Use of Dihalohydrin Precursors of Butadiene Diepoxide in the Chemical Modification of Cotton Cellulose

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Synopsis

Dihalohydrin precursors of *meso*-butadiene diepoxide or *d,l*-isomers of butadiene diepoxides have been reacted with cotton cellulose. It has been shown that *d,l*-2,3-dibromo-1,4-butanediol, *d,l*-2,3-dichloro-1,4-butanediol, *meso*-2,3-dichloro-1,4-butanediol, and *meso*-1,4-dichloro-2,3-butanediol can be added to cotton in small amounts (1–4%) to increase both dry and wet crease resistance of the fabric. Several methods of application were investigated, and two methods for the *in situ* formation of the butadiene diepoxides in cotton and their subsequent reaction with cellulosic hydroxyls rather than solvolysis have been proposed. Both processes call for the application of the dihalohydrin from an aqueous solution and subsequent treatment of the dried fabric by either of the following: (*1*) absolute alcoholic solution of NaOH or (*2*) concentrated aqueous solution of Na_4SiO_4 saturated with NaCl. With the former, a slow curing of the dehydrohalogenated sample in a sealed polyethylene bag at room temperature or a rapid high temperature cure could be used; with the latter, increased dry and wet crease resistance was obtained only with a rapid high temperature cure. Use of aqueous orthosilicate solutions offers a potential commercial application, since the dihalohydrins are relatively inexpensive and such a process avoids handling of the volatile and relatively toxic butadiene diepoxides. Typical fabric properties obtained with the various methods are included.

INTRODUCTION

Results of an extensive study of acid- and base-catalyzed reactions between cotton cellulose and isomeric butadiene diepoxides have been reported.[1,2] Differences in the base-catalyzed cellulose-butadiene diepoxide reaction rates observed with the *meso*-isomer (BDE) and the *d,l*-isomers (BDO) have been attributed to the greater solubility of BDO, particularly in concentrated aqueous sodium hydroxide solutions, as evidenced by different distribution coefficients for BDO and BDE between CCl_4 and aqueous base phases.[3] Selection of experimental concentrations of base and butadiene diepoxide allowed for any predetermined add-on and any degree of wet or dry crease recovery in cottons finished with base catalysis. However, the add-ons of either BDE[1] or BDO[4] to cotton with

acid catalysis could not be varied as could those of other diepoxides.[5] Although the relatively expensive BDO and BDE showed low efficiencies under conditions of acid catalysis, they were nevertheless excellent crease-proofing agents for cotton, even at negligible add-ons.

The objectives of this investigation were the *in situ* preparation of BDO or BDE in cotton by dehydrohalogenation of their less expensive and less toxic dihalohydrin precursors and the subsequent reaction of these die-poxides with cellulosic hydroxyls rather than with solvent media or other diepoxide molecules. The attainment of both objectives in an all-aqueous medium of sodium hydroxide either in a one-step or two-step process regardless of order of addition of reagents was not realized. The objectives have been obtained, however, by (a) the use of alcoholic solutions of caustic or (b) by the use of concentrated aqueous solutions of sodium orthosilicate, preferably saturated with sodium chloride, as the dehy-drohalogenation agents.

Dehydrohalogenation

In the synthesis of nonvolatile epoxides by dehydrohalogenation, the halohydrins are usually dissolved in a water-immiscible solvent such as ether or chloroform and then contacted with dry or nearly dry hydroxide, Na_4SiO_4, or other alkali.[6,7] Such processes, which are not applicable to a three-phase system involving cotton, prevent intimate mixture of the epoxide with ions of salts of alkali so that the rapid dehydrohalogenation takes place before the slower hydrolysis of the oxirane rings. The choice of methanol or ethanol as the dehydrohalogenating medium in this study was based on the following facts: (a) BDO reacted with cotton which had been activated with methanolic NaOH;[2] (b) ethylene oxide has been reacted with sodium alcoholates under mild conditions[8] to from monoalkyl ethers of glycol, but high temperature and pressure are required if the alcohol rather than the alkoxide is used;[9] (c) cellulosic hydroxyls, like those of other polyols, should be more acidic than those in simple alcohols,[10] and therefore since the latter do not form alkoxides easily with NaOH they should not be too competitive with cellulosic alkoxides for reaction with BDO or BDE; (d) Gerzon[11] reported that N,N,N-tris(3-chloro-2-hydroxypropyl)amine can be dehydrohalogenated in the presence of methanol diluted with ether; and (e) epoxide ring openings in ethanol have been investigated by others.[12,13] Dry alcoholic solutions of alkali hydroxides function as dehydrohalogenating agents because they are less "ionic" than corresponding aqueous solutions because of ion pair associa-tions even in dilute solutions.[14]

EXPERIMENTAL

Materials

Research grade d,l-2,3-dibromo-1,4-butanediol, m.p. 128°C., d,l-2,3-dichloro-1,4-butanediol, m.p. 65°C., and meso-2,3-dichloro-1,4-butanediol, m.p. 119°C., were obtained from Koppers Company, Inc.

Pure *meso*-1,4-dichloro-2,3-butanediol, m.p. 121°C., was prepared from 1,4-dichloro-2,3-epoxybutane obtained from Union Carbide Chemical Co. by a previously reported method.[6]

Dehydrohalogenation of Dihalohydrin on Cotton

a. Aqueous Solutions of Dihalohydrin—Two-Step Process. When the precursor is applied from aqueous solution, a critical sequence of addition of reactants is required. A typical application consisted of twice padding the fabric with an aqueous solution containing 5–20% of the dihalohydrin to approximately 100% wet pickup. Of the dihalohydrin precursors, only the *d,l*-2,3-dichloro-1,4-butanediol was soluble in water to the extent of 15–20% at 25°C. Others were dissolved in water at 75°C. and the hot solutions were used in the pad baths to prevent crystallization of the dihalohydrins on the surface of the cotton. After being padded, the fabrics were dried in an oven at 110°C. for 5 min., twice padded with alcoholic NaOH (3–10%) solutions and cured by either of the following methods: (*1*) the fabric was placed in a sealed polyethylene bag for periods in the range of 16–24 hr. at 25°C., or (*2*) the fabric was placed in an oven at 100–125°C. for a rapid cure. If the fabric after being padded with alcoholic caustic was allowed to stand in the open for 24 hr. (or even a few hours), enough moisture was taken up to give negative results.

b. Alcoholic Solutions of Dihalohydrin—One-Step Process. The fabrics were twice padded in methanolic or ethanolic solutions containing 10–20% of the dihalohydrin and enough NaOH or KOH to give a slight excess of base over that required for the dehydrohalogenation. The fabrics were then cured either by a slow process at 25°C. in a sealed polyethylene bag or rapidly in an oven at 100–125°C.

c. Use of "Controlled Alkali" in Aqueous Media for Dehydrohalogenation—Two-Step Process. This method was the same as the two-step procedure discussed above except that the dehydrohalogenation process or second step was accomplished by use of aqueous "controlled alkali." Previous work with cellulose–epichlorohydrin reactions[15,16] showed that certain silicates, phosphates, and azides, or aqueous solutions of caustic soda and sodium chloride could be used as dehydrohalogenating agents to produce dry resiliency in cottons. Preliminary experiments with precursors of BDO and BDE revealed that sodium carbonate, trisodium phosphate, sodium tetrapyrophosphate, sodium metasilicate, and caustic soda in the presence of concentrated sodium chloride as dehydrohalogenating agents were ineffective in producing increased dry crease recovery in cotton. Sodium orthosilicate, however, which may be considered as a mixture of caustic soda and the metasilicate, was an effective dehydrohalogenating agent and produced chemically modified cottons possessing both high and dry and high wet crease resistance.

Textile Testing

After completion of all etherifying reactions, the treated fabrics were washed free of reactants with tap water, then with dilute acetic or nitric

acids, rinsed in tap water, and finally in distilled water. Those fabrics cured in the presence of silicates were also given a mild hydrofluoric acid wash, and rinsed thoroughly in tap water. After a final rinse in distilled water, the fabrics were ironed dry at 160°C. and conditioned for 24 hr. before being weighed and tested.

The following textile tests were carried out according to the American Society for Testing Materials Specifications or Federal Specifications Standard Methods: breaking strengths by the strip method (80-thread count width) on a Scott Tester,[17a] tearing strengths by the Elmendorf method,[17b] and crease recovery angles by the Monsanto method[17c] with a 500-g. weight.

RESULTS AND DISCUSSION

Data in Table I are typical of add-ons and crease angles obtained by application of the dihalohydrin by the two-step process a followed by slow curing at room temperature in a sealed polyethylene bag. In general, a slight excess of base over that required to dehydrohalogenate the dihalohydrin was required. Usually, best results were obtained with a molar ratio of hydroxide/dihalohydrin of approximately 2.5. At this molar ratio, the d,l-2,3-dichloro-1,4-butanediol, which was the most soluble of the

TABLE I
Properties of Fabrics Treated with Dihalohydrins by a Two-Step Slow-Cure Process[a]

Pad baths		Mole ratio NaOH/ dihalo- hydrin	Add-on, %	Crease angles, (W + F)°	
Dihalohydrin and concentration, %	NaOH, %			Wet	Dry
d,l-2,3-Dibromo-1,4-butanediol					
10	5.0	2.8	1.4	245	230
15	7.5	2.8	1.7	243	245
15	7.5	2.8	2.3	243	261
d,l-2,3-Dichloro-1,4-butanediol					
12	5.0	1.6	0.2	215	235
20	10.0	2.0	2.4	246	230
10	5.0	2.0	1.0	230	232
15	10.0	2.6	6.1	225	255
$meso$-2,3-Dichloro-1,4-butanediol					
10	5.0	2.0	0.3	248	237
15	10.0	2.6	1.8	242	248
$meso$-1,4-Dichloro-2,3-butanediol					
15	7.5	2.0	loss	180	216
15	10.0	2.6	2.8	230	253
Control	—	—	—	156	185
Control	2.0	—	—	180	180

[a] 80 × 80 fabric padded with aqueous solution of dihalohydrin, dried 5 min. at 105°C., padded with absolute ethanolic solutions of NaOH, and cured 17–24 hr. in sealed polyethylene bags at 25°C.

four dihalohydrins in water, gave the largest add-ons to cotton. However, neither the dry nor wet crease resistance was increased over that resulting with lower add-ons of the other dihalohydrins. Also, with the most soluble d,l-2,3-dichloro-1,4-butanediol, 95% ethanol could be substituted for absolute ethanol as the solvent for NaOH. Use of 95% ethanolic solutions of NaOH with the other halohydrins resulted in lower wet and dry crease angles at equivalent weight gains. When the dihalohydrins were applied out of absolute methanol rather than aqueous solutions in the first step, increased dry crease resistance, but no increased wet resistance, was obtained. For example, application of 15% meso-1,4-dichloro-2,3-butanediol in absolute methanol, followed by application of 10% NaOH in methanol, gave negligible add-ons to cotton cured in polyethylene bags at 25°C., dry crease angles of 250(W+F)°, but no improvement in wet crease angles over that of the control fabric. This phenomenon of improved dry crease resistance without improved wet crease resistance has been observed with cotton finished with certain diepoxides in nonaqueous solvents which do not swell cotton. In general, fabrics having dry crease angles approximating 260(W+F)° by this method experienced 30–40%

TABLE II

Properties of Fabrics Treated with Dihalohydrins by a Two-Step Fast-Cure Process[a]

Pad baths		Mole ratio hydroxide/ dihalohydrin	Add-on, %	Crease angles, (W + F)°	
Dihalohydrin and concentration, %	NaOH, %			Wet	Dry
d,l-2,3-Dibromo-1,4-butanediol					
10	5.0	2.8	0.0	214	216
20	10.0	2.8	1.0	189	189
d,l-2,3-Dichloro-1,4-butanediol					
12	5.0	1.6	1.2	208	205
10	5.0	2.0	2.0	190	217
15	7.5	2.0	0.1	193	203
20	10.0	2.0	0.1	202	228
15	10.0	2.6	2.6	196	214
15	10.0[b]	2.6	4.2	231	248
meso-2,3-Dichloro-1,4-butanediol					
10	5.0	2.0	1.0	221	249
15	10.0[b]	2.6	1.4	213	231
meso-1,4-Dichloro-2,3-butanediol					
15	7.5	2.0	Loss	172	193
20	10.0	2.0	Loss	178	198
15	7.5[b]	2.0	1.2	202	248
15	10.0[b]	2.6	1.8	204	250
Control	—	—	—	145	195
Control	2.0	—	—	175	180

[a] 68 × 72 fabrics padded with aqueous solutions of dihalohydrin, dried 5 min. at 105°C., padded with absolute ethanolic solution of NaOH, and cured 5 min. at 105°C.

[b] Base dissolved in absolute methanol.

TABLE III

Properties of Fabrics Treated with Dihalohydrins by a One-Step Slow-Cure Process[a]

| Pad baths | | Mole ratio hydroxide/ dihalohydrin | Add-on, % | Crease angles, (W + F)° | | Breaking strength, % retained | Tearing strength, % retained |
Dihalohydrin and concentrations, %	NaOH, %			Wet	Dry		
d,l-2,3-Dibromo-1,4-butanediol							
15	7.5	2.8	1.7	230	246	67	60
20	10.0	2.8	1.5	227	230	70	56
d,l-2,3-Dichloro-1,4-butanediol							
15	7.5	2.0	1.5	221	235	76	54
20	10.0	2.0	1.2	215	220	77	58
meso-2,3-Dichloro-1,4-butanediol							
10	10.0	4.0	1.7	215	218	—	—
10	10.0	4.0	1.4	207	224	—	—
meso-1,4-Dichloro-2,3-butanediol							
15	7.5	2.0	Loss	189	174	100	75
20	10.0	2.0	Loss	193	172	100	70
Control	—	—	—	145	195	—	—

[a] 68 × 72 fabric twice padded to 100% pickup with absolute ethanolic solution of dihalohydrin and base and cured in a sealed polyethylene bag for 20 hr. at room temperature.

losses in breaking strength and 40–50% losses in tearing strength even with the add-ons of less than 2%. These losses in tensile strength for comparable dry angles were equivalent to those obtained by both acid and base catalyzed reactions with BDO or BDE and cotton.

Table II contains some typical data obtained by the two-step process a followed by a rapid oven cure at 110°C. In brief, this faster curing process was not as effective as the slower curing process at 25°C. in a sealed polyethylene bag. The data also indicated that methanolic base solutions gave better results than ethanolic base solutions by this fast curing technique. The increases in wet recovery over the control value were greater than the corresponding increases for the dry recovery values. However, only dry crease angles as high as 250(W+F)° were realized in a few instances.

These investigations also included application of the dihalohydrins from dioxane rather than aqueous solutions and reversal of the sequence of application of base and halohydrins in the two-step process. All of these procedures resulted in very small add-ons, wet crease angles varying in the range 200–220(W+F)°, and dry crease angles less than that of the control.

Shown in Table III are typical add-ons, crease angles, and tensile properties for fabrics finished by a one-step application of the dihalohydrins from absolute ethanolic solution containing NaOH and subsequently cured in a sealed polyethylene bag at room temperature. Use of a rapid oven cure by this one-step process failed to increase either wet or dry crease resistance.

Weight gains were realized with use of several aqueous alkali solutions in process c, but wet and dry crease angles were increased only when the dehydrohalogenation occurred in concentrated solutions of sodium orthosilicate and a rapid oven cure was used. Slow cures at room temperature in sealed polyethylene bags even with 20% Na_4SiO_4 saturated with NaCl did not produce increased dry crease resistance. Typical data in Table IV show that the concentration of Na_4SiO_4 in the aqueous phase is critical.

That the amount of water present at time of dehydrohalogenation is critical is evidenced by (1) lack of production of dry resiliency when practical grade KOH, which has a larger moisture content than NaOH, is substituted in process a, (2) negative results when fabrics dehydrohalogenated in alcoholic base are exposed to atmospheric conditions rather than being placed in sealed polyethylene bags, and (3) necessity of high temperature cure in use of process c.

The use of aqueous orthosilicate solutions might have commercial possibilities, since the dihalohydrin precursors are relatively inexpensive and such a process would avoid the handling of the volatile and relatively toxic butadiene diepoxides.

Although the rate of hydrolysis of butadiene diepoxide increases with the increase in caustic concentration up to 23% NaOH,[3] the efficiencies of both the BDO-cotton[1] and BDE-cotton reactions[2,18] attain a maximum at

TABLE IV
Effect of Various Alkalies in Aqueous Solutions as Dehydrohalogenating Agents in a
Two-Step Process[a]

Pad baths		Add-on, %	Crease angles, Monsanto $(W + F)°$	
Dihalohydrin, %	Base and concentration, %		Wet	Dry
Control	—	—	145	195
20	NaOH, 10	0	150	180
20	NaOH, 10; sat'd. NaCl	1.8	197	219
15	Na_4SiO_4, 15	1.1	196	211
15	Na_4SiO_4, 15; sat'd. NaCl	1.4	222	218
15	Na_4SiO_4, 20	2.3	237	233
20	Na_4SiO_4, 20; sat'd. NaCl	2.4	254	242
20	Na_4SiO_4 20	6.1	242	225
20	Na_4SiO_4, 20; sat'd. NaCl	7.0	235	237
20	Na_4SiO_4, 15; sat'd. NaCl	6.3	208	239

[a] 68 × 72 fabrics padded with aqueous solutions of d,l-2,3-dichloro-1,4-butanediol, dried 5 min. at 105°C., padded with aqueous solutions of indicated alkali, and cured 5 min. at 120°C.

that caustic concentration causing maximum swelling of the cotton fiber. For dilute concentrations of base, such as those used in these dehydrohalogenating experiments, only about 5% of the amount of butadiene diepoxide hydrolyzed added to the cotton.[1,3,18] With the dihalohydrin precursors and a slight excess of base, usually about one-fourth of the theoretical amount of diepoxide generated added to the cotton. In a few instances, as high as three-fourths of the theoretically available diepoxide added to cotton. Therefore, the efficiency of these dihalohydrin-cotton reactions are higher than those of the BDO– or BDE–cotton reactions in the presence of very dilute aqueous base.

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Résumé

On a fait réagir les dihalohydrines précurseurs du diépoxyde de *meso*-butadiène ou des isomères *d,l* des diépoxydes de butadiène avec la cellulose de coton. Il a été démontré que *dl*,-2,3-dibromo-1,4-butanediol, *d,l*-2,3-dichloro-1,4-butanediol, *meso*-2,3-dichloro-1,4-butanediol, et *meso*-1,4-dichloro-2,3-butanediol peuvent être additionnés au coton en faible quantité (1–4%) pour augmenter la résistance du tissu au plissage à sec et à l'humidité. On a étudié plusieurs méthodes d'application et on a proposé 2 méthodes pour la formation *in situ* du diépoxyde de butadiène dans le coton et la réaction ultérieure avec les hydroxyles cellulosiques (de préférence à la solvolyse). Les deux procédés demandent l'application de dihalohydrine dans une solution aqueuse et un traitement subséquent du tissu sec par l'un des réactifs suivants: (*1*) solution de NaOH dans l'alcool absolu ou (*2*) solution aqueuse concentrée de Na₄SiO₄ saturée avec NaCl. Avec la première solution on peut faire soit un traitement lent d'un échantillon déhydrohalogéné dans un sac de polyéthylène scellé à température de chambre, soit un traitement rapide à haute température; pour la seconde, seul le traitement rapide à haute température a donné une plus grande résistance aux plis à sec et à l'humidité. L'utilisation de solutions aqueuses d'orthosilicate offre une possibilité d'application commerciale puisque les dihalohydrines sont relativement bon marché et un tel procédé évite la manipulation des diépoxydes de butadiène volatils et relativement toxiques. Les propriétés typiques des tissus obtenus avec différentes méthodes sont inclues.

Zusammenfassung

Dihalohydrinvorstufen von *Meso*butadiendiepoxyd oder *d,l*-Isomeren von Butadiendiepoxyden wurden mit Baumwollzellulose zur Reaktion gebracht. Es wurde gezeigt dass zur Vergrösserung der Trocken- und Nass Knitterfestigkeit des Gewebes geringe Beträge (1–4%) von *d,l*-2,3-Dibrom-1,4-butandiol, *d,l*-2,3-Dichlor-1,4-butandiol, *Meso*-2,3-dichlor-1,4-butandiol und *Meso*-1,4-dichlor-2,3-butandiol der Baumwolle zugesetzt werden können. Mehrere Anwendungsmöglichkeiten wurden untersucht und zwei Methoden der *in-situ*-Bildung von Butadiendiepoxyden in Baumwolle und ihre darauffolgende Reaktion mit Zellulosehydroxylen bevorzugt vor einer Solvolyse, wurden vorgeschlagen. Beide Prozesse verlangen Anwendung von Dihalohydrin in wässriger Lösung und darauffolgende Behandlung des getrockneten Gewebes mit einem der nachfolgenden Systeme: (*1*) absolutalkoholische Lösung von NaOH oder (*2*) konzentrierte wässrige Lösung von Na₄SiO₄, gesättigt mit NaCl. Mit ersterer kann eine langsame

Nachbehandlung der dehydrohalogenierten Probe in einer verschlossenen Polyäthylenhülle oder eine schnelle Hochtemperaturnachbehandlung angewendet werden; mit letzterer wurde eine vergrösserte Nass- und Trockenknitterfestigkeit nur mit einer schnellen Hochtemperaturnachbehandlung erreicht. Die Verwendung von wässriger Orthosilikatlösung bietet eine mögliche kommerzielle Verwertung, da die Dihalohydrine relativ billig sind, und dieser Prozess eine Verwendung der flüchtigen und relativ giftigen Butadiendiepoxyde vermeidet. Typische, mit den verschiedenen Methoden erhaltene Gewebeeigenschaften werden angegeben.