soda causes addition to cellulose at much lower concentrations but never imparts dry crease resistance. If used at 20–30% concentrations, NaOH

TABLE IV
Properties of Fabrics^a Pretreated with Soluble Silicates of SiO₂:Na₂O Ratio >1

Silicate ^b	SiO ₂ / Na ₂ O	Active ingred., %	Concent. in pad bath, %	Wt. gain, %	Monsanto crease angles (W + F), deg.	
					Wet	Dry
B-W	1.6	51.1	21.5	3.7	221	236
			27.0	5.2	260	270
Starso	1.8	37.5	21.5	2.6	221	220
			27.0	3.7	238	231
C	2.0	54.0	21.5	1.8	233	208
			27.0	3.4	228	226
K	2.9	42.9	21.5	6.1	205	189
N	3.2	37.6	21.5	10.1	200	163
S	3.7	32.0	21.5	12.6	205	155

^a 80° fabric pretreated with silicate solution before 30 min. immersion in epichlorohydrin at 80°C.

^b Philadelphia Quartz Company label.

as a pretreatment for application of epichlorohydrin causes disintegration of the cloth or gives a boardlike material unsuitable for fabric use.

Variations of both wet and dry crease angles of fabric treated with 100% epichlorohydrin at 80°C. with concentrations of sodium metasilicate solutions used in pretreatments are shown in Figure 2. These data show that the wet crease angles are higher than dry crease angles when concentrations less than 16% metasilicate are used. With higher concentrations of metasilicate solution used in pretreatment, the wet crease angles decrease and the dry crease angles remain essentially the same. Similar variations in crease angles with concentrations of pad bath have been observed with orthosilicate solutions. Addition of epichlorohydrin to cellulose pretreated with the trisodium phosphate is much slower at 80°C., and the maximum in wet crease recovery has not been observed.

Since successful results were obtained with ortho- and metasilicates (SiO₂:Na₂O mole ratios of 0.5 and 1, respectively), other water-soluble silicates of ratios >1 were used in pretreatments. Typical data, recorded in Table IV, indicate that as the (SiO₂:Na₂O) ratio increases up to 2 there is a decrease in weight gains and, in most cases, in crease recovery properties of the cotton. Higher weight gains recorded in Table IV for the K, N, and S silicates (Philadelphia Quartz Company labels) having SiO₂:Na₂O ratios of approximately 3 or greater were due to deposition of SiO₂ in the fibers. Such samples were not washed with hydrofluoric acid, and showed a high ash content. Results obtained with the B-W sample (ratio 1.6) at 27% active ingredient in the pad bath are exceptional and indicate that commercially available sodium sesquisilicate (ratio 1.5) would be a useful pretreating agent.

Concentrated alkali or alkaline salt solutions have certain physico-chemical properties not well understood, and it is doubtful whether the

measured pH's of such solutions are meaningful. However, since it is now known that caustic soda solutions are not very useful in obtaining dry crease recovery in the cellulose-epichlorohydrin reactions and that under similar conditions sodium silicate solutions do assist, the claims of the alkali and detergent industries in regard to "controlled alkali" takes on added significance. Sodium orthosilicate ($2\text{Na}_2\text{O}\cdot\text{SiO}_2$) does not give $(\text{SiO}_4)^{4-}$ in water but, rather, $(\text{SiO}_3)^{--}$, OH^- , and Na^+ , and may, for practical purposes, be considered a mixture of caustic and sodium metasilicate. Such solutions were shown by Kohlrausch^{38,39} and Harman⁴⁰ to exhibit poor conductance at concentrations as high as $2N_w$, which is even less concentrated than the solutions employed here. Harman claimed that in concentrated solution there may be little ionization or there may be complex or colloid formation. Hydrolysis in such solutions is low, only 15–17%, at $2N_w$. A rationalization of this finding could mean that the hydroxyl ions are less mobile because of hydrogen bonding with silicic acid, which implies complex formation. In any event, in the cellulose-epichlorohydrin reaction more cellulose product leading to improvement in dry crease recovery results in unit time when $(\text{SiO}_3)^{--}$ is present with OH^- than when only OH^- is present.

Trisodium phosphate, the dodecahydrate of commerce, shows high conductivity and is strongly hydrolyzed,⁴¹ and its peculiar retentivity for alkali has been well discussed.^{42–44} The salt used in this work contained 1.8% free NaOH.

Microscopical Examinations

The swelling or dissolution of fibers in cupriethylenediamine (cuene) is used as a criterion of degree of crosslinking. Observations with the light microscope of samples of longitudinal fibers immersed in 0.5M cuene reveal by type and amount of swelling the degree of crosslinking at the fiber level. Similarly, examinations with the electron microscope of thin fiber cross sections (800–1000 Å) after immersion in cuene for 30 min. reveal swelling patterns which can be used for further differentiation of the amounts of crosslinking.^{45,46} Comparisons made by such microscopical techniques indicated that the cellulose-epichlorohydrin reaction at 80°C. after pretreatments with concentrated silicates or phosphates gave a modified cotton that differed from that obtained after pretreatments with sodium hydroxide of various strengths. Even after pretreatments with dilute NaOH, the fibers and cross sections were more swollen in cuene than were those pretreated with the silicates or phosphates. In Figure 3, typical electron micrographs are given for comparative purposes. The best evidence of crosslinking, as indicated by least amount of swelling (Fig. 3, *a*), is observed on thin sections of samples pretreated with 21% sodium metasilicate before application of epichlorohydrin at 80°C. for 30 min. The effects of similar applications of epichlorohydrin after pretreatments with 3 and 8% aqueous NaOH are illustrated by the swelling patterns of ultrathin sections in Figure 3, *b* and *c*. Although these fibers

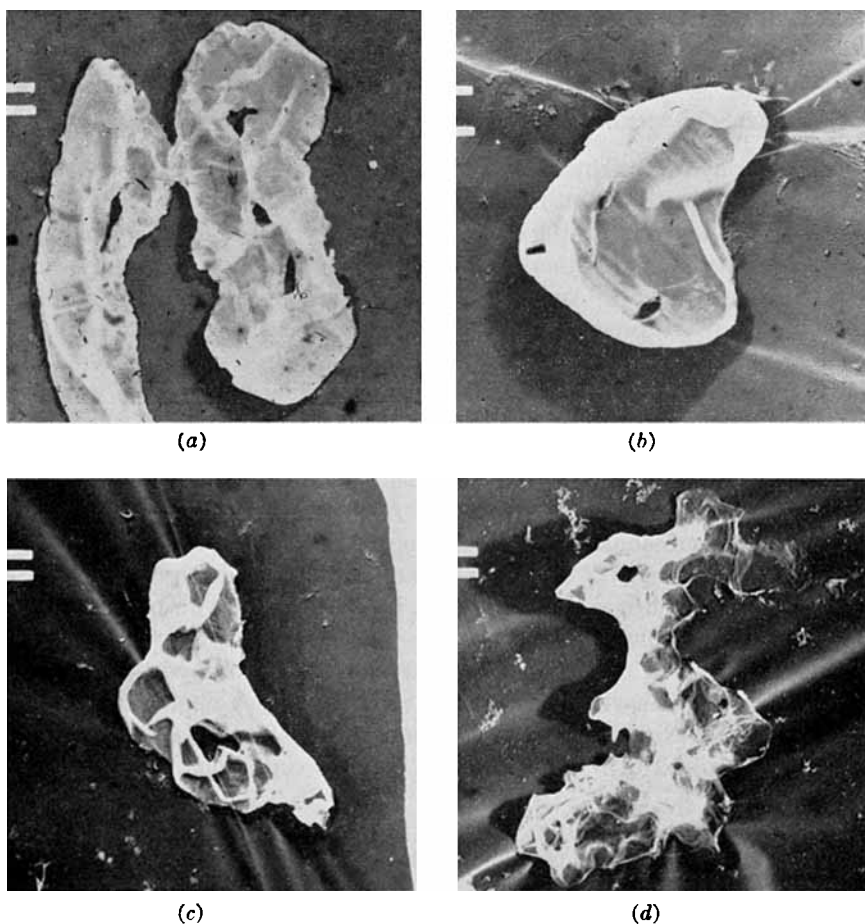


Fig. 3. Electron micrographs taken of ultrathin cross sections of cotton fibers taken from finished fabrics, after 30 min. immersion in cuene. Epichlorohydrin applied to fabrics at 80°C. for 30 min. after the following pretreatments: (a) 21% Na_4SiO_4 ; (b) 3% NaOH ; (c) 8% NaOH ; (d) fabric pretreated with 2% NaOH and then solvent-extracted with acetone and ether before immersion in 20% epichlorohydrin in CCl_4 at 25°C. for 16 hrs. (a, c, d, 2800 \times ; b, 9,000 \times .)

and cross sections did not dissolve in cuene, there was evidence of some decrease in section thickness during swelling, and the amount of dissolution from the first to the second to the third sample correlates with decrease in dry crease resistance of the fabrics (Fig. 3). While all these fabrics possessed high wet crease resistance, only that of *a* in Figure 3 possessed high dry crease resistance. For comparative purposes, there is included an electron micrograph of the typical swelling pattern of ultrathin sections of fibers from a fabric pretreated with aqueous 2% NaOH and then solvent-extracted with acetone and ether before application of 20% epichlorohydrin in CCl_4 at 25°C. (Fig. 3, *d*). The greater part of such thin cross sections

dissolved in cuene; this is taken to indicate a smaller amount of crosslinking at this level than exhibited by the samples described above.

Effects of Monoepoxides and Diepoxides on Crease Recovery

Epichlorohydrin might be said to be acting similarly to monoepoxides⁴⁷ in its reaction with cotton in the presence of caustic soda inasmuch as it increases the wet but not the dry crease recovery. It is believed that only cellulose hydroxy alkyl ethers or linear graft polymers thereof are formed with monoepoxides.¹¹ Another usual criterion of crosslinking, that of insolubility of the product in cuene, should be considered along with the crease resistance properties of the product. It is clear from previous work in this laboratory and in others that cuene insolubility of cotton results if cellulose is truly crosslinked. In many instances, only very small add-ons of a difunctional reagent, of the order of a few hundredths of a (D.S.), can result in the desired properties and cuene insolubility. However, it has also been shown that cuene insolubility can result when monoepoxides, which are not crosslinkers, are added to cotton,¹¹ but at much larger additions. For example, a 12% add-on of butylene monoxide to cotton results in a product which is soluble in cuene, but a larger add-on of this monoepoxide causes insolubility in cuene.

A comparison of crease angles imparted by epichlorohydrin to cotton cellulose pretreated with 10% NaOH with the angles imparted by some typical monoepoxides and certain chlorohydrins after the same pretreatment is given in Table V. Under the imposed conditions, which are not

TABLE V
Effects of Monoepoxides and Certain Chlorohydrins on Crease Resistance of Cotton^a

Etherifying agent	Add-on, wt.-%	Monsanto crease angles (W + F), deg.	
		Wet	Dry
Allyl glycidyl ether	9.0	211	176
Butylene oxide ^b	1.1	210	167
Butyl glycidyl ether	1.5	232	170
Glycidyl diethylamine	1.2	216	155
Glycidaldehyde ^c	40.0	243	176
Phenyl glycidyl ether	1.0	204	177
Styrene oxide	0.0	198	168
3-Chloro-1,2-propanediol	0.0	189	183
1,3-Dichloro-2-propanol	0.0	207	172
Epichlorohydrin	10.1	323	218
Control	—	166	196
Control treated with 10% NaOH	—	200	184

^a 80² fabric pretreated to 100% wet pickup with 10% NaOH, then treated with etherifying agent for 30 min. at 80°C.

^b Reacted at 60°C.

^c Reacted violently, removed at once.

ideal for such a variety of compounds, there was some improvement in wet crease resistance in only a few instances. Only those epoxides resulting in wet crease angles significantly above 200° ($W + F$), produced by base pretreatment, are considered to improve wet crease resistance. The dry crease resistance was either little affected, or less than that of the control fabrics for all except the epichlorohydrin-treated fabrics. In other experiments, where the fabric was treated first with 1,3-dichloro-2-propanol, glycidol, or *N*(3-chloro-2-hydroxypropyl) cyclohexylamine, dried, then treated with base and cured at 80°C . for 15 min., fabrics of 2% weight gains resulted. These fabrics had dry crease angles of only 162° ($W + F$), and only the one treated with 1,3-dichloro-2-propanol had significant improvement in wet crease resistance (255° $W + F$).

TABLE VI
Base-Catalyzed Cellulose-Ethylene Oxide Reaction*

Time of reaction, min.	Add-on, wt.-%	Monsanto crease angle ($W + F$), deg.	
		Wet	Dry
45	1.7	210	141
90	10.0	211	106
180	11.5	Dissolves	87
300	32.0	Dissolves	78
Control (6% moisture regain)	—	166	196
Control treated with 15% NaOH	—	204	186
Control over P_2O_5	—	—	260

* 80^2 fabric pretreated with 15% NaOH and then treated for indicated time intervals in 15% by volume solution of ethylene oxide in CCl_4 at 25°C .

Results with ethylene oxide, as recorded in Table VI, are particularly instructive. Even at a low add-on, the very slight improvements in wet crease resistance were accompanied by large decreases in the dry crease angles. Recorded also in Table VI are the dry crease angles for thoroughly dried cotton, cotton of 6% moisture regain, and cotton pretreated with 15% NaOH. Changes in these dry angles show effects of water and caustic on hydrogen bonding of cotton cellulose. Data in Table VI indicate that these effects are not as great as those caused by presence of hydrophilic hydroxyethyl groups, which permit water to penetrate the lattice with consequent solubilization of the chains, first in weak alkali and finally in water at a D.S. of 1.4. Similar solubilizations of ethyl and methyl celluloses occur at a low D.S., but solubility in organic solvents rather than in water results at a higher D.S. of these hydrophobic groups.^{48,49}

Usually, only wet crease recovery is improved when cotton reacts with certain monoepoxides by base catalysis. With diepoxides and base catalysis, wet crease recovery is improved initially. This can be explained

either by the crosslinking in the swollen state or a large degree of mono attachment of the reagent initially.

Intrachain linking involving hydroxyls on carbons 2 and 3 is largely ruled out by the experiments of Croon and Lindberg,⁵⁰ who showed that relative rate constants involved in epoxide reactions at hydroxyls on carbons 6, 2, and 3 were 10:3.5:1, respectively. With dilute base, use of certain diepoxides can result in improvement in dry crease recovery, indicating that a certain number of diepoxide molecules succeed in crosslinking cotton. Epichlorohydrin, a potential diepoxide, usually produces only wet crease recovery unless certain precautions are taken. These include control of the amount of swelling of cellulose, the amount of water imbibed, and the hydroxide ion mobility, which is lowered in concentrated silicate and other alkaline salt solutions.

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Synopsis

As a phase of an investigation of the cellulose-epoxide reactions, experiments have been performed in which epichlorohydrin reacted with cotton cellulose in the presence of sodium hydroxide and various salts. Acidic and basic salts, as well as those which are relatively neutral in aqueous solutions, were used in pretreatments for the cellulose-epichlorohydrin reaction. No reaction with cellulose occurred in the presence of acid salts and only very slow addition of epichlorohydrin to cellulose in the presence of neutral salts; the greatest reaction was produced with basic salts. Particular emphasis was given to use of certain salts known to cause epichlorohydrin to undergo a type of cyclization reaction. Previously published methods, used for imparting both wet and dry crease resistance to cotton fabrics by means of diepoxides in the presence of NaOH, have resulted in wet crease resistance only when applied to the application of epichlorohydrin. Among the basic salts investigated, 20% solutions of sodium azide used in pretreatments were found to produce low weight gains of epichlorohydrin and a fair degree of dry and wet crease resistance in cotton after a slow reaction at 25°C. or a faster reaction at 80°C. The greatest improvement in dry crease resistance with epichlorohydrin was obtained by pretreatments with concentrated solutions of sodium orthosilicate, sodium metasilicate, or trisodium phosphate at 80°C. The effects of amount of water at time of reaction as well as speeds of reaction with the various pretreatments have been considered. Optical and electron microscopical examinations of fibers and ultrathin cross sections of fibers, respectively, after immersion in cupriethylene diamine (cuene) have indicated that the cellulose-epichlorohydrin reaction at 80°C. after pretreatment with concentrated solutions of silicates or phosphates differed from that after pretreatment with sodium hydroxide at all concentrations. Even when the

pretreatments were with dilute sodium hydroxide, the epichlorohydrin-reacted fibers were more swollen in cuene than were those treated fibers which had been pretreated with the concentrated silicates or trisodium phosphate solutions. Decrease in amount of swelling and dissolution in cuene was found to correlate with increase in dry crease resistance of the fabrics. While all these treated fabrics possessed high wet crease resistance, only those pretreated with the aforementioned concentrated salt solutions possessed good dry crease resistance. Effects of base-catalyzed addition of certain monoepoxides to cotton on the resultant crease resistance properties of the fabrics have been reported and compared with properties imparted by epichlorohydrin. Attempts have been made to explain why the number of cellulose crosslinks formed per unit of time by epichlorohydrin is greater, when silicates or phosphates at high concentrations are present with hydroxyl ions, than when hydroxyl ions only are present.

Résumé

Dans le cadre des recherches sur les réactions cellulose-époxyde, on a effectué des expériences dans lesquelles on a fait réagir de l'épichlorhydrine avec de la cellulose de coton en présence d'hydroxyde de sodium et divers sels. On a utilisé des sels acides et basiques, de même que ceux qui sont relativement neutres dans les solutions aqueuses, comme prétraitements à la réaction cellulose-épichlorhydrine. Alors qu'il ne se produisait pas de réaction avec la cellulose en présence de sels acides, et seulement une addition très lente de l'épichlorhydrine sur la cellulose en présence de sels neutres, la réaction a été la plus importante en utilisant des sels basiques comme prétraitements. On a attaché une importance particulière à l'utilisation de certains sels dont on savait qu'ils entraînaient de la part de l'épichlorhydrine un type de réaction de cyclisation. Des méthodes publiées précédemment, qui attribuaient à des tissus de coton traités par les diépoxydes en présence de NaOH une résistance au chiffonnement à la fois humide et sec, ont produit une résistance au chiffonnement humide, uniquement lorsqu'appliquées à l'application de l'épichlorhydrine. Parmi les sels basiques étudiés on a trouvé que des solutions à 20% d'azoture de sodium utilisées dans les prétraitements, produisaient de faibles gains en poids d'épichlorhydrine et une assez bonne résistance au chiffonnement sec et humide par rapport au coton après une réaction lente à 25°C. ou une réaction plus rapide à 80°C. On a obtenu les améliorations les plus grandes en ce qui concerne la résistance au chiffonnement sec avec l'épichlorhydrine par des prétraitements avec des solutions concentrées d'orthosilicate de sodium, métasilicate de sodium ou phosphate trisodique à 80°C. On a considéré les effets de la quantité d'eau sur le temps de réaction ainsi que les vitesses de réaction avec les différents prétraitements. Des examens aux microscopes optique et électronique des fibres et de sections transversales ultraminces de fibres après immersion dans la cupriéthylène-diamine (cuène) ont montré que la réaction cellulose-épichlorhydrine à 80°C. après des prétraitements avec des solutions concentrées de silicates ou de phosphates différait de celle après des prétraitements avec de l'hydroxyde de sodium à toutes les concentrations. Même lorsque les prétraitements étaient effectués avec de l'hydroxyde de sodium dilué, les fibres qui avaient réagi avec l'épichlorhydrine étaient plus gonflées dans le cuène que les fibres traitées ayant subi un prétraitement avec des solutions concentrées de silicates et phosphate trisodique. On a trouvé qu'une diminution du gonflement et la dissolution dans le cuène correspondait à une augmentation de la résistance au chiffonnement sec des tissus. Alors que tous ces tissus traités possédaient une grande résistance au chiffonnement humide, uniquement ceux traités par les solutions concentrées des sels mentionnés possédaient une grande résistance au chiffonnement à sec. On rend compte des effets de l'addition, (catalysé par les bases), de certains monoépoxydes au coton, sur les propriétés résultantes de résistance au chiffonnement des tissus; on les compare aux propriétés dues à l'épichlorhydrine. On a essayé d'expliquer pourquoi il se formait plus de ponts celluloseux par unité de temps au moyen de l'épichlorhydrine lorsque des silicates ou des

phosphates en fortes concentrations étaient présents en même temps que des ions hydroxyles que lorsque les ions hydroxyles étaient seuls.

Zusammenfassung

Als ein Teil einer Untersuchung von Cellulose-Epoxyreaktionen wurden Versuche zur Reaktion zwischen Epichlorhydrin und Baumwollcellulose in Gegenwart von Natriumhydroxyd und verschiedenen Salzen ausgeführt. Saure und basische Salze sowie solche, die in wässriger Lösung relativ neutral sind, wurden als Vorbehandlung für die Cellulose-Epichlorhydrinreaktion angewendet. Während in Gegenwart saurer Salze keine Reaktion mit Cellulose und in der von neutralen Salzen nur eine sehr langsame Addition von Epichlorhydrin an Cellulose eintritt, wird durch Verwendung basischer Salze zur Vorbehandlung das höchste Ausmass an Reaktion erreicht. Besonders berücksichtigt wurde die Verwendung gewisser Salze, deren cyclisierender Einfluss auf Epichlorhydrin bekannt ist. Früher veröffentlichte Methode zur Erzielung einer Knitterfestigkeit von Baumwollgeweben im nassen und trochenen Zustand durch Diepoxyde in Gegenwart von NaOH führten bei der Übertragung auf Epichlorhydrin nur zu einer Nassknitterfestigkeit. Unter den untersuchten basischen Salzen führte die Verwendung einer 20% Lösung von Natriumazid zur Vorbehandlung zu einer geringen Gewichtszunahme an Epichlorhydrin und einer annehmbaren Trocken- und Nassknitterfestigkeit von Baumwolle nach langsamer Reaktion bei 25°C oder rascherer Reaktion bei 80°C. Die grösste Verbesserung der Trockenknitterfestigkeit wurde mit Epichlorhydrin nach Vorbehandlung mit konzentrierter Natriumorthosilikat-, Natriummetasilikat- oder Trinatriumphosphatlösung bei 80°C erhalten. Der Einfluss der Wassermenge während der Reaktion und die Geschwindigkeit der Reaktion bei verschiedener Vorbehandlung wurden untersucht. Optische und elektronenmikroskopische Untersuchung von Fasern bzw. ultradünnen Faserschnitten nach Immersion in Cupriäthylendiamin (Cuen) zeigte, dass die Cellulose-Epichlorhydrinreaktion bei 80°C nach Vorbehandlung mit konzentrierten Silikat- oder Phosphatlösungen sich von der nach Vorbehandlung mit Natriumhydroxyd bei allen Konzentrationen unterschied. Sogar bei Vorbehandlung mit verdünntem Natriumhydroxyd waren die Fasern nach Reaktion mit Epichlorhydrin in Cuen stärker gequollen als diejenigen behandelten Fasern, die mit konzentrierter Silikat- oder Trinatriumphosphatlösung vorbehandelt worden waren. Die Abnahme der Quellung und Lösung in Cuen zeigte eine Korrelation zu der Zunahme der Trockenknitterfestigkeit der Gewebe. Während alle behandelten Gewebe eine hohe Nassknitterfestigkeit besaßen, wiesen nur die mit den oben erwähnten konzentrierten Salzlösungen vorbehandelten hohe Trockenknitterfestigkeit auf. Der Einfluss einer basenkatalysierten Addition gewisser Monoepoxyde an Baumwolle auf die Knitterfestigkeit der Gewebe wurde beschrieben und mit der Wirkung von Epichlorhydrin verglichen. Erklärungsversuche für die Bildung einer grösseren Zahl von Cellulosevernetzungen pro Zeiteinheit durch Epichlorhydrin bei gleichzeitiger Anwesenheit von Silikaten oder Phosphaten in hoher Konzentration und Hydroxylionen, als mit Hydroxylionen allein, werden gegeben.

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