Crosslinking of Cotton Cellulose with Diglycidyl Ether

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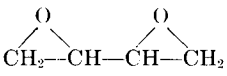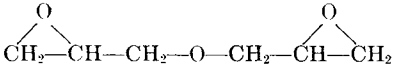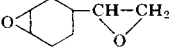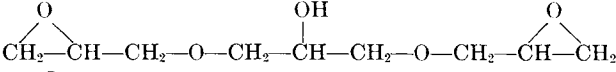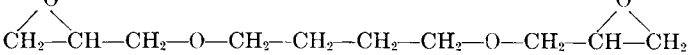
Introduction

The cool, porous comfort of cotton and other cellulosic fiber garments is far superior to that obtainable in present day synthetic fibers. However, in recent years, there have been a large number of synthetic fibers available for use in garments that have excellent wash-wear properties. In efforts to obtain "easy care" properties for cotton competitive with those available in some of the synthetics, chemical and textile manufacturers have spent considerable research effort in developing chemical treatments for cotton.

The mechanism by which chemical treatments impart crease recovery to cellulosic fabrics is not completely understood. However, it is generally accepted that chemical crosslinking within the cotton fiber is a basic requirement for improved wrinkle resistance.[1,2] Polymer formation within the cotton fiber is considered to improve the wash-wear rating and muss resistance and to give a fuller hand. Until recently, most of the resin-formers or crosslinkers used were N-methylol compounds. Major ad-

vantages of the N-methylol compounds are that they will react in and with cellulose under easily controlled conditions, and they are relatively inexpensive. Most of these compounds are derivatives of either urea, triazine, or triazones having free NH groups which tend to pick up chlorine from hypochlorite bleach baths. The N-methylol compounds are not as resistant to laundering as desired since, under various conditions, the crosslinks are hydrolyzed, resulting in the loss of creaseproofing effects. Under certain conditions, formaldehyde or other obnoxious odors are given off.

In efforts to overcome these defects, numerous other compounds have been used for crosslinking cellulose. Diepoxides, reactive difunctional chloro compounds, divinyl sulfone, di- and triaziridinyl compounds, and diisocyanates have been extensively studied.[1-6] The diepoxy compounds are particularly interesting. They react with cellulose under a variety of conditions to give creaseproofing effects which are exceptionally durable. Some react with swollen cellulose to give predominantly wet crease recovery, and under other conditions, to

TABLE I
Properties of Some Diepoxides

Name	Formula	Theoretical epoxide equivalent weight	Boiling point, °C.
Butadiene dioxide	CH_2—CH—CH—CH_2 (diepoxide)	43	145/750 mm.
Diglycidyl ether	CH_2—CH—CH_2—O—CH_2—CH—CH_2	65	227
Vinylcyclohexene dioxide	O⟨ ⟩—CH—CH_2 (with epoxide)	70	227
Eponite 100 (principal monomer)	CH_2—CH—CH_2—O—CH_2—CH—CH_2—O—CH_2—CH—CH_2 (OH)	102	270
Araldite RD-2 (principal monomer)	CH_2—CH—CH_2—O—CH_2—CH_2—CH_2—CH_2—O—CH_2—CH—CH_2	101	270

give both dry and wet crease recovery. Diglycidyl ether (DGE) was chosen for extensive study because of its many advantages over other diepoxides. It has a high epoxide equivalent, fairly low vapor pressure, and is completely water-soluble. Properties of some diepoxides are compared in Table I.[7-10] Since it has been shown by Galligan,[4] McKelvy,[8] and others that diepoxides only slightly less volatile could be satisfactorily dried and cured, it seemed probable that DGE could be cured at reasonable temperatures to give good efficiency.

Butadiene dioxide is an efficient crosslinking agent for cellulose under selected conditions only. It is so reactive that aqueous solutions hydrolyze readily, and to be efficient it must be applied to fabric from alcoholic, acetone, dioxane, or other non-aqueous solutions containing a catalyst.[8,11,12] DGE is somewhat less reactive than butadiene dioxide and gives equal results from alcoholic or water solutions containing acidic catalysts.

DGE is classified as moderately to highly toxic on ingestion, inhalation, or skin exposure. Its warning properties are poor, as it has a heavy ether odor which is not irritating at the time of inhalation. Prolonged exposure to the vapors must be avoided and a threshold limit of 0.1 ppm has been recommended by the manufacturer.[9] Therefore, all work with DGE must be done under well ventilated conditions.

One of the possible crosslinking reactions of DGE with cellulose is given in eq. (1). As can be seen, the product contains hydroxyl groups which offer possibilities for further crosslinking between the DGE moieties as well as polymer formation.

$$CH_2\text{—}CH\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH\text{—}CH_2 + 2 \text{ Cell- OH} \xrightarrow{H^+}$$

$$\text{Cell—O—}CH_2\text{—}CH\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH\text{—}CH_2\text{—}O\text{— Cell}$$
$$\underset{OH}{\qquad} \underset{OH}{\qquad} \tag{1}$$
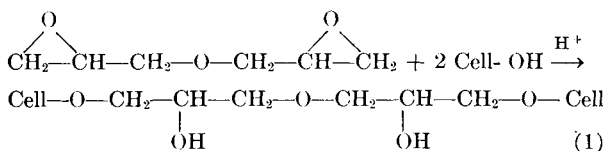
Materials and Methods

The work reported here was carried out on bleached, undyed, 136 × 60 broadcloth weighing 3.5 oz./yd.[2] Fabric samples were padded to 100% wet pickup in the formulations which contained 0.05% Triton X-100 to insure even wetting, dried, and/or cured as specified. The treated fabric was given a "wet" cure in a laboratory model Monforts Reactor,[13] which consists of an electrically heated, stainless steel cylinder that can be rotated to enclose the sample between the cylinder and a $^3/_{16}$-in. sheet of butyl rubber. Dry wrinkle recovery was determined by the Monsanto method,[14a]

the wet by the procedure of Lawrence and Phillips,[15] tensile strength by the grab method,[14b] and tear strength by the Elmendorf method,[14a] at 65% R.H. and 70°F. Crease recovery angles reported are the totals of those measured in the warp and filling directions.

Experimental and Discussion

For the diglycidyl ether reaction with cellulose, the base-catalyzed reaction was of particular interest since basic catalysts, under the proper conditions, exhibit less degrading effects on cotton than acidic catalysts. This reaction was attempted with the use of several concentrations of sodium hydroxide and sodium carbonate. Samples were padded in a solution containing 10% DGE and catalyst as indicated. "Dry" cures were carried out in a hot air oven and wet cures as previously described. Tables II and III compare fabric properties imparted by dry and wet cures of

TABLE II
Effect of Dry Cure and Alkaline Catalysts on Fabric Treated with 10% DGE and Dried-Cured 3 Min. at 135°C.

Catalyst	Catalyst, %	Crease recovery angle		Warp tensile, lb.	Warp tear, lb.
		Dry	Wet		
NaOH	1.0	204°	208°	59.9	1.10
	3.0	245°	248°	53.5	1.10
	5.0	233°	229°	56.3	1.05
	7.0	203°	217°	59.0	1.10
Na₂CO₃	1.0	191°	171°	71.8	1.21
	3.0	176°	151°	76.0	1.27
	5.0	181°	152°	72.5	1.16
	7.0	172°	159°	69.3	1.27
Untreated blank		145°	115°	97.0	1.80

TABLE III
Effect of Wet Cure and Alkaline Catalysts on Fabric Treated with 10% DGE and Wet-Cured 1 Min. at 135°C.

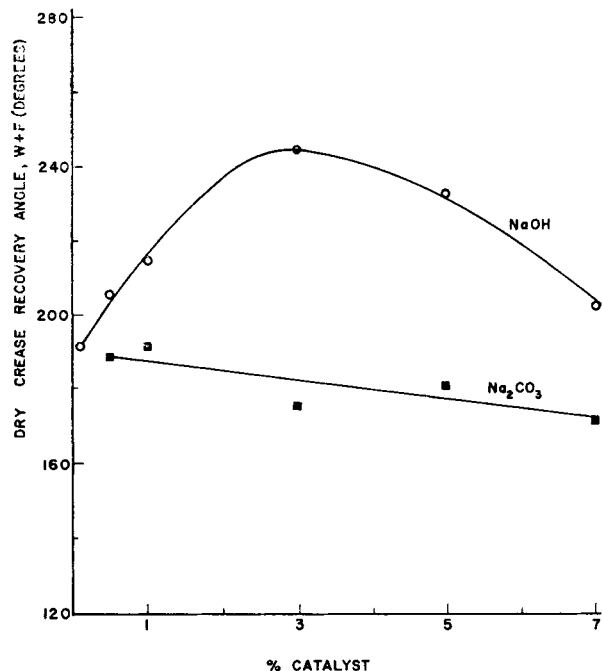| Catalyst	Catalyst, %	Crease recovery angle		Warp tensile, lb.	Warp tear, lb.
		Dry	Wet		
NaOH	1.0	171°	177°	68.0	1.54
	3.0	176°	192°	67.3	1.32
	5.0	183°	213°	60.5	1.10
	7.0	199°	196°	67.0	1.38
Na₂CO₃	1.0	159°	135°	88.2	1.66
	3.0	154°	155°	84.8	1.71
	5.0	158°	133°	88.0	1.93
	7.0	157°	118°	84.0	1.60
Untreated blank		145°	115°	97.0	1.80

Fig. 1. Crease recovery angles produced by 10% DGE and alkaline catalysts. Dried-cured at 135°C. for 1 min.

DGE with alkaline catalysts. Figure 1 indicates that sodium hydroxide exhibits its highest activity for a pad-dry-cure process at a concentration of 3%. Sodium carbonate has little effect on the reaction in the range of concentrations studied and probably causes hydrolysis at a high rate while acting as an inefficient catalyst. The probable explanation for this decrease above 3% NaOH lies in increased rates of hydrolysis and/or polymer formation.

DGE was applied to the surface of fabric samples which had been padded in 14% NaOH in efforts to obtain high wet crease recovery. The treated fabrics were either rolled up in polyethylene and held 15 hr. at room temperature or given a wet high temperature cure. Both methods stiffened the fabric appreciably, indicating polymer formation. The resulting crease recovery angles are given in Table IV.

The catalytic effect of zinc fluoborate was investigated by treating samples with a series of solutions in which the concentrations of zinc fluo-

TABLE IV

Recovery angles (warp + filling)	Rolled and held 15 hr.	Wet cure, 1 min. 135°C.
Dry crease recovery angle	185°	198°
Wet crease recovery angle	272°	215°

TABLE V

Effect of Zinc Fluoborate Concentration on Physical Properties of Fabric with 10% DGE Dried-Cured 7 Min. at 150°C.

Zinc fluoborate, %	Crease recovery angle		Warp tensile, lb.	Warp tear, lb.
	Dry	Wet		
0	161°	162°	90.0	1.65
0.2	219°	204°	56.0	1.10
0.4	282°	255°	53.5	0.77
0.6	272°	266°	47.0	0.77
0.8	273°	254°	55.5	0.88

borate and DGE were treated as independent variables. Samples were padded to 100% wet pickup and dried-cured in the oven at 150°C. for 7 min. Under these conditions, 10% DGE with 0.5% zinc fluoborate gives a weight gain of approximately 7%. Table V indicates that wet and dry crease recovery angles increase with increasing amounts of zinc fluoborate up to a concentration of 0.4% for dry crease recovery and 0.6% for wet crease recovery. As illustrated in Figure 2, the dry crease recovery decreases slightly and then levels out above this catalyst concentration. Wet crease recovery behaves similarly, but slightly more catalyst is required to achieve a
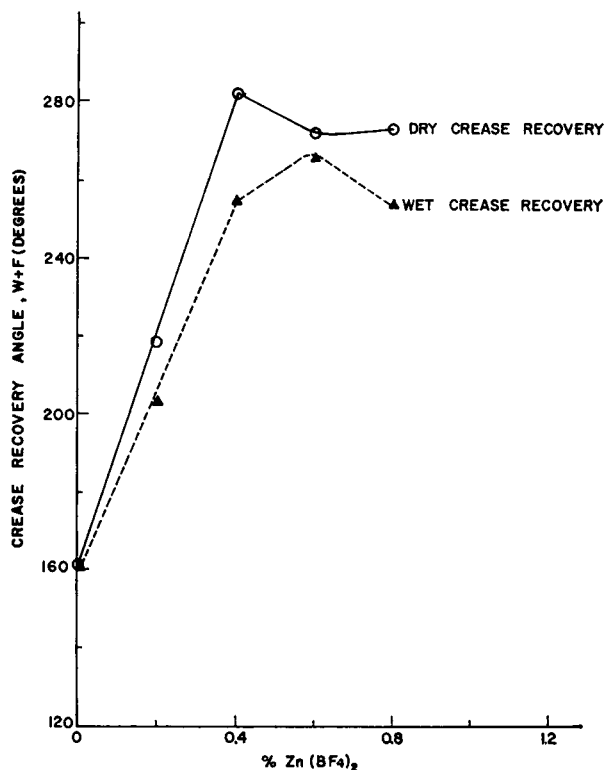

Fig. 2. Crease recovery angles produced by 10% DGE and zinc fluoborate catalyst. Dried-cured 150°C. for 7 min.
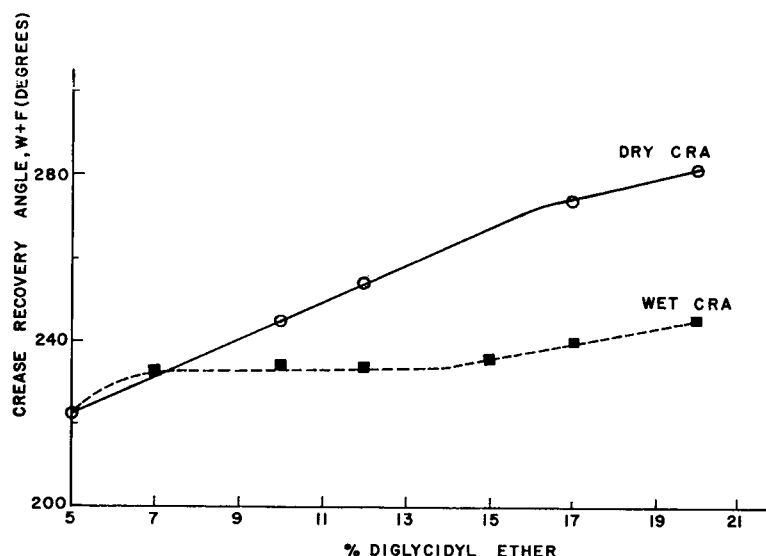
Fig. 3. Effect of DGE concentration on crease recovery, 0.5% zinc fluoborate catalyst. Dried-cured 150°C. for 7 min.

maximum in the curve. This would indicate that more catalyst is needed to promote the reaction before the fibers are dried and collapsed to give higher wet crease recovery.

With zinc fluoborate as a catalyst, the DGE concentration was varied in an attempt to study its relation to crease recovery angle. The catalyst concentration was maintained constant. Dry crease recovery increased in a linear manner to 17% DGE, at which point the line decreased somewhat in a slope as shown in Figure 3. Wet crease recovery showed an initial small increase to 7% DGE and leveled off to a concentration of 15–17%. Properties of fabric treated with various concentrations of DGE are shown in Table VI.

Zinc fluoborate in the wet cure process with DGE promoted polymerization and resulted in only slight improvements in crease recovery. Tear

strengths showed some increase under these conditions, apparently as a result of internal softening from polymer formed.

The effect of pad bath concentration and there-

TABLE VI
Effect of DGE Concentration on Physical Properties of Fabric with 0.5% Zinc Fluoborate Dried-Cured 7 Min. at 150°C.

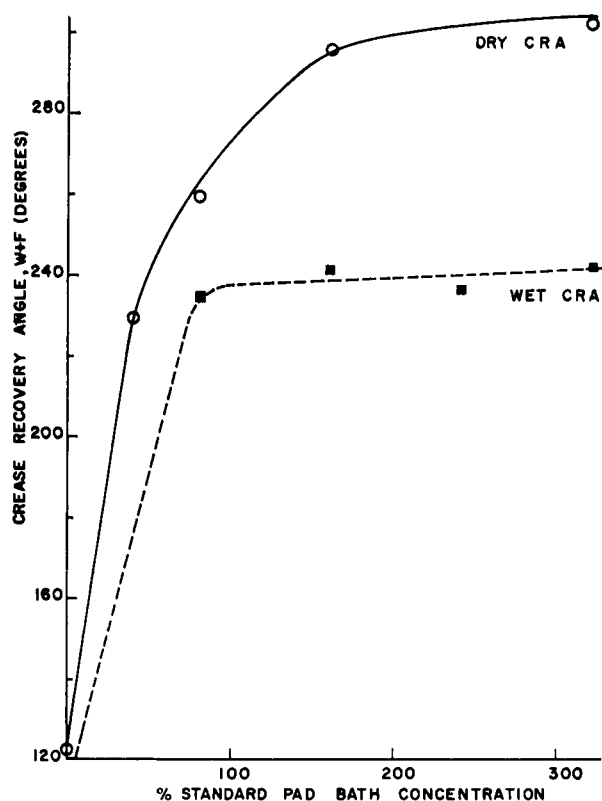| DGE, %	Crease recovery angle		Warp tensile, lb.	Warp tear, lb.
	Dry	Wet		
5	223°	223°	56.0	0.99
7	249°	233°	55.0	1.05
10	245°	235°	55.5	1.05
12	254°	234°	51.5	0.88
15	278°	236°	51.0	0.88
17	274°	240°	49.5	0.77
20	281°	245°	48.5	0.77

Fig. 4. Crease recovery vs. pad bath concentrations. Standard pad bath concentration was 10% DGE, 0.5% zinc fluoborate. Dried-cured 150°C. for 7 min.

TABLE VII
Durability of the DGE Finish to Home Washes

Sample	Dry crease recovery angle			Wet crease recovery angle		
	Original	5 Washes	10 Washes	Original	5 Washes	10 Washes
1	258°	278°	244°	245°	254°	239°
2	264°	283°	248°	244°	248°	236°
3	264°	282°	246°	248°	236°	232°
4	267°	284°	254°	247°	238°	231°
Average	263°	282°	248°	246°	244°	234°

TABLE VIII
Comparison of DGE- and Triazine-Finished Fabric

Finish	% Agent applied	Crease recovery angle		Warp tensile, lb.	Warp tear, lb.
		Dry	Wet		
Triazine (solids)	2	238°	221°	63.0	1.21
	4	274°	243°	61.3	1.02
	6	282°	248°	58.5	1.21
DGE	5	225°	223°	56.0	0.99
	10	257°	235°	50.5	0.83
	17	274°	240°	49.5	0.77
	20	281°	245°	48.5	0.77
Untreated broadcloth		145°	115°	97.0	1.80

fore, to some degree, the effect of polymer formation on the fabric was studied. Figure 4 shows that wet and dry crease recovery increased rapidly with pad bath concentration to a concentration of approximately 50–75% of the standard bath concentration [10% DGE, 0.5% Zn(BF₄)₂]. At this point, the wet crease recovery levels off and shows no improvement even up to 320% of the standard bath concentration. The dry crease recovery increases with decreasing slope to a concentration of approximately 175%, above which point there is no further significant increase in dry crease recovery. At 400% of the standard pad bath concentration, the fabric was so brittle that it disintegrated upon handling.

To determine durability to laundering, the crease recovery angle was measured before and after five and ten home washes on samples which had been padded with 10% diglycidyl ether, and 0.5% zinc fluoborate. The results shown in Table VII indicate that dry crease recovery increased after five washes and decreased after ten washes. The wet crease recovery remained essentially constant for five washes and decreased slightly after ten washes. This would seem to indicate that polymer was removed by washing. Polymer on the exterior of the fiber apparently caused the material to be slightly brittle. Removal of this polymer reduced the brittleness and increased dry crease recovery.

To demonstrate the relations between dry crease recovery and tensile strength, results obtained with a
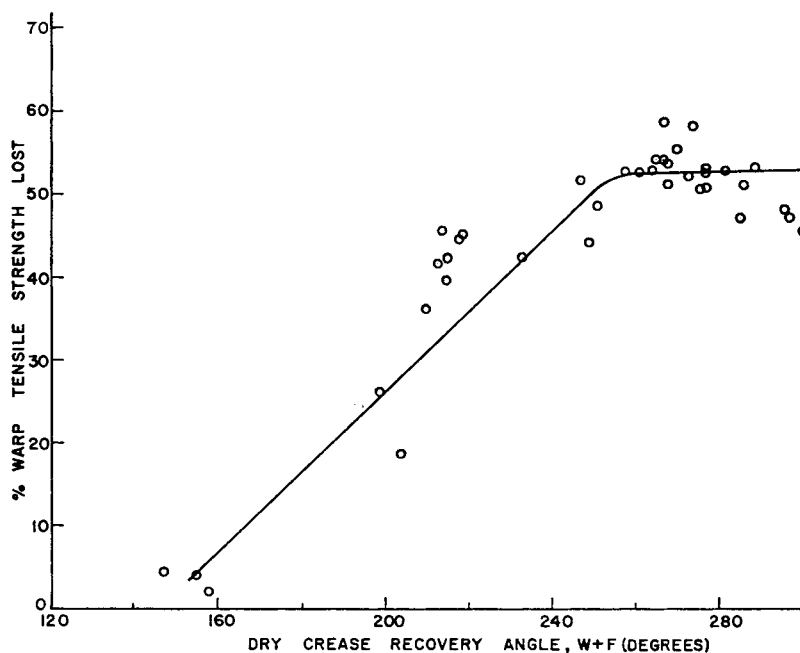

Fig. 5. Strength loss vs. dry crease recovery angle.

large number of samples which had been prepared under various curing conditions are shown in Figure 5. Tensile strength and dry crease recovery seem to be linearly related to a tensile loss of 50%, after which additional crease recovery has little effect on the tensile strength.

The physical properties of fabric treated with DGE and a triazine, compared in Table VIII, indicated the low efficiency and excessive strength loss on the DGE as compared to the triazine finish.

Summary

The reaction between diglycidyl ether, a difunctional epoxide, and cotton cellulose has been studied with respect to catalysis, pad bath concentration, and crease recovery–strength relationships. Sodium hydroxide exhibits maximum catalytic activity at about 3% concentration, while sodium carbonate shows decreasing activity with increasing concentration over a range of 1 to 7%. Zinc fluoborate functions as a catalyst at all concentrations used, reaching a maximum at 0.4% for dry crease recovery and at 0.6% for wet crease recovery in a solution containing 10% DGE. DGE is less efficient and results in greater strength losses than methylol–triazine finishes, thus limiting the commercial usefulness of DGE as a crease-proofing agent unless exceptional durability is required.

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Synopsis

Certain diepoxides react with cellulose under a variety of conditions to give covalent crosslinks. The ether linkages formed with diepoxides are stable to hydrolysis and offer advantages over crosslinks formed with N-methylol compounds. Diglycidyl ether (DGE) has many advantages over other diepoxides. It has a high epoxide equivalent, low vapor pressure, and is completely water-soluble. Both epoxide groups have equal reactivity and their reaction with cellulose can be catalyzed by acids or bases. Fabric properties obtained with DGE with the use of acidic and basic catalysts at various temperatures and concentrations are compared. DGE applied with acidic catalysts by the conventional pad-dry-cure process gave both dry and wet crease recovery. The same catalyst in a wet-cure process promoted polymerization instead of crosslinking and resulted in only slight improvement in crease recovery, but did increase the tear strength. Under conventional conditions of drying and curing, weakly basic catalysts did not promote crosslinking. However, concentrations of sodium hydroxide around 3% gave both dry and wet crease recovery. Strong concentrations of sodium hydroxide at room temperature or in a wet-cure process promoted crosslinking and gave predominantly wet crease recovery.

Résumé

Certains diépoxydes réagissent avec la cellulose dans de nombreuses conditions différentes pour donner des liaisons pontées covalentes. Les liaisons éther formées avec les diépoxydes sont stables par hydrolyse et offrent des avantages par rapport aux liaisons reticulées formées avec les composés N-méthylol. L'éther diglycidyle (DGE) a de nombreux avantages par rapport a d'autres diépoxydes. Celui-ci a un équivalent époxyde élevé, une faible tension de vapeur, et est complètement soluble dans l'eau. Les deux groupes époxy ont une réactivité identique et leur réaction avec la cellulose peut être catalysée par des acides ou des bases. Les propriétés technologiques obtenues avec le DGE en utilisant des catalyseurs acide et basiques à des températures et des concentrations différentes sont comparées. Le DGE appliqué par catalyse acide au moyen du processus conventionnel du "pad dry cure" donne à la fois un recouvrement sec et humide. Le même catalyseur dans un processus de "wet cure" provoque une polymérisation au lieu d'une réaction de reticulation et il s'en suit seulement une faible amélioration dans le recouvrement du pli, sans augmentation de la force de cisaillement. Dans les conditions conventionnelles de séchage et de cuisson, les catalyseurs faiblement basiques ne provoquent pas une réticulation. Cependant, des concentrations en hydroxyde de sodium d'environ 3% donnaient un recouvrement du pli à la fois sec et humide. De fortes concentrations d'hydroxyde de soude à température ambiante ou dans un processus "wet-cure" provoquent une réticulation et donnaient préférentiellement un recouvrement du pli humide.

Zusammenfassung

Bestimmte Diepoxyde reagieren unter verschiedenartigen Bedingungen mit Cellulose unter Bildung kovalenter Vernetzungsstellen. Die mit Diepoxyden gebildeten Ätherbindungen sind gegen Hydrolyse beständig und bieten Vorteile gegenüber der Vernetzung mit N-Methylolverbindungen. Diglycidyläther (DGE) ist wesentlich günstiger als andere Diepoxyde. Er besitzt ein hohes Epoxydäquivalent, geringen Dampfdruck und ist vollständig wasserlöslich. Beide Epoxydgruppen besitzen die gleiche Reaktivität und ihre Reaktion mit Cellulose kann durch Säuren oder Basen katalysiert werden. Die Eigenschaften von Geweben, die mit DGE unter Verwendung saurer oder basischer Katalysatoren bei verschiedenen Temperaturen und Konzentrationen erhalten wurden, werden verglichen. Die Verwendung von DGE mit sauren Katalysatoren bei der üblichen Trockenbehandlung ergibt Knitterfestigkeit im trockenen und feuchten Zustand. Der gleiche Katalysator gab bei nasser Behandlung Polymerisation anstatt Vernetzung und verbesserte die Knitterfestigkeit nur geringfügig, erhöhte aber die Reissfestigkeit. Unter den gewöhnlichen Trocknungs- und Behandlungsbedingungen lieferten schwach basische Katalysatoren keine Vernetzung. Konzentrationen an Natriumhydroxyd um 3% ergaben jedoch Knitterfestigkeit sowohl im trockenen als auch nassen Zustand. Hohe Konzentrationen von Natriumhydroxyd bei Zimmertemperatur oder bei Nassbehandlung führten zur Vernetzung und erzeugten vorwiegend Knitterfestigkeit im feuchten Zustand.