Diethylaminoethyl Cellulose–Epoxide Reactions*

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Synopsis

Reactions of various monoepoxides and diepoxides with diethylaminoethyl (DEAE) cellulose in the absence and presence of external catalysts have been studied. In the absence of additional catalysts, many epoxides which did not react with the unmodified cotton reacted with DEAE-cotton. Others, which reacted with unmodified cotton in the presence of external bases, imparted different properties when catalyzed by the builtin tertiary amino groups of DEAE-cotton. For example, epichlorohydrin reacted with DEAE-cotton to produce a fabric with excellent conditioned recovery, good wet recovery, and strong-base anion exchange properties. The same epoxide imparted only wet crease recovery to cotton when the reaction was catalyzed by external bases. Phenyl glycidyl ether and styrene oxide reacted with DEAE-cotton to produce a fabric with twentyfold improvement in resistance to flex abrasion. With 8% aqueous NaOH as an external catalyst, the DEAE-cotton displayed greater reactivity with all epoxides than did the unmodified fabric. DEAE-cotton–diepoxide reactions with added base catalyst generally resulted in a decrease in the conditioned recovery angle and an increase in the wet recovery angle. When $Zn(BF_4)_2$ was used as an additional catalyst, again the DEAE fabrics displayed the greater reactivity toward the monoepoxides; but the unmodified cotton was more reactive toward the diepoxides than was the DEAE-cotton. The $Zn(BF_4)_2$–monoepoxide-treated DEAE fabrics had higher wet recovery angles but lower dry recovery angles than the corresponding epoxide-finished control cottons. Butadiene diepoxide was the only diepoxide investigated which imparted higher dry recovery angles to the DEAE-cotton than to the unmodified cotton control in the presence of $Zn(BF_4)_2$. Tertiary amino groups in DEAE-cottons act as an internal catalyst for the opening of the oxirane rings, direct the site for reaction in the absence of additional catalysts, and react with some epoxides to form quaternary nitrogen groups.

INTRODUCTION

Cotton fabrics converted to weak-base anion exchangers (DEAE-cellulose) by reaction with β-chloroethyldiethylamine hydrochloride in the presence of bases[1] were subsequently quaternized with alkyl halides.[2,3] Recently, it has been shown that the quaternized products from the reaction of DEAE-cellulose with epichlorohydrin at 95°C. were strong-base anion exchange fabrics possessing excellent dry crease recovery, 300(W + F)°,

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and good wet crease recovery, $280(W + F)°$.[2]   Previously it had been shown that epichlorohydrin in the liquid phase did not react with unmodified cotton in the absence of a catalyst or under conditions of acid catalysis; with external base catalysis, only wet crease recovery was imparted to the fabric.[4]   It was only in the presence of very concentrated solutions of certain salts that conditioned crease recovery was imparted to cotton by epichlorohydrin under conditions of base catalysis.[5]   It was, therefore, of interest to study the effects of other epoxides on fabric properties of DEAE-cottons.

This paper reports the fabric properties imparted to DEAE-cotton by various mono- and diepoxides.   The epoxide reactions were: (1) without external catalyst, (2) with NaOH catalyst, and (3) with $Zn(BF_4)_2$ catalyst. The anion exchange properties of treated DEAE-cottons were determined to indicate whether or not quaternization of the tertiary amino groups of DEAE-cottons had occurred during the epoxide reactions.   Properties of the DEAE-cottons treated with epoxides were compared with fabric properties of unmodified cottons treated with the respective epoxides under similar experimental conditions.

EXPERIMENTAL

Materials

Reagents

Reagent grade chemicals were used without further purification.   The β-chloroethyldiethylamine hydrochloride was obtained from Matheson, Coleman and Bell.   The various epoxides, their chemical structures, and sources of supply are listed in Table I.

Conductivity water was used in preparation of all solutions used in titrations.   The pH of the water was maintained at 7 by flushing out all titration vessels with dry nitrogen before the addition of the cellulose anion exchangers.
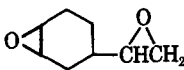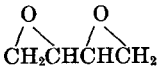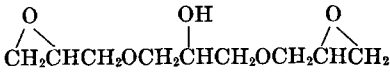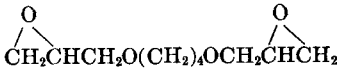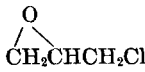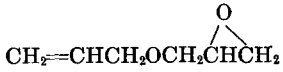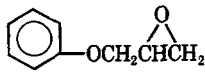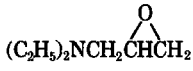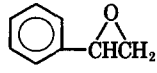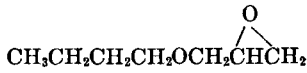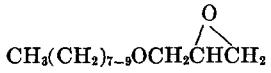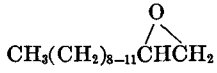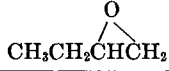
Fabrics

An 80×80 cotton print cloth weighing 3.12 oz./yd.[2] was desized, scoured, and then processed in commercial peroxide bleaching equipment. This fabric was used as untreated cotton controls and for further chemical modifications.

DEAE-Cottons.   The DEAE-cellulose was prepared according to the method of Hartmann.[1]   Fabric samples were padded with 10% aqueous solution of 2-chloroethyldiethylamine hydrochloride, dried at 60°C. for 5 min., and then reacted overnight at room temperature in 25% aqueous NaOH.   Fabrics were thoroughly washed in tap water until free of excess hydroxyl ions and air-equilibrated for 24 hr. before being tested for fabric properties or being subjected to further chemical modification.   Usually, a nitrogen content of only 0.2–0.3% was obtained in a single treatment.

To achieve higher nitrogen contents, it was necessary to react cotton several times with 2-chloroethyldiethylamine hydrochloride according to the above procedure.

TABLE I
List of Epoxides

Epoxide	Structure	Source
Vinylcyclohexene dioxide	(cyclohexene dioxide ring) O / $CHCH_2$ epoxide	U.C.[a]
Butadiene diepoxide	$CH_2CHCHCH_2$ with two epoxide O	Koppers[b]
Eponite 100	$CH_2CHCH_2OCH_2CHCH_2OCH_2CHCH_2$ with epoxide O, OH, epoxide O	Shell[c]
Araldite RD-2	$CH_2CHCH_2O(CH_2)_4OCH_2CHCH_2$ with two epoxide O	Ciba[d]
Epichlorohydrin	CH_2CHCH_2Cl with epoxide O	Shell
Allyl glycidyl ether	$CH_2{=}CHCH_2OCH_2CHCH_2$ with epoxide O	Shell
Phenyl glycidyl ether	(phenyl)$-OCH_2CHCH_2$ with epoxide O	Shell
Glycidyldiethylamine	$(C_2H_5)_2NCH_2CHCH_2$ with epoxide O	U.C.
Styrene oxide	(phenyl)$-CHCH_2$ with epoxide O	U.C.
Araldite RD-1	$CH_3CH_2CH_2CH_2OCH_2CHCH_2$ with epoxide O	Ciba
P & G epoxide No. 7	$CH_3(CH_2)_{7-9}OCH_2CHCH_2$ with epoxide O	P & G[e]
C_{11}–C_{14} epoxide	$CH_3(CH_2)_{8-11}CHCH_2$ with epoxide O	A-D-M[f]
Butylene oxide	$CH_3CH_2CHCH_2$ with epoxide O	U.C.

[a] Union Carbide Corp., Chemical Division, New York, N. Y.
[b] Koppers Company, Inc., Research Division, Pittsburgh, Pa.
[c] Shell Chemical Corp., A Division of Shell Oil Co., New York, N. Y.
[d] Ciba Products Corp., Kimberton, Pa.
[e] Procter & Gamble Industrial Chemicals Development, Cincinnati, Ohio.
[f] Archer-Daniels-Midland Co., Minneapolis, Minnesota.

Application of Epoxides

(1) No External Catalyst. The undiluted epoxides were brought to 95°C. in covered cylinders in a constant temperature oven. Appropriate quantities of DEAE-cotton fabrics as well as unmodified cottons were placed in the cylinders and held at the specified temperature for definite periods of time. Since butylene oxide boils lower than 95°C., and an azeotrope of epichlorohydrin with water boils at approximately 95°C., these two epoxides were reacted with fabrics at their respective reflux temperatures. All treated samples were washed in absolute methanol, tap water, and then distilled water. They were ironed dry and allowed to air-equilibrate at room temperature for at least 24 hr. prior to determination of add-ons and fabrics properties.

(2) NaOH Catalyst. Fabrics were padded to 100% wet pickup with 8% aqueous NaOH. The padded DEAE-cotton and the padded unmodified cotton control were placed in the same container with excess epoxide at room temperature for a given period. Then they were removed, washed in dilute acetic acid, tap water, and finally in distilled water. The fabrics were ironed dry and allowed to equilibrate at least 24 hr. at room temperature before weight add-ons and fabrics properties were determined.

(3) Zn(BF$_4$)$_2$ Catalyst. Fabrics were padded twice to 100% wet pickup with a methanolic solution which was 0.05M with respect to Zn(BF$_4$)$_2$ and contained 20% by weight of the epoxide. The wet fabrics were placed immediately in an oven at 125°C. for 5 min. They were washed in pyridine absolute methanol, tap water, and finally distilled water. They were ironed dry and allowed to equilibrate at room temperature for 24 hr. before being weighed and tested for fabric properties.

Potentiometric Titrations

The anion exchange fabrics in salt form were ground to pass a 20-mesh screen. Regeneration to the base form was brought about with excess 0.05M NaOH according to experimental procedures described previously.[3] The exchanger in base form was dried over P$_2$O$_5$ under vacuum to constant weight before elemental analyses and anion exchange capacities were determined. An accurately weighed sample of approximately 0.8 meq. of replaceable anion was placed in a specially designed titration flask containing exactly 50.00 ml. of 1M NaCl salt solution prepared with conductivity water and kept in a nitrogen atmosphere. Experimental details for titrations were as previously reported.[3] All pH measurements were made with either a Beckman Model GS or a Model 101900 pH meter to ±0.05 pH units.

Textile Testing

Breaking strengths were determined by the strip method (80-thread count width) on a Scott tester,[6] conditioned (dry) crease recovery angles by the Monsanto Method[7] with a 500-g. weight, wet crease recovery angles as described previously,[8] and abrasion resistance values by the flex method.[9]

Microscopical Examinations

Methods of optical microscopy were applied to observe the amount of swelling and dissolution of the epoxide-treated fabrics in $0.5M$ cupriethylenediamine (cuene).   More detailed information concerning the sites of crosslinking was obtained from electron micrographs of ultrathin cross sections of fibers removed from finished fabrics.   The techniques applied for the preparation of electron micrographs of fiber cross-sections which had been treated with methacrylate to produce layer expansion have been described previously.[10]

RESULTS AND DISCUSSION

DEAE-Cotton–Epoxide Reactions in Absence of Catalyst

Earlier work showed that various epoxides could be added to cellulose only in the presence of selected acid or base catalysts.[11,12]   DEAE-cotton, which has the following chemical structure for its ionized form, reacted

$$Cell—O—CH_2CH_2\overset{\oplus}{N}:H \qquad ^{\ominus}OH$$
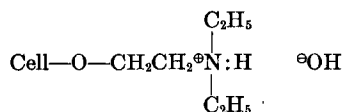
with many epoxides without the addition of an external catalyst.

The tertiary amino groups in DEAE-cotton act as built-in catalysts for the opening of epoxide rings.   The intermediate formed between the catalyst and oxirane ring can react with the amino groups to form quaternary amino groups, or react with hydroxyls to form linear grafts and crosslinks between cellulose chains through ether linkages, or can cause formation of homopolymers of the monomeric epoxides.   The following equations are illustrative of the types of reactions with monoepoxides which might lead to the formation of quaternary groups as in III or linear grafts

$$Cell—OCH_2CH_2{}^+N:H \qquad ^-OH + RCHCH_2 \rightarrow \tag{1}$$

$$\left[Cell—O—CH_2CH_2N: \quad + \; ^-OH + RCHCH_2 \right] \; or$$

I

$$\left[Cell—O—CH_2CH_2{}^+N:H \; + RCHCH_2 \right]$$

II

$$I \rightarrow \text{Cell—OCH}_2\text{CH}_2{}^+\overset{\overset{\text{C}_2\text{H}_5}{|}}{\underset{\underset{\text{C}_2\text{H}_5}{|}}{\text{N}}}\text{:CH}_2\overset{\overset{\text{OH}}{|}}{\text{C}}\text{HR} \quad {}^-\text{OH} \quad \text{or}$$

III

$$\text{RCHCH}_2\overset{\diagdown}{\underset{\text{OH}}{}}\text{—O—Cell—OCH}_2\text{CH}_2{}^+\overset{\overset{\text{C}_2\text{H}_5}{|}}{\underset{\underset{\text{C}_2\text{H}_5}{|}}{\text{N}}}\text{:H} \quad {}^-\text{OH} \quad (2)$$

IV

$$II \rightarrow \text{RCHCH}_2\overset{}{\underset{\underset{\text{OH}}{|}}{}}\text{O—Cell—OCH}_2\text{CH}_2{}^+\overset{\overset{\text{C}_2\text{H}_5}{|}}{\underset{\underset{\text{C}_2\text{H}_5}{|}}{\text{N}}}\text{:H} \quad {}^-\text{OH} \quad (3)$$

IV
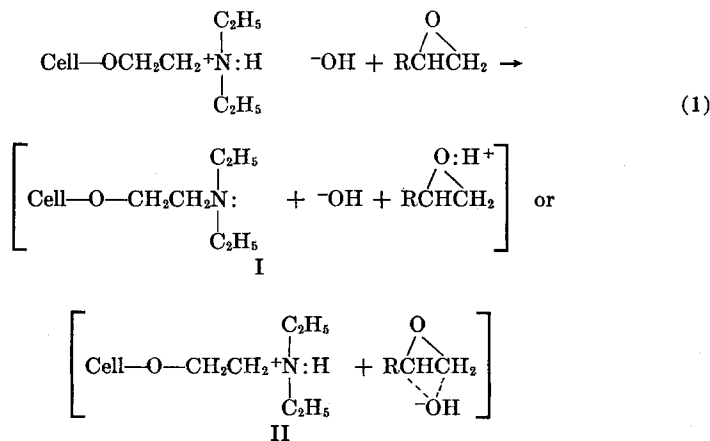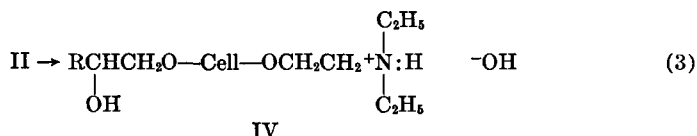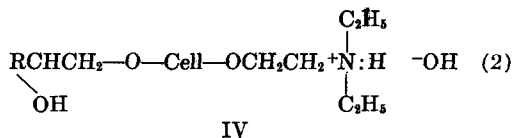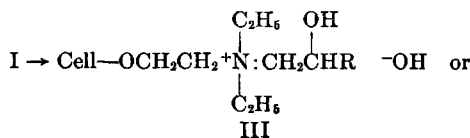
of epoxides as in IV. In addition, the intermediates of diepoxides can react with only cellulosic hydroxyls to crosslink cellulose chains, react with amino groups to crosslink chains, or react with a combination of both amino and cellulosic hydroxyl groups. Schematic structures in Figure 1 are illustrative of the various possible crosslinks (VI, VII, and VIII) which can be formed between cellulosic chains of DEAE-cottons. Evidence of reaction of epoxides with tertiary amino groups resulting in formation of quaternary groups such as those present in compounds III, VI, and VII was obtained from the potentiometric titration curves of the finished fabrics. Quaternary nitrogen groups titrated as strong-base anion exchangers, whereas DEAE-cellulose itself titrated as a weak-base anion exchanger.
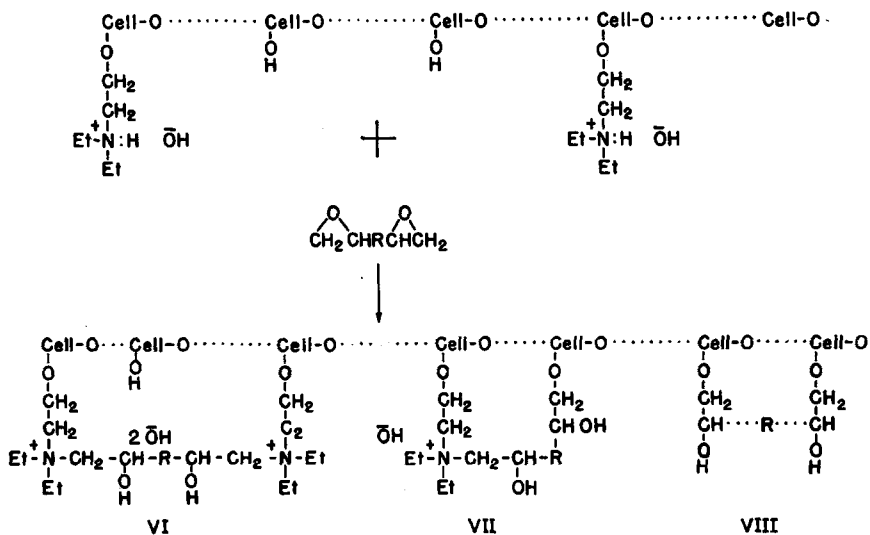

Fig. 1. Types of crosslinks possible in DEAE-cellulose reactions with diepoxides in absence of catalysts.

TABLE II
DEAE-Cotton Cellulose-Epoxide Reaction with No Added Catalyst[a]

Epoxide	Nitrogen, %	Reaction time, hr.	Wt. gain, %	Crease recovery[b] angle (W + F)°		Breaking str., % retained	Flex abrasion, cycles
				Wet	Cond.		
Vinylcyclohexene	1.02	7	2.7	220	215	—	520
dioxide	1.22	7	8.4	216	223	—	679
	0.0	7	0.0	173	181	—	374
Butadiene diepoxide	1.02	2	3.0	245	260	33	589
	1.22	2	4.6	219	263	38	258
	0.0	2	1.0	185	199	68	331
Eponite 100	1.02	7	1.6	259	201	84	825
	1.22	7	2.6	258	194	85	769
	0.0	7	0.0	181	179	—	394
Araldite RD-2	1.02	7	9.9	251	233	40	350
	1.22	7	11.4	239	224	73	359
	0.0	7	0.4	156	179	—	310
Epichlorohydrin[c]	0.27	3	5.1	262	229	—	—
	0.71	3	9.2	265	284	—	—
	1.23	3	15.2	243	288	—	—
	0.0	3	0.0	170	176	—	—
Allyl glycidyl ether	1.02	5	15.3	286	181	71	790
	1.22	5	17.3	268	198	79	839
	0.0	5	1.1	177	173	—	434
Phenyl glycidyl	1.02	0.5	51.4	207	181	35	>10,000
ether	1.22	0.5	71.0	233	200	—	>10,000
	0.0	0.5	0.0	160	172	—	374
Glycidyldiethyl-	1.02	7	1.8	257	179	91	558
amine	1.22	7	1.8	243	183	92	598
	0.0	7	0.0	150	175	—	470
Styrene oxide	1.02	5	38.0	228	174	82	>10,000
	1.22	5	34.1	190	184	89	>10,000
	0.0	5	0.0	151	178	—	396
Araldite RD-1	1.02	1	11.3	245	126	88	532
	1.22	1	23.2	264	103	88	2321
	0.0	1	0.0	151	178	—	396
P & G epoxide No. 7	1.02	7	21.0	210	201	86	495
	1.22	7	18.7	196	211	96	540
	0.0	7	0.0	170	176	—	420
C_{11}–C_{14} epoxide	1.02	7	3.2	214	206	86	495
	1.22	7	3.7	217	205	85	566
	0.0	7	1.0	170	177	63	352
Butylene oxide[c]	1.02	6	11.2	237	168	88	815
	1.22	6	15.5	202	120	84	928
	0.0	6	1.2	152	172	88	550
Control DEAE	1.02	—	—	209	188	—	542
	1.22	—	—	217	225	—	530
Control cotton	0.0	—	—	170	176	—	420

[a] Fabrics immersed in epoxide at 95°C. for indicated time.
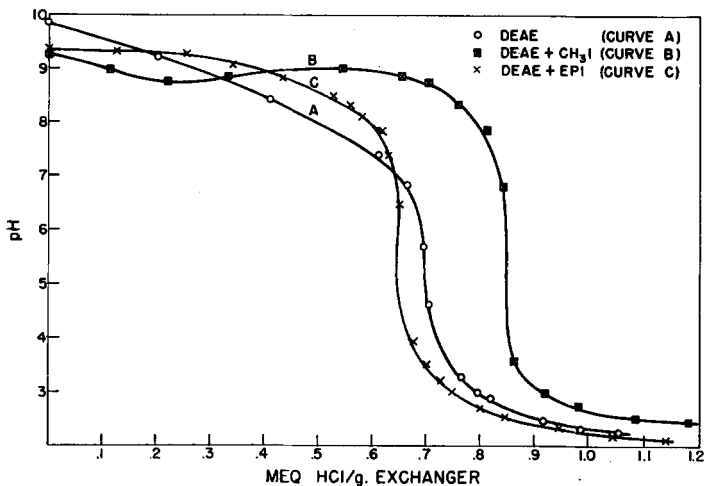[b] Average of three Monsanto crease angles.
[c] Reacted at reflux temperature.

Fig. 2. Potentiometric titration curves of DEAE-cotton (curve A), DEAE-cotton quaternized with CH₃I (curve B), and DEAE-cotton treated with epichlorohydrin (curve C). All curves are for the titration of the regenerated base in 50 ml. of 1M NaCl vs. standardized 0.1N HCl. Curve A represents 1.0643 g. (0.779 meq.); curve B, 1.0072 g. (0.900 meq.); and curve C, 1.0890 g. (0.923 meq.).

In Table II are summarized the fabric properties of DEAE-cottons after treatments with various epoxides for the indicated times at 95° in the absence of external catalysts. Included are the properties for unmodified cottons (0.0% N) treated similarly with the respective epoxides. All epoxides reacted to some degree with the DEAE-cotton. Only a few were able to produce even a very small add-on to the unmodified fabric. Phenyl glycidyl ether was extremely reactive toward DEAE-cotton. As with styrene oxide treatment, it produced a fabric with extremely high flex abrasion resistance properties. This improvement may be a result of polymer grafted to the fiber. Blouin and co-workers[13] have been able to improve the resistance to flex abrasion of irradiated cotton by graft polymerization of vinyl acetate. Only epichlorohydrin and butadiene diepoxide imparted good conditioned recovery angles to DEAE-cotton. The other diepoxides improved only the wet recovery angles of the DEAE-cotton. DEAE-cottons finished with monoepoxides had conditioned recovery angles lower than the original DEAE-cotton control.

In Figure 2 are the potentiometric titration curves of: (A) DEAE-cotton containing 0.90 meq. nitrogen/g. product; (B) a DEAE-cotton quaternized by treatment with CH₃I and containing 0.78 meq. nitrogen per gram product; and (C) a DEAE-cotton treated with epichlorohydrin and containing 0.85 meq. nitrogen per gram product. A comparison of these curves indicates that epichlorohydrin has quaternized a portion of the tertiary amino groups of DEAE-cotton.

In Figure 3 are shown titration curves of DEAE-cottons which had been treated with: (A) epichlorohydrin, (B) vinylcyclohexene dioxide, (C)
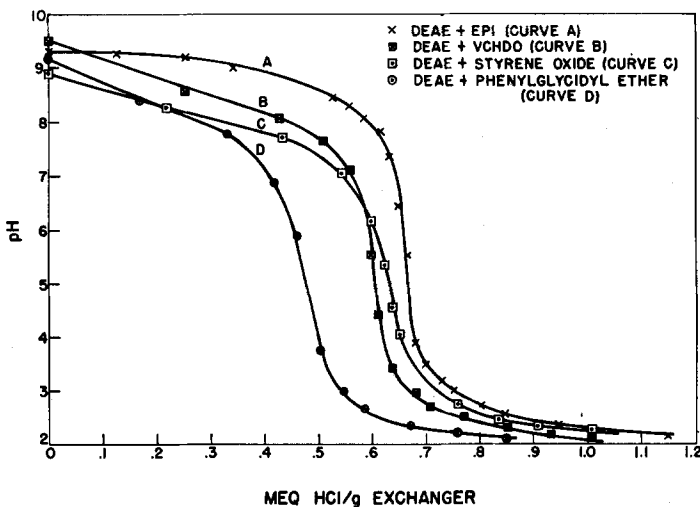
Fig. 3. Potentiometric titration curves of DEAE-cotton after treatment with the following epoxides: (A) epichlorohydrin, (B) vinylcyclohexene dioxide, (C) styrene oxide, (D) phenyl glycidyl ether. All curves are for the following weights of the regenerated base forms in 50 ml. of $1M$ NaCl vs. standardized $0.1N$ HCl: (A) represents 1.0072 g. (0.900 meq.); (B) 1.27500 g. (0.829 meq.); (C) 1.34125 (0.686 meq.); and (D) 1.28984 g. (0.6910 meq.). All titrations were in 50 ml. of $1M$ NaCl vs. standardized $0.1N$ HCl.

styrene oxide, and (D) phenyl glycidyl ether. These titration curves were compared to those of weak-base and quaternary-base exchangers. In addition, for each titration curve, the change in pH with percentage of base exchanger neutralized was considered. These changers were compared with similar changes observed with weak-base anion exchangers and with quaternary-base anion,exchangers. It was concluded that none of the epoxides completely quaternized all of the amino groups of DEAE-cotton. The partial conversion to quaternary nitrogen groups was greater with epichlorohydrin and vinyl cyclohexene dioxide than with styrene oxide or with phenyl glycidyl ether. Partial conversion to the quaternary-base anion exchanger was also shown in the titration curve of a DEAE fabric which had been treated with P & G Epoxide No. 7. The titration curves of the DEAE-cottons which had been treated with allyl glycidyl ether, Araldite RD-2, and the C_{11}–C_{14} monoepoxide were like that of the original DEAE-cotton.

The original DEAE-cottons dissolved immediately in $0.5M$ cuene. The diepoxide-treated DEAE fabrics were insoluble in cuene to various degrees. Those treated with vinylcyclohexene dioxide, butadiene diepoxide, and epichlorohydrin were completely insoluble after a 30-min. immersion in $0.5M$ cuene. The other diepoxide-treated DEAE fabrics showed partial dissolution after a 30-min. immersion. Treatment of DEAE-cotton with monoepoxides incapable of crosslinking resulted in finished fabrics of different degrees of solubility in $0.5M$ cuene. Some,

(a)

(b)

(c)
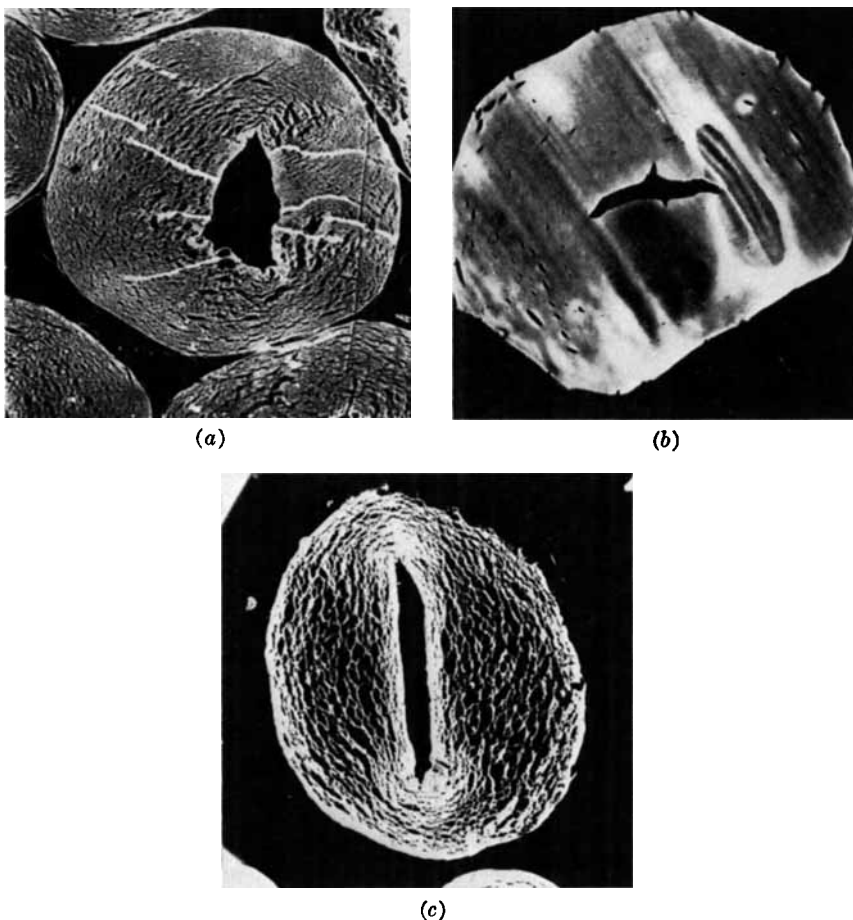
Fig. 4. Typical expansion patterns of cotton fibers. (a) DEAE-cotton. (b) DEAE-cotton treated with epichlorohydrin. (c) Unmodified cotton treated with epichlorohydrin.

such as the styrene oxide-treated DEAE-cotton, only swelled in cuene; the DEAE-cotton treated with glycidyldiethylamine was completely soluble in cuene.

In Figure 4 are typical electron micrographs of ultrathin cross-sections of fibers showing expansion patterns. The absence of crosslinks is indicated by the formation of concentric layers in cotton fibers expanded by preswelling in water and methanol and subsequent polymerization of methacrylate within the cell wall of the fiber. Lack of separation of the layers by such expansion techniques is indicative of crosslinking. The electron micrograph of DEAE-cotton (Fig. 4a) shows layering. After treatment of DEAE-cotton with epichlorohydrin (Fig. 4b), the electron micrograph of the fiber cross-section shows only a few isolated holes. The cotton control fiber treated with epichlorohydrin gives an electron micro-

TABLE III
DEAE-Cotton Cellulose–Epoxide Reaction with 8% Aqueous NAOH Catalyst[a]

Epoxide	Nitro-gen, %	Reac-tion time, hr.	Wt. gain, %	Crease recovery[b] angle $(W + F)$[c]		Break-ing str., % re-tained	Flex abra-sion, cycles
				Wet	Cond.		
Vinylcyclohexene	1.02	2	2.4	245	145	100	851
dioxide	1.22	2	2.5	207	177	96	864
	0.0	2	1.3	172	181	85	723
Butadiene diepoxide	1.02	0.5	10.3	305	170	45	720
	1.22	0.5	10.6	299	177	45	1301
	0.0	0.5	3.5	266	234	55	590
Eponite 100	1.02	2	13.3	308	186	48	872
	1.22	2	12.1	313	152	59	983
	0.0	2	3.5	224	222	67	552
Araldite RD-2	1.02	2	9.0	301	150	56	1079
	1.22	2	9.4	302	136	67	1379
	0.0	2	1.4	203	181	74	471
Epichlorohydrin	0.29	2	7.4	316	182	—	—
	0.74	2	8.2	317	230	—	—
	1.22	2	9.2	320	206	—	—
	0.0	2	3.6	264	192	—	—
Allyl glycidyl ether	0.02	2	10.4	246	132	71	738
	1.22	2	10.4	234	116	96	911
	0.0	2	2.5	201	184	85	502
Phenyl glycidyl ether	1.02	2	2.0	251	146	90	566
	1.22	2	1.6	247	148	100	543
	0.0	2	1.0	188	170	88	266
Glycidyldiethylamine	1.02	18	5.1	244	161	95	737
	1.22	18	4.9	236	178	97	666
	0.0	18	4.5	187	179	81	485
Styrene oxide	1.02	2	1.0	216	195	100	754
	1.22	2	1.0	211	195	95	662
	0.0	2	1.6	185	186	92	498
Araldite RD-1	1.02	2	2.1	184	166	93	709
	1.22	2	1.5	206	161	96	689
	0.0	2	1.1	180	163	96	489
P & G epoxide No. 7	1.02	18	0.4	205	146	—	394
	0.0	18	0.0	182	192	—	321
C_{11}–C_{14} epoxide	1.02	18	1.3	225	172	100	670
	1.22	18	2.1	236	167	85	421
	0.0	18	0.0	182	134	85	467
Butylene oxide	1.02	18	14.4	231	135	90	475
	1.22	18	13.4	271	165	86	421
	0.0	18	4.1	214	167	85	467
Control DEAE	1.02	—	—	209	188	—	542
	1.22	—	—	217	225	—	530
Control cotton	0.0	—	—	170	176	—	420

[a] Fabrics twice padded with base and then immersed in epoxide for indicated times; all titrated as weak-base anion exchangers.

[b] Average of three Monsanto crease angles.

graph (Fig. 4c) showing layering of the type characteristic of an unmodified cotton fiber.

DEAE-Cotton–Epoxide Reactions with 8% NaOH Catalyst

When NaOH is present, both DEAE-cotton and the unmodified cotton were reactive to many of the epoxides. Data in Table III show that all epoxides, except styrene oxide, were more reactive with DEAE-cotton than with unmodified cotton.

In almost all cases, the epoxide treatment of DEAE-cottons produced an improvement in the wet recovery angle and a decrease in the conditioned recovery value. Even small add-ons of such monoepoxides as phenyl glycidyl ether and glycidyldiethylamine produced a significant improvement in the wet crease recovery angles of the DEAE-cottons. Larger add-ons of butylene oxide produced an even greater improvement in wet crease recovery. Such data show that a difunctional crosslinking agent is not necessarily required for the production of wet crease recovery in chemically modified cotton fabrics.

Base-catalyzed epoxide reactions improved the flex abrasion values of both the DEAE-cottons and the unmodified cotton. The increase was never more than threefold.

The titration curves of the DEAE-cottons pretreated with aqueous NaOH and then treated with either mono- or diepoxides showed no changes from the titration curve of the original DEAE fabrics. This would indicate that epoxides did not quaternize the nitrogen groups under these conditions of added external base catalysis.

In Figure 5 are typical electron micrographs showing expansion patterns of cross-sections of fibers of a DEAE-cotton (a) and of an unmodified

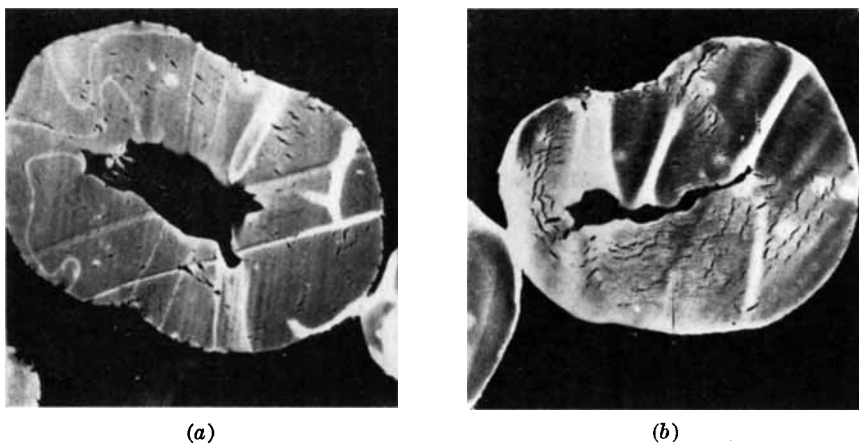(a)   (b)

Fig. 5. Typical expansion patterns of cotton fibers. (a) DEAE-cotton treated with 8% aqueous NaOH and then with epichlorohydrin to give an add-on of 9.25%. (b) Unmodified cotton treated with 8% aqueous NaOH and then with epichlorohydrin to give an add-on of 3.6%.

cotton (*b*) which had been pretreated with aqueous 8% NaOH and then treated with epichlorohydrin. Both show very little layering. This would seem to indicate that both contain crosslinks.

TABLE IV

DEAE–Cotton Cellulose–Epoxide Reaction with $Zn(BF_4)_2$ Catalyst[a]

Epoxide	Nitro-gen, %	Wt. gain, %	Crease recovery[b] angle $(W + F)°$		Break-ing str., % re-tained	Flex abra-sion, cycles
			Wet	Cond.		
Vinylcyclohexene dioxide	1.02	3.5	263	155	95	390
	1.22	3.7	273	138	92	461
	0.0	11:8	247	208	70	339
Butadiene diepoxide	1.02	8.5	241	281	38	362
	1.22	6.4	282	259	47	591
	0.0	4.6	253	284	47	152
Eponite 100	1.02	12.9	286	235	53	643
	1.22	10.3	286	227	63	593
	0.0	19.8	307	259	68	377
Araldite RD-2	1.02	11.8	293	223	53	347
	1.22	11.0	264	218	60	444
	0.0	18.2	298	274	58	390
Allyl glycidyl ether	1.02	6.6	265	190	79	601
	1.22	6.5	260	189	81	488
	0.0	5.8	238	225	67	408
Phenyl glycidyl ether	1.02	6.8	242	167	89	597
	1.22	7.3	248	172	85	464
	0.0	1.7	189	158	58	206
Glycidyldiethylamine	1.02	1.9	224	143	79	358
	1.22	2.7	218	171	77	563
	0.0	1.0	176	161	91	353
Styrene oxide	1.02	4.4	238	110	96	735
	1.22	4.4	226	131	92	600
	0.0	1.4	185	187	60	303
Araldite RD-1	1.02	2.2	207	178	99	735
	1.22	0.6	198	142	79	709
	0.0	1.7	179	182	60	526
C_{11}–C_{14} epoxide	1.02	1.8	235	145	100	362
	1.22	3.0	236	141	95	430
	0.0	0.7	173	173	71	516
Butylene oxide	1.02	2.3	257	148	88	494
	1.22	2.6	231	142	84	494
	0.0	0.3	190	176	51	321
P & G Epoxide No. 7	0.60	0.5	243	166	86	314
	1.02	—	209	188	—	542
	0.0	0.4	186	175	48	155
Control DEAE	1.22	—	217	225	—	530
Control cotton	0.0	—	170	176	—	420

[a] Fabric twice padded with methanolic solution of $0.05M$ $Zn(BF_4)_2$ and 20% epoxide, cured 5 min. at 125°C. (All finished DEAE fabrics titrated as weak-base exchangers.)

[b] Average of three Monsanto crease angles.

The fibers from unmodified cotton as well as DEAE-cotton which had been treated with butylene oxide, glycidyldiethylamine, C_{11}–C_{14} Epoxide, styrene oxide, and Araldite RD-1 dissolved in $0.5M$ cuene. The other epoxide-treated fibers either swelled to some degree or ballooned in spots when immersed in $0.5M$ cuene. The effect was independent of the nature of the starting fabric. The only exceptions were the DEAE fabrics treated with allyl glycidyl ether or Eponite 100 which were more resistant to swelling than were the similarly treated unmodified fabrics. However, the latter had smaller add-ons of the epoxides.

DEAE-Cotton—Epoxide Reaction in the Presence of $Zn(BF_4)_2$ Catalyst

In the absence of additional catalyst or with NaOH catalysis, the DEAE fabrics were more reactive toward the epoxides than were the unmodified fabrics. Data in Table IV indicate that this is also true with $Zn(BF_4)_2$ catalysis except for three diepoxides. With vinylcyclohexene dioxide, Eponite 100, and Araldite RD-2, the add-on to the unmodified fabric was twice that to the DEAE-cotton. In almost all instances, the wet recovery angle of the treated DEAE-cotton was higher or equal to that of the treated unmodified cotton. The dry recovery angle of the finished DEAE fabric was either lower than or equal to that of the epoxide-treated control cotton. Resistance to flex abrasion was not improved in any of the treatments and all finished fabrics titrated as weak-base anion exchangers. Epichlorohydrin did not react with either fabric in the presence of $Zn(BF_4)_2$.

Fabrics treated with Araldite RD-2, phenyl glycidyl ether, allyl glycidyl ether, vinylcyclohexene dioxide, Eponite 100, and butadiene diepoxide did not dissolve in $0.5M$ cuene within 30 min.

SUMMATION

So far, this study has not made it possible to generalize as to effects of epoxides on the properties of cottons or DEAE-cottons. However, it is evident that built-in basic catalysts affect crease recovery properties differently than do external base catalysts. Some of the more interesting results of this study are as follows:

Vinylcyclohexene dioxide, which does not react with cotton when uncatalyzed or base-catalyzed by NaOH, reacted with DEAE-cotton to give as high as 8% add-on in the absence of external catalyst. However, there was no significant improvement in wet or conditioned recovery angles and only partial conversion to the quaternary base form. At smaller add-ons to DEAE-cottons in the presence of both NaOH and $Zn(BF_4)_2$ catalysis, there was improvement in wet recovery angles only, a lowering of conditioned recovery angles, and no evidence of conversion

to the quaternary base. Under like conditions of catalysis, there was no decrease in conditioned recovery angles of the control cottons.

In the absence of added catalysts, butadiene diepoxide did not add appreciably to cotton, but did improve significantly the conditioned recovery angles of DEAE-cottons at add-ons as low as 3%. Even with NaOH catalysis, the add-ons to DEAE-cotton were threefold greater than to the unmodified cotton. The latter had improved conditioned and wet recovery angles, but the finished DEAE-cotton had only high wet crease recovery angles. With $Zn(BF_4)_2$ catalysis, the add-ons of butadiene diepoxide to DEAE-cottons were greater than to the unmodified cottons. In the latter, wet and conditioned recovery were improved, but only wet crease recovery was improved in the DEAE fabrics.

Unlike butadiene diepoxide, which imparted high dry crease recovery to DEAE-cotton and no improvement in its wet crease recovery in the absence of catalysts, Eponite 100, which is principally the diglycidyl ether of glycerol, imparted only high wet crease recovery to DEAE-cotton even at add-ons of less than 3%. With NaOH catalysis, results with Eponite were similar to results with BDO. With $Zn(BF_4)_2$ catalysis, the unmodified cotton had about twice the add-on of the DEAE-cotton, and all treated fabrics had approximately 300 $(W + F)°$ values for wet crease recovery angles. Improvements in dry crease recovery angles were negligible for the DEAE-cottons and high for the unmodified cottons.

Results with Araldite RD-2, the diglycidyl ether of 1,4-butanediol, were almost identical with corresponding Eponite 100 results.

The Araldite RD-1, which is the glycidyl ether of 1-butanol, added to DEAE-cotton as did Araldite RD-2, the diglycidyl ether of 1,4-butanediol. Both monoepoxide and diepoxide treatments resulted in similar improvements in wet crease recovery of the DEAE-cottons at like add-ons. However, the conditioned crease recovery angle of the DEAE-cotton finished with the monoepoxide was halved, whereas the diepoxide did not alter the conditioned recovery angle.

When the glycidyl group was attached to an unsaturated group, as in allyl glycidyl ether or phenyl glycidyl ether, the add-ons to DEAE-cotton in the absence of catalyst were large. However, the only improvement noted was with the allyl glycidyl ether which improved only the wet crease recovery angles. The phenyl glycidyl ether improved only the flex abrasion values.

Use of three monoepoxides in which the oxirane was a terminal group attached to various chain lengths as in butylene oxide, the P&G Epoxide No. 7, and the C_{11}–C_{14} Epoxide, as well as of styrene oxide, resulted in significant add-ons to DEAE-cotton only, but no improvement in conditioned or wet crease recovery angles.

If a decrease in conditioned recovery angles is an indication of quaternization of amino groups, the greatest degree of quaternization occurred with Araldite RD-1 and butylene oxide in the uncatalyzed DEAE-cotton–

epoxide reactions. With NaOH catalysis, conditioned recovery angles were lower in the DEAE-cottons than in the control fabrics after reaction with all epoxides except epichlorohydrin. With additional $Zn(BF_4)_2$ catalysis, all monoepoxides except phenyl glycidyl ether lowered the conditioned crease recovery angles of the DEAE-cottons. Only vinylcyclohexene dioxide of the diepoxide series lowered the conditioned crease recovery angles of the DEAE-cottons in the presence of $Zn(BF_4)_2$ catalysis.

Use of cotton chemically modified to introduce built-in catalysts for subsequent chemical modification of cotton in the absence of external catalysts offers interesting potential. Many chemical finishing agents which did not react with unmodified cotton with external catalysts might react with cotton if an intermediate is formed within the cellulose matrix. The use of a built-in basic group to open a variety of epoxide rings, some of which did not add to cotton with external base catalysts, as well as the use of built-in acid groups to catalyze acid-catalyzed cellulose reactions with other finishing agents, is undergoing further investigation.

References

1. M. Hartmann, U. S. Pat. 1,777,970 (Oct. 7, 1930).

2. D. M. Soignet, R. J. Berni, and R. R. Benerito, *Textile Res. J.*, **36**, 978–989 (1966).

3. R. R. Benerito, B. B. Woodward, and J. D. Guthrie, *Anal. Chem.*, **37**, 1693 (1965).

4. J. B. McKelvey, R. R. Benerito, R. J. Berni, and B. G. Burgis, *J. Appl. Polymer Sci.*, **7**, 1371 (1963).

5. J. B. McKelvey, R. R. Benerito, R. J. Berni, and C. A. Hattox, *Textile Res. J.*, **34**, 759 (1964).

6. Am. Soc. Testing Mater. Specifications. ASTM Designation 1739–59, Philadelphia, Pa.

7. U. S. Federal Supply Service, Federal Specifications CC-T-19 lb, Method 5212, Washington, D. C., U. S. Government Printing Office (1951).

8. R. A. Fujimoto, R. M. Reinhardt, and J. D. Reid, *Am. Dyestuff Reptr.*, **52**, 329 (1963).

9. Am. Soc. Testing Mater. Specifications. ASTM Designation D1175-64T, Philadelphia, Pa.

10. M. L. Rollins, J. H. Carra, E. J. Gonzales, and R. J. Berni, *Textile Res. J.*, **36**, 185 (1966).

11. J. B. McKelvey, B. G. Webre, and E. Klein, *Textile Res. J.*, **29**, 918 (1959).

12. R. R. Benerito, B. G. Webre, and J. B. McKelvey, *Textile Res. J.*, **31**, 757 (1961).

13. F. A. Blouin, N. J. Morris, and J. C. Arthur, *Textile Res. J.*, **36**, 309 (1966).

Résumé

Des réactions de différents monoépoxydes et diépoxydes sur la cellulose diéthylaminoethylée (DEAE) en absence et en présence de catalyseurs externes ont été étudiées. En absence de catalyseurs additionnels, de nombreux époxydes qui ne réagissaient pas avec

des cotons non-modifiés, réagissaient avec la coton-DEAE. D'autres qui réagissaient avec le coton non-modifié en présence de base externes, donnaient des propriétés différentes lorsqu'ils étaient catalysés par les groupes amines tertiaires incorporés au coton-DEAE. Par exemple, l'épichlorohydrine réagissait avec le coton-DEAE et produisait un tissu avec un recouvrement conditionné excellent une bonne résistance à l'humidité et des propriétés d'échange d'anions élevés. Le même époxyde fournissait uniquement un recouvrement humide au coton lorsque la réaction était catalysée par des bases externes. L'éther phényl glycidylique et l'oxyde de styrène réagissaient avec le coton-DEAE et produisaient un tissu avec une amélioration de 20 fois la résistance à l'abrasion par fraction. Avec de la soude aqueuse à 8% comme catalyseur externe, le coton DEAE manifestait une plus grande réactivité à tous les époxydes, que le tissu non-modifié. Les réactions diépoxydes de coton-DEAE avec le catalyseur basique additionné connaissent généralement une décroissance de l'angle de recouvrement conditionné et un accroissement dans l'angle de recouvrement humide. Lorsque $Zn(BF_4)_2$ était utilisé comme catalyseur additionnel, de nouveau les tissus DEAE avaient une réactivité plus grande pour les monoépoxydes; mais le coton non-modifié, était plus réactionnel vis à vis des diépoxydes que ne l'était le coton-DEAE. Les tissus DEAE traités au $Zn(BF_4)_2$-monoépoxyde avaient des angles de recouvrement humide plus élevés mais des angles de recouvrement sec plus bas, que les cotons de contrôle traités aux époxydes. Le diépoxyde de butadiène était le seul diépoxyde étudié, qui ait donné des angles de recouvrement sec plus élevés au coton-DEAE qu'au coton non-modifié de contrôle en présence de $Zn(BF_4)_2$. Des groupes amines tertiaires agissent dans les cotons-DEAE comme un catalyseur interne pour l'ouverture des anneaux oxiraniques, dirigent le site de la réaction, en absence de catalyseur additionné, et réagissent avec certains époxydes pour former des groupes azotés quaternaires.

Zusammenfassung

Reaktionen verschiedener Monoepoxyde und Diepoxyde mit Diäthylaminoäthyl-(DEAE)-cellulose in Gegenwart und Abwesenheit zugesetzter Katalysatoren wurden untersucht. In Abwesenheit zusätzlicher Katalysatoren reagierten viele Epoxyde, die mit unmodifizierter Baumwolle keine Reaktion zeigten, doch mit DEAE-Baumwolle. Andere, welche mit unmodifizierter Baumwolle in Gegenwart zugesetzter Basen reagierten, lieferten bei Katalyse durch die eingebauten tertiären Aminogruppen der DEAE-Baumwolle andersartige Produkte. Zum Beispiel reagierte Epichlohrydrin mit DEAE-Baumwolle unter Bildung eines Gewebes mit ausgezeichneter Konditionierungsbeständigkeit, guter Nassfestigkeit und Anionenaustauscher-Eigenschaften entsprechend einer starken Base. Das gleiche Epoxyd verlieh der Baumwolle bei Katalyse der Reaktion mit zugesetzten Basen nur eine Nass-Knitterfestigkeit. Phenylglycidyläther und Styroloxyd reagierten mit DEAE-Baumwolle unter Bildung eines Gewebes mit zwanzigfach verbesserter Biege-Abriebfestigkeit. Mit 8% igem wässrigem NaOH als zugesetztem Katalysator zeigte DEAE-Baumwolle gegen alle Epoxyde eine grössere Reaktionsfähigkeit als das unmodifizierte Gewebe. Die Reaktion von DEAE-Baumwolle mit Diepoxyd bei Zusatz eines basischen Katalysators führte zu einer Neigungsabnahme der Konditionierungsbeständigkeit und einer Zunahme der Nassfestigkeit. Bei Verwendung von $Zn(BF_4)_2$ als zusätzlichem Katalysator zeigen wieder die DEAE-Gewebe die grössere Reaktionsfähigkeit gegen die Monoepoxyde; die unmodifizierte Baumwolle dagegen war gegen die Diepoxyde reaktionsfähiger als DEAE-Baumwolle. Die mit $Zn(BF_4)_2$-Monoepoxyd behandelten DEAE-Gewebe besassen die grössere Neigung in der Nassfestigkeit aber die niedrigere in der Trockenfestigkeit, als die entsprechenden mit Epoxyd behandelten Baumwoll-Kontrollproben. Butadiendiepoxyd war das einzige untersuchte Diepoxyd, das der DEAE-Baumwolle eine höhere Neigung der Trockenfestigkeit verlieh, als der unmodifizierten Baumwoll-Kontrollprobe in Gegen-

wart von $Zn(BF_4)_2$. Tertiäre Amingruppen in DEAE-Baumwolle wirken als innerer Katalysator für die Öffnung der Oxiranringe, geben die Richtung für den Reaktionsort in Abwesenheit zusätzlicher Katalysatoren und reagieren mit einigen Epoxyden unter Bildung quaternärer Stickstoffgruppen.