

## Cellulose-*d,l*-Butadiene Diepoxide Reactions Catalyzed by Lewis Acids\*

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### Synopsis

The reactions between cotton cellulose and the racemic mixture of *d,l*-isomers of butadiene diepoxide (BDO) in the presence of various Lewis acids have been studied. In particular, the zinc fluoborate-catalyzed reaction has been studied in various solvent media, with various mole ratios of reactants, and at various times and temperatures of cure. It has been shown that BDO will add to cotton from aqueous solutions to form products possessing dry and wet crease resistance provided the concentration of BDO is greater than 20%. Substitution of methanol for water results in excellent dry and wet crease resistant cottons after application of BDO at low concentrations followed by curing at relatively low temperatures (100–125°C.). In the wide epoxide/catalyst/AGU molar ratios investigated, weight gains were found to be relatively independent of concentrations used, but improvements in dry and wet crease angles depended on molar ratios of reactants. Application of BDO in methanolic solutions to cellulose of diverse accessibilities resulted in greatest improvement in crease recovery properties at lowest weight gain in ramie, the cellulose of highest crystallinity value. In addition, it was shown that BDO reacts with a number of chemically modified cottons. Dry crease resistance was improved in cottons acetylated to a low degree of substitution, dialdehyde cotton, and carboxymethylated cottons. Improvement in dry crease resistance was not observed in cottons acetylated to a high degree of substitution or in cyanoethylated cottons. The latter exhibited substantial improvement in wet crease resistance only. Possible reaction mechanisms have been considered.

### INTRODUCTION

Recently, it was reported that *meso*-butadiene diepoxide (BDE) could be used to crosslink cotton cellulose under conditions of both acid and base catalysis.<sup>1</sup> With the availability of the *d,l*-racemic mixture of butadiene diepoxide (BDO),<sup>2</sup> work in our laboratories showed that although the *meso*- and *d,l*-isomers behaved similarly in their reactions with cellulose in some instances, there were enough differences in their physical properties, such as boiling points and solubilities, to warrant further investigations. For example, BDO was found to be much more soluble in high concentrations

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of aqueous caustic solutions than BDE and did not form a solid polymer as did the latter. The BDO could be used to crosslink cellulose pretreated with solutions of NaOH as concentrated as 23% with resultant formation of etherified cottons possessing both wet and dry crease resistance, whereas BDE required concentrations of base less concentrated than 6% for the production of dry crease resistance. The subject of base catalysis has been reported previously,<sup>3</sup> and a future report will deal with the *in situ* formation of the isomeric butadiene diepoxides by the dehydrohalogenation of their precursors within the cellulose fiber.<sup>4</sup> The present work reports the findings of an extensive study of the reactions between BDO and cotton cellulose in the presence of various Lewis acids, and in particular the zinc fluoborate-catalyzed reaction. The effects of solvent media, molar ratios of reactants, and reaction temperatures have been investigated. In addition, cellulose of diverse accessibility, such as ramie and viscose, and a number of chemically modified cottons were reacted with BDO, and the properties of the resultant products compared with those obtained with cotton.

## EXPERIMENTAL

### Materials

Research grade racemic mixture of *d,l*-isomers of butadiene diepoxide (BDO), b.p. 145°C. and epoxy equivalent of 2.32 eq./100 g. as determined by the method of Durbetaki<sup>5</sup> was obtained from Koppers Company, Inc. Other properties of BDO are adequately described in the technical literature.<sup>2</sup>

The inorganic fluoborates and many BF<sub>3</sub> complexes of organic compounds used as catalysts were obtained from the Harshaw Chemical Company.

The PF<sub>5</sub> derivatives and adducts used as catalysts were obtained from the Ozark-Mahoning Company.

### Fabric Description

An 80 × 80 cotton print cloth weighing 3.12 oz./yd.<sup>2</sup> was desized, scoured, and then processed in commercial peroxide bleaching equipment. The majority of experiments were with samples measuring approximately 13 × 13 in. and weighing 10–12 g. All chemically modified cottons used for comparative purposes were laboratory preparations. The partially acetylated fabrics were of a 48 × 44 construction originally and prepared as previously reported.<sup>6</sup> The cyanoethyl, dialdehyde, and carboxymethyl cottons were prepared as previously reported<sup>7–9</sup> and were chemically modified 80 × 80 print cloths.

The ramie fabric was a sample of 39 × 39 men's suiting cloth of unknown origin obtained from the microscopy section. The viscose, a plain weave 75 × 80 fabric, was given a mild soap-soda scour.

### Application of BDO

A freshly prepared aqueous or methanolic solution containing known weight percentages of the diepoxide and catalyst was used to twice pad cloth to a 90–100% wet pickup. Samples were oven-cured at the indicated temperature. After curing was completed, samples were washed in methanol, then in dilute base or acid, to neutralize the catalyst, finally washed in distilled water, ironed dry (160°C.), and conditioned 24 hr. before weight gains and fabric properties were determined.

### Textile Testing

The following textile tests were carried out according to ASTM or Federal Specifications Standard Methods: breaking strengths by the strip method on a Scott Tester;<sup>10a</sup> tearing strengths by Elmendorf method;<sup>10b</sup> and crease recovery angles by Monsanto method.<sup>10c</sup>

### Microscopical Examination

Methods of optical microscopy were applied to observe the amount of swelling and dissolution of BDO-treated fibers after immersion in 0.5*M* cupriethylenediamine (cuene). More detailed information concerning the extent of crosslinking was obtained from electron micrographs by use of specialized techniques on ultrathin (500–800 Å.) cross sections of treated fibers which had been immersed in 0.5*M* cuene. These techniques have been described previously.<sup>11–13</sup>

## RESULTS AND DISCUSSION

### Change in Mole Ratios of Reactants

A series of methanolic solutions in which the weight percentages of both BDO and zinc fluoborate catalyst were varied are listed in Table I. Resultant weight gains obtained after curing fabrics at 100°C. for 5 min., crease angles, breaking strengths, and tearing strengths are also given. The series of solutions was designed to investigate effects of change in mole ratios of epoxide/Zn(BF<sub>4</sub>)<sub>2</sub>/AGU (anhydroglucose units of cotton cellulose) on weight gains and crease resistance properties of resultant fabric. These data indicate that the crease angles imparted depend upon the mole ratios of all reactants. Although the weight gains are very small in all instances, the crease resistance of the fabric varied greatly. For each AGU/Zn(BF<sub>4</sub>)<sub>2</sub> ratio, the wet and dry crease angles increased with increase in BDO/Zn(BF<sub>4</sub>)<sub>2</sub> mole ratio. In general, best crease resistance was obtained at the AGU/Zn(BF<sub>4</sub>)<sub>2</sub> mole ratio of 50. In every instance, dry crease angles were equal to or greater than wet crease angles.

A similar series of experiments in which water was the solvent resulted in similar weight gains. However, there was no significant improvement in either wet or dry crease resistance, and negligible changes in breaking strengths and tearing strength at all mole ratio of reactants investigated.

TABLE I  
Effect of Composition of Padding Solutions of BDO on Weight Gains and Fabric Properties\*

Composition of pad baths		Mole ratios		Weight gain, %	Crease angles (W + F) <sup>o</sup>		Breaking strength, % retained	Tearing strength, % retained
		BDO/ Zn(BF <sub>4</sub> ) <sub>2</sub>	AGU/ Zn(BF <sub>4</sub> ) <sub>2</sub>		Wet	Dry		
5.3	5.26	50		0.3	203	63.6	70.0	
7.7	7.89	"		0.6	200	71.0	55.2	
10.0	10.53	"		1.0	241	58.9	58.0	
12.2	13.16	"		1.5	231	63.6	50.7	
14.3	15.79	"		2.1	266	60.4	46.9	
16.3	18.42	"		2.8	231	54.1	43.8	
21.7	21.06	"		2.5	272	52.7	51.3	
4.3	5.26	67		0.2	200	61.2	66.0	
5.4	7.02	"		0.7	239	61.1	62.0	
8.5	10.53	"		0.9	236	58.3	58.7	
14.5	21.06	"		2.1	238	52.6	50.7	
2.8	5.26	100		0.3	197	70.0	72.7	
5.4	10.53	"		0.5	222	60.9	64.7	
7.9	15.79	"		1.1	232	57.2	58.7	
10.3	21.06	"		1.5	234	57.2	54.7	
2.3	8.48	200		0	192	78.3	79.3	
2.8	10.53	"		0	186	77.9	83.3	
5.5	21.06	"		0.6	212	61.9	69.3	
8.1	31.56	"		0.6	200	73.8	67.0	
10.5	42.12	"		0.8	216	71.6	63.0	
Control	—	—		—	158	44.06 lb. (W), 36.88 lb. (F)	1200 g. (W), 840 g. (F)	

\* 80 X 80 fabrics twice padded to 100% wet pickup with freshly prepared methanolic solutions and cured immediately at 100°C. for 5 min.

Moisture content and regain values of all finished fabrics, regardless of final crease resistance imparted or solvents used, were not significantly different from the respective control values.

In Figure 1, changes in crease angles with changes in BDO/ $\text{Zn}(\text{BF}_4)_2$  mole ratios for an AGU/ $\text{Zn}(\text{BF}_4)_2$  ratio of 50 are shown for both aqueous and methanolic solutions. This graph illustrates the great improvement in crease resistance with increase in epoxide/catalyst ratio when methanolic solutions of BDO are used.

BDO is different from other diepoxides studied previously<sup>14</sup> in that weight gains of other diepoxides could be varied considerably by varying the mole ratios of reactants. These investigators have been unable to

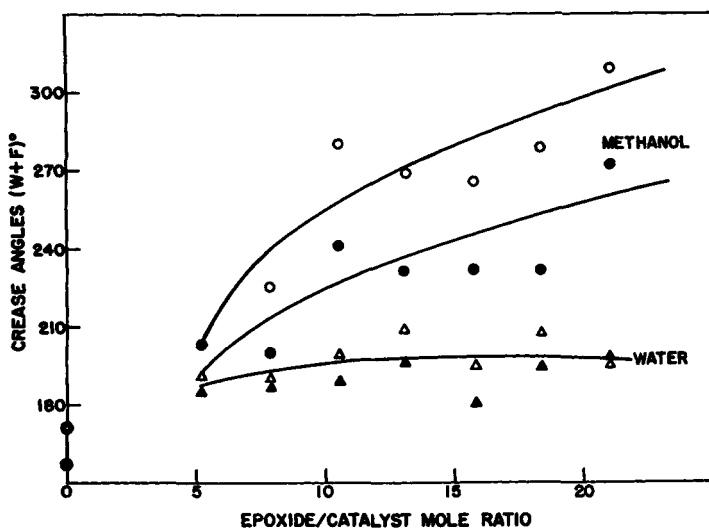


Fig. 1. Variation of crease angles with BDO/ $\text{Zn}(\text{BF}_4)_2$  molar ratio at constant AGU/ $\text{Zn}(\text{BF}_4)_2$  mole ratio of 50: (O) dry angles obtained with methanol as solvent; ( $\Delta$ ) dry angles obtained with water as solvent; ( $\bullet$ ) wet angles obtained with methanol as solvent; ( $\blacktriangle$ ) wet angles obtained with water as solvent. In water, both wet and dry angles follow lowest curve.

obtain large weight gains of either BDO or BDE to cotton under condition of zinc fluoroborate catalysis regardless of mole ratio of reactants, solvent media, time, or temperature of cure used. It was thought originally that the speed of hydrolysis of BDO in the presence of acid or  $\text{Zn}(\text{BF}_4)_2$  interfered with the cellulose-BDO reaction and accounted for the very small add-ons at all molar ratios of reactants. Therefore, the kinetics of the hydrolysis of both BDO and BDE have been investigated.<sup>15</sup> At catalyst concentration which gave the optimum add-on to cellulose, the specific reaction rate constants for opening of both oxirane rings are not larger than those of other diepoxides which were found to give much larger add-ons to cotton.<sup>14</sup> With vinylcyclohexene diepoxide,<sup>16</sup> the ratio of the specific reaction rate constants for opening of the first and second oxiranes,  $k_2/k_1$ ,

was less than unity, whereas this ratio was greater than unity for BDO and BDE under similar conditions of catalysis.

### Cellulose-BDO-Zn(BF<sub>4</sub>)<sub>2</sub> Reaction in Water

The BDE did not add appreciably to cotton padded with aqueous solutions of 10–15% diepoxide and 1% Zn(BF<sub>4</sub>)<sub>2</sub> catalyst and cured 5 min. at 125°C.<sup>1</sup> Weight gains were absent or slight, and no crease recovery properties were noted. Similar results have been obtained with BDO in which the epoxide/catalyst ratio varied from 5 to 21 and the AGU/catalyst ratios varied from 50 to 200. Weight gains were 0.8–1.2%; usual tensile strength losses were 10%, and the maximum strength loss was 20%. Crease angles were almost unchanged. While the results obtained were negative as far as crease recovery is concerned, they show that there is little basis for believing that the catalyst seriously damages the fabric. Schroeder and Condo<sup>17</sup> recommended with certain other diepoxides a curing temperature of 165°C., but for our work 100–125C. was ample, since some epoxide rings open with greater facility.

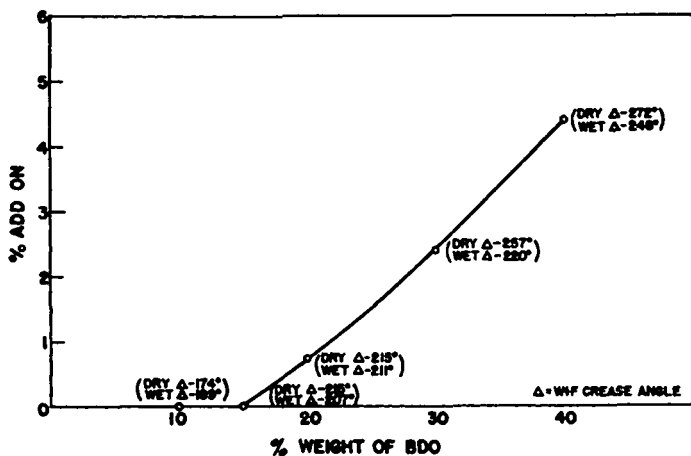


Fig. 2. Variations of add-ons of BDO and crease angles of finished cottons with concentrations of BDO used in aqueous pad baths of molar ratios of BDO/Zn(BF<sub>4</sub>)<sub>2</sub> = 10.

Attempts were also made to ascertain if any conditions existed in aqueous solution by which BDO could be added to cotton to cause improved crease recovery. Variations of weight gains and crease angles with the weight per cent of BDO used in aqueous pad baths are shown in Figure 2. It can be seen that an addition of BDO does occur at a 40% concentration in water and the add-on rapidly diminishes as the epoxide concentration is lowered. At every concentration level, the efficiency of the process is low. A concentration of 30–40% is required before useful properties are observed. In such epoxide solutions there is still more than enough water present to hydrolyze the epoxide, and there is obviously a sufficient fraction of the

epoxide available to react with the cellulose. Data in Figure 2 were obtained at a constant epoxide/catalyst ratio of 10/1. In another series of reactions in aqueous-organic mixtures at this same epoxide/catalyst ratio, it was found that when at least 50% of the solvent was inert methanol, isopropanol, or dioxane, a 20% by weight BDO solution gave the desired improvement in both wet and dry crease resistance at low add-ons to cotton.

Numerous other experiments unreported here have shown that desirable fabric properties are not obtained when BDO vapors at 25 or 85°C. are allowed in contact with cloth containing the catalyst either in presence of methanol or water. Weight gains were obtained however. Treating the cloth with aqueous catalyst solution, followed by acetone and ether extractions, removes much of the water. When such pretreated cloth was treated with alcoholic BDO solution up to 85°C. in a 5-min. cure, no weight gains or improved properties resulted.

### Other Lewis Acid Catalysts

In our cellulose-epoxide research program, one objective has been to find more efficient acidic catalysts than zinc fluoborate for cellulose-epoxide reactions. After investigations of cellulose-diepoxy reactions with a long list of catalysts including almost all known types of  $\text{BF}_3$  addition products, no catalyst has been tested which is superior to the Zn or Cd salts of fluoboric acid when all fabric properties are considered. In aqueous solutions, none caused BDO properly to crosslink cotton when the epoxide concentration was 10–12%. Catalysts investigated included  $(\text{CH}_3)_3\text{N} \rightarrow \text{O} \cdot \text{BF}_3$ ,  $\text{NH}_4\text{BF}_4$ ,  $\text{NH}_3 \cdot \text{BF}_3$ , various cyclic ether adducts of  $\text{BF}_3$ , amine or amide complexes of  $\text{BF}_3$ , alcohol or glycol adducts. Also investigated were  $\text{PF}_5$  derivatives and adducts, such as phenyldiazonium fluophosphate and ammonium hexafluorophosphate. The inefficient complexes tested were either insoluble in water, too acidic, too easily hydrolyzed, or did not evolve  $\text{BF}_3$  or  $\text{PF}_5$  at temperatures less than the boiling point of BDO. Others, which were as efficient catalysts as zinc and cadmium fluoborates, such as diazonium fluoborates and fluophosphates and  $\text{BF}_3$ -aniline adduct, caused discoloration of the cotton fabrics.

### Crosslinking of Cellulose of Diverse Accessibilities

Since the cotton, ramie, and viscose fabrics were not of the same construction, crease recovery values are reported as per cent improvements in Table II. Data in Table II show that weight gains are not directly proportional to the calculated values of accessibility. Better correlation is obtained with crystallinity values as determined by acid hydrolysis<sup>18</sup> than by x-ray diffraction methods.<sup>19</sup> Calculated accessibility values<sup>20</sup> show cotton to be only slightly more accessible than ramie. As measured by weight gains, the accessibility of ramie is only a twentieth of that of cotton. The number of crosslinks in cotton, assuming that all weight gains of BDO are involved in crosslinking, is of the order of one per 25 anhydroglucose units. The amazingly small weight gain of ramie accompanied by the

TABLE II  
Effects of BDO on Different Types of Cellulose<sup>a</sup>

Cellulose type	Crystallinity, %			Accessibility, % <sup>d</sup>	Weight gain %	Crease recovery			
	Acid hydrolysis <sup>b</sup>	X-Ray <sup>c</sup>	(W + F) <sup>o</sup>			Increase, %		Wet	Dry
						Wet	Dry		
Ramie	95	70	215	33	—	128	—	14	77
Ramie + BDO	—	—	246	—	0.1	226	—	—	—
Cotton	83	70	166	38	—	196	—	37	34
Cotton + BDO	—	—	228	—	1.9	263	—	—	—
Viscose	68	40	188	71	—	213	—	2	2
Viscose + BDO	—	—	192	—	2.9	260	—	—	—

<sup>a</sup> Fabrics twice padded to 100% pickup with freshly prepared methanolic solutions of 10% BDO and 1% Zn(BF<sub>4</sub>)<sub>2</sub>; cured 5 min. at 125°C.

<sup>b</sup> According to Philipp, Nelson, and Ziffle.<sup>16</sup>

<sup>c</sup> According to Hermans.<sup>17</sup>

<sup>d</sup> According to Valentine.<sup>20</sup>



highest crease recovery improvement under identical conditions indicates that much is still to be learned about the phenomena involved and suggests that perhaps BDO in the presence of certain catalysts causes rearrangements of normal hydrogen bonding of cellulose in addition to forming covalent links. Since cotton cellulose I is known to have relatively few hydroxyl groups available for reaction, perhaps larger morphological units than individual chain molecules such as lamellae or microfibrils are linked by BDO, and these units are doubtlessly dependent upon the type and size of crystals in the macro structure.

In order to determine uniformity of reaction and obtain some indication of the extent of crosslinking in the three types of cellulose reacted with BDO under identical conditions, the whole fibers and ultrathin cross sections of fibers removed from finished fabrics were examined after immersions of 30 min. in 0.5*M* cuene. The controls of all three types of cellulose

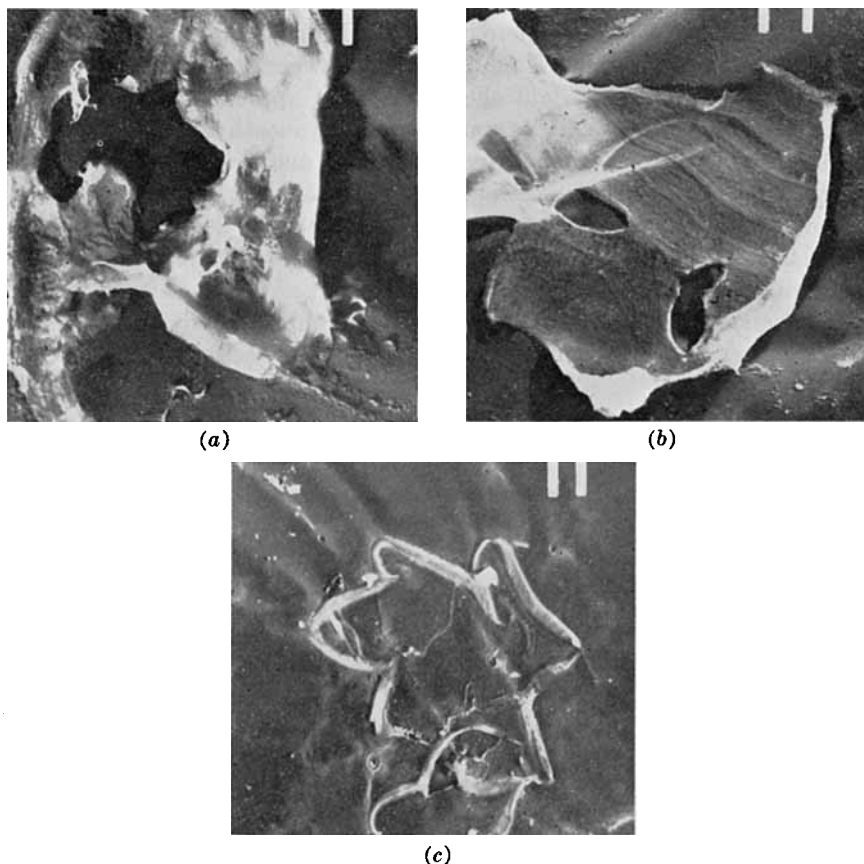


Fig. 3. Electron micrographs of ultrathin cross-sections of BDO-treated fibers after 30 min. of immersion in 0.5*M* cupriethylenediamine: (a) cotton, (b) ramie, and (c) viscose rayons. All fabrics finished with 10% BDO and 1%  $Zn(BF_4)_2$  in methanol by pad-day cure (125°C.) method. Platinum shadowing,  $\times 6,000$ .

dissolved immediately in 0.5*M* cuene. Optical microscopic observations on the whole fibers and electron micrographs of the ultrathin sections of the BDO-treated fabrics showed that cotton had the greatest degree of crosslinking at both the fiber and 800–1000 Å levels. Both ramie and rayon had been reacted to a smaller degree at the fiber level. The reaction appeared to have occurred on the surface of the ramie but throughout the rayon fibers. With the latter, the reaction was least uniform. Electron micrographs of ultrathin cross sections taken from BDO-treated cotton, rayon, and ramie fabrics after an immersion in 0.5*M* cuene for 30 min. are shown in Figures 3*a*, 3*b*, and 3*c*, respectively.

### Crosslinking of Chemically Modified Cottons with BDO

In general, when untreated cotton is reacted with methanolic solutions containing 10% BDO and 1% Zn(BF<sub>4</sub>)<sub>2</sub> by the pad-dry cure method, only small add-ons are observed but at least a 50% improvement in both wet and dry crease recovery angles are realized. Data in Table III are typical of the results obtained when similar treatments were applied to chemically modified cottons. These data show that only approximately 20% improvements in wet crease angles resulted when cyanoethylated, acetylated, and dialdehyde cottons were reacted with BDO, and that no improvement in wet crease recovery was experienced by the carboxymethylated cotton. However, the latter and the cotton acetylated to a low degree of substitution (0.23) showed greatest improvement in dry crease recovery after treatment with BDO.

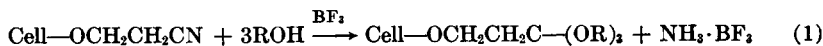
The cyanoethylated cotton showed the least improvement in dry crease recovery after BDO addition, and is one of the few cases known to these in-

TABLE III  
Effect of Addition of BDO to Chemically Modified Cottons<sup>a</sup>

Modification	Degree of substitution	BDO add-on, %	Crease Angles, (W + F) <sup>o</sup>		% Improvement	
			Wet	Dry	Wet	Dry
Cyanoethylated	0.42	—	199	189	—	—
Cyanoethylated + BDO	—	1.3	252	205	26	8
Carboxymethylated (acid)	0.10	—	243	173	—	—
Carboxymethylated, + BDO	—	2.2	249	234	2	37
Acetylated	0.23	—	151	155	—	—
Acetylated + BDO	—	1.3	188	223	24	44
Acetylated	0.60	—	124	156	—	—
Acetylated + BDO	—	1.7	152	193	22	23
Dialdehyde	0.14	—	180	203	—	—
Dialdehyde + BDO	—	1.0	214	268	19	32
Untreated	0	—	159	186	—	—
Untreated + BDO	—	1.2	259	280	63	50

<sup>a</sup> All fabrics were twice padded to 100% wet pickup with freshly prepared methanolic solutions of 10% BDO and 1% Zn(BF<sub>4</sub>)<sub>2</sub>, and cured at 125°C. for 5 min.

investigators where a cellulose-diepoxide reaction catalyzed by  $\text{Zn}(\text{BF}_4)_2$  in methanol produced wet crease recovery only. It should be noted in passing that cyanoethylated cotton has been crosslinked by melamine<sup>21</sup> and dimethylolethylene urea.<sup>22</sup> With cyanoethylated cotton the following reaction<sup>23</sup> was also considered:



ROH might conceivably be furnished by cellulose itself or by added polyols. In the absence of added polyols, there was considerable improvement in the wet crease recovery of cyanoethylated cotton at approximately 1% add-on of BDO. When either ethylene glycol or  $\alpha$ -chloroglycerol was included in the reaction mixture, slight weight gains of BDO were observed, but there was no improvement in either wet or dry crease recovery angles over that of the cyanoethylated control fabrics.

Improvements in dry crease recovery of the carboxymethylated and acetylated cottons of low degree of substitution and of the dialdehyde cotton formed by the periodate oxidation, which preferentially oxidizes adjacent hydroxyls on C<sub>2</sub> and C<sub>3</sub> of cellulose, indicate that reaction of BDO with the primary hydroxyls of cellulose is required for dry crease resistance. The dialdehyde cotton after BDO treatment showed the same solubility behavior in NaOH as did the control dialdehyde cotton. Only a slightly less intense yellow color than that of the control after dyeing both in the same bath with 2,4-dinitrophenylhydrazine was observed.

A series of fabrics containing 6, 13.6, 20.5, 28.5, and 35.3% acetyl were reacted with methanolic solutions containing 10% BDO and 1%  $\text{Zn}(\text{BF}_4)_2$ . The percentage weight gains of BDO were 1.3, 1.7, 4.5, 5.3, and 6.8%, respectively, and all fabrics experienced approximately 25% improvement in wet crease recovery angles over the control acetylated fabrics. However, only the one of lowest degree of substitution showed an approximate 50% improvement in dry crease angles. The fabric of highest acetyl content experienced a 14% decrease in dry crease recovery and the others showed approximately 25% increase in dry crease angles. Microscopical examinations of acetylated fabrics after BDO treatment showed that the fibers ballooned slightly after long immersions in acetone and cuene, but did not dissolve. Probably, the more open structure of the fabrics acetylated to higher acetyl contents accounts for the higher weight gains of BDO.

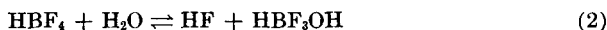
### Mechanism

In the cellulose-BDO reaction catalyzed by  $\text{Zn}(\text{BF}_4)_2$ , very little reaction and no recovery occur unless the relative amount of water is decreased either by increasing the concentration of epoxide or by use of a nonaqueous solvent such as alcohol. Even when the concentration of BDO in aqueous solutions is increased to 40%, only a small fraction reacts with cotton. At such high concentrations of BDO, perhaps the rate of ring opening is changed because of changes in dielectric properties of the medium or, more

likely, enough BDO remains on the fabric to cause a bulk polymerization after the initial loss of some water during the curing process. In all cellulose-epoxide reactions, there is a competing reaction between water and epoxide. Yet, the presence of at least some water is essential as the ring openings by either  $SN^1$  or  $SN^2$  mechanisms involve ionic species. It has been established that cotton at or near 100% R.H. contains about 23% water; the molar ratio  $H_2O/AGU$  thus approximates 2. Normally, cotton contains 6% water which approximately corresponds to a molar ratio of 0.5. It has been postulated<sup>24</sup> that of the three cellulosic hydroxyls, the one on  $C^6$  has the greatest affinity for water. It is also this primary hydroxyl which is the main site of the epoxide reactions.<sup>1</sup>

The complete elucidation of hydrogen bonding network in cotton cellulose has not been attained in spite of many recent ingenious suggestions. The greater strength of wet cotton over that of dry has been attributed to a more even distribution of interchain stresses in the wet state. This involves movement of portions of chains as postulated by Lang and Mason.<sup>25</sup> The  $C_6$  hydroxyls, which have the greatest affinity for water, may be bonded through water to other hydroxyls or oxygens intra- or intermolecularly.<sup>26-28</sup> When water is completely removed from cotton, the freed hydroxyl groups might bond with one another, and as suggested by Neale,<sup>29</sup> as water vapor enters thoroughly dried cellulose, it might form interchain links utilizing the less sterically hindered  $C_6$  hydroxyl sites.

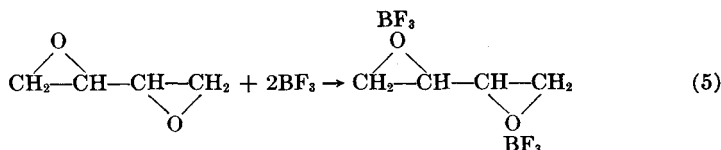
Fluoboric acid, present in the catalyst solution, undergoes hydrolysis in a stepwise fashion according to eq. (2):<sup>30</sup>



At the end point of hydrolysis,  $F^-$ ,  $BF_4^-$ , and  $BO_2^-$  anions exist. Dry zinc fluoborate, on the other hand, decomposes according to eq. (3):<sup>31</sup>



The liberated  $BF_3$  can activate the cellulose and BDO according to eqs. (4) and (5).



Some of the activated diepoxide then reacts with activated cellulosic hydroxyls, at least some of which form crosslinks. Activation of cellulose ethers with resultant formation of graft polymers is very small as evidenced by very small weight gains in all instances of acid catalysis. Data in Table I indicate that eq. (5) is much more important than eq. (4) in the crosslinking mechanism.

One objection to the above mechanism is the failure of monoepoxides to add to cellulose under similar conditions.<sup>32</sup> However, monoepoxides are known to either cyclize to *p*-dioxane derivatives<sup>33-37</sup> or isomerize to aldehydes or ketones which further react to produce acetals or ketals.<sup>35,38,39</sup> Certain diepoxides are also known to cyclize to furanoid derivatives<sup>40</sup> in the presence of acids. Such reactions would interfere with homopolymerizations and account for the relatively low efficiencies of certain cellulose-epoxide reactions. The zinc or cadmium fluoborate acts as a latent catalyst in BDO solutions and cannot be replaced by fluoboric acid, as the latter causes rapid heating and loss of epoxide reagent on mixing.

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

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### Résumé

On a étudié les réactions entre la cellulose de coton et le mélange racémique des isomères *d,l* du diépoxyde de butadiène (BDO) en présence de différents acides de Lewis. En particulier la réaction catalysée par le fluoroborate de zinc a été étudiée dans différents solvants, avec des rapports molaires variables des réactifs à différents temps et températures de traitement. On a montré que le BDO s'additionne au coton en solution aqueuse pour former des produits possédant une résistance au plissage à sec et à l'humidité pourvu que la concentration en BDO soit plus grande que 20%. La substitution de méthanol à l'eau produit des cotons très résistants au pli à sec et à l'humidité, après une application de BDO à faible concentration suivie d'un traitement à des températures relativement basses (100-125°C). Dans des larges rapports molaires époxyde/catalyseur/AGU examinés, les gains de poids ont été trouvés relativement indépendants des concentrations utilisées mais l'amélioration de la résistance aux plis à sec et à l'humidité dépendait des rapports molaires des réactifs. L'application de BDO en solution méthanolique à des celluloses de diverses accessibilités provoque une très grande amélioration des propriétés de recouvrement au froissage, une cellulose de très haute cristallinité. En outre, il a été démontré que BDO réagit avec de nombreux cotons modifiés chimiquement. La résistance au pli à sec a été améliorée dans les cotons acétylés à un D.S. bas, dans des cotons dialdéhydes, et dans des cotons carboxyméthylés. Une amélioration dans la résistance au pli à sec n'a pas été observée dans les cotons acétylés à haut D.S. ou dans des cotons cyanoéthylés. Ces derniers révèlent une forte amélioration dans la résistance à l'humidité seulement. On a considéré les mécanismes de réactions possibles.

### Zusammenfassung

Die Reaktion zwischen Baumwollzellulose und einer racemischen Mischung von *d,l*-Isomeren von Butadiendiepoxyden (BDO) in Anwesenheit verschiedener Lewisäuren wurde untersucht. Im besonderen wurde die Zinkfluorborat-katalysierte Reaktion in verschiedenen Lösungsmitteln mit verschiedenen Molverhältnissen der Reaktanten und

bei verschiedener Behandlungsdauer und -temperatur untersucht. Es wurde gezeigt, dass, unter der Voraussetzung einer BDO-Konzentration grösser als 20%, BDO in wässriger Lösung sich mit Baumwolle unter Bildung eines Produkts mit Trocken- und Nassknitterfestigkeit verbindet. Ersetzen von Wasser durch Methanol ergibt eine ausgezeichnet trocken- und nassknitterfeste Baumwolle, wenn BDO in geringen Konzentrationen zugefügt wird und die Nachbehandlung bei relativ niedrigen Temperaturen (100–125°C) erfolgt. Bei dem untersuchten grossen Epoxyd-Katalysator-AGU-Molverhältnis ist die Gewichtszunahme von der verwendeten Konzentration relativ unabhängig, die Verbesserung des Trocken- und Nassknitterwinkels jedoch hängt von dem Molverhältnis der Reaktanten ab. Anwendung von Methanollösung auf Zellulose von verschiedener Angreifbarkeit ergab eine gute Verbesserung der Knitterfestigkeitseigenschaften bei niedrigstem Gewichtszuwachs bei Ramie, der Zellulose mit der höchsten Kristallinität. Ausserdem reagiert BDO mit einer Anzahl von chemisch modifizierten Baumwollen. Trockenknitterfestigkeit wurde bei zu einem niedrigen D.S.-Wert acetylierter Baumwolle, Dialdehydbaumwolle und carboxymethylierter Baumwolle verbessert. Eine Verbesserung der Trockenknitterfestigkeit konnte bei zu einem hohen D.S.-Wert acetylierter und bei cyanäthylierter Baumwolle nicht beobachtet werden. Letztere zeigte lediglich eine Verbesserung der Nassknitterfestigkeit. Mögliche Reaktionsmechanismen werden in Betracht gezogen.

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