

# Paper Strengthening by Starch Xanthate-Alkyl Diepoxide Adducts

By G. G. Maher, C. R. Russell and C. E. Rist, Peoria, Illinois (USA)

*The reaction between starch xanthate and alkyl diepoxide formed gels in concentrated solution (6–8 %) or turbid suspensions in dilute solution (0.1–1.0 %); the gelling varied with the nature of the epoxide. The gel or suspension was dispersed and added to wood pulp suspension and therefrom paper products of improved strength characteristics were formed. Also the reaction was conducted in the presence of paper furnish. Handsheets made from furnish containing a 2.5 % additive level based on fiber content had burst, folding endurance, and wet and dry breaking length values 1.6, 4.6, 4.2 and 1.4 times, respectively, those of control papers. Improvement in properties was somewhat independent of the xanthate's degree of substitution but dependent on the reaction time (either separate from or in presence of fiber) and the order of addition of epoxide and xanthate.*

(Zusammenfassung Seite 389; Résumé à la page 389)

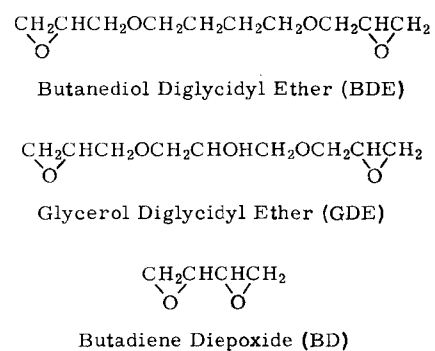
## Introduction

Starch xanthate has been reacted with divalent metal ions or oxidized to the xanthide to produce crosslinked materials that are strengthening agents for various wood pulp products [1–3]. Starch xanthate has also been crosslinked by reaction with organic compounds-polyacrolein [4], low-molecular-weight polyfunctional amines [5] and polyethylenimine (PEI) [6]. The product from the PEI reaction significantly improved burst, dry and wet tensile and fold endurance properties of paper [7].

This study reports the reinforcement of paper by the cross-linked product from reaction of starch xanthate with alkyl diepoxide. The reaction of diepoxy compounds with carbohydrates has been known and its usefulness evidenced in making gel filtration substrates from dextran [8] and crease resistant fabrics from cotton cellulose [9]. Also starch has been treated with diepoxide to crosslink for higher viscosity and reduced retrogradation tendencies [10]. Like those hydroxy-containing macromolecules, some thiol-containing proteins have been crosslinked with diepoxides [11]. The reaction between diepoxide and monomeric, monofunctional xanthate (a dithiocarbonate) has been studied, but polyxanthates have not been involved [12]. The work reported here then broaches the idea of using diepoxides to crosslink in heterogeneous medium an insoluble cellulose and a soluble starch xanthate under conditions that may link molecules of cellulose to cellulose, cellulose to starch and starch to starch. The processes and products evolved in this study have been patented [13]. A separate paper on the xanthate-epoxide reaction is being written.

for starch by a cuprimetric method and for xanthate groups by an acidimetric method; and from these values, the D.S. and dry substance sodium starch xanthate (hereafter also called simply xanthate) content, based on the anhydroglucose unit, were calculated, all as described previously [14].

The diepoxides were obtained from commercial production sources, and were used without any purification or treatment. Araldite RD-2<sup>1)</sup>, trade name for 1,4-bis(2,3-epoxypropoxy) butane or 1,4-butanediol diglycidyl ether (BDE) (technical grade), was received from Ciba Products Company, Fair Lawn, New Jersey 07410, USA. Acrite 100, trade name for 1,3-bis(2,3-epoxypropoxy) 2-propanol or glycerol diglycidyl ether (GDE) (technical grade), came from Shell Chemical Company, Union, New Jersey 07083, USA. 1,2:3,4-Diepoxo butane or butadiene dioxide (BD) was obtained from Columbia Organic Chemicals Co., Inc., Columbia, South Carolina 29209, USA (Fig. 1).



S 67. 1

Figure 1. Structures of diepoxides.

The pulp was unbleached, sulfate, US western softwood of 800 ml SR freeness, containing 75 % moisture. Ninety grams of this pulp were soaked in ca. 600 ml of water and gently disintegrated in a Waring Blendor prior to final dilutions for use in treatment and paper production.

<sup>1)</sup> The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

## Experimental

### Materials

The xanthates were prepared from corn starch by the continuous method developed in this Laboratory [14, 15]. They were stored in a refrigerator as the sodium salt in pH 11 aqueous solutions of 8–13 % concentration and were used within several weeks after preparation since there is some decomposition and loss in degree of substitution (D.S.) after that time. The xanthate solutions were analyzed

The reaction between sodium starch xanthate and diepoxide was conducted either separate from the pulp, that is, *ex situ* with subsequent mixing of the adduct and pulp media, or in the presence of the pulp, that is, *in situ*.

In the *ex situ* reaction a typical recipe and procedure were as follows: To 15 ml of water was added 0.5 ml (0.55 g) of BDE. Then 15 g of an 8.96 % 0.24 D.S. sodium starch xanthate solution was weighed in and mixed rapidly until reaction was underway, as evidenced by thickening and clouding. In this particular reaction, the ratio of epoxide group to xanthate group was 3/1. The mixture was kept at room conditions for 1 h, and after this time the mix was a soft, yellowish, opaque, slow-running gel that was stirred into about 400 ml of water to disperse.

The dispersed gel was stirred into a 1400-ml suspension of 90 g of the pulp (22.5 g dry weight fibers). Any additional reaction between epoxide and xanthate hence became an *in situ* type. The treated pulp suspension was set at room conditions for 3 h, at which time the pulp had settled about one-third through the volume in the 2-liter beaker. Some clear water was decanted and then the beaker was inverted over an 18 mesh wire screen to drain and form a thin mat. The mat was dried in the room air for several days. When handsheets were to be made, the dispersed gel was added to a 2 % pulp suspension (15 g dry weight fibers in 750 ml water) in a Waring Blendor, gently stirring. This mixture was diluted to 6250 g with water and dropped to pH 7 with hydrochloric acid and processed into handsheets by standard procedures.

The variables that were manipulated in the foregoing procedures were the D.S. of the xanthate, the structure of the diepoxide, the concentrations and relative amounts of xanthate and diepoxide, the duration of the *ex situ* reaction, the amount of reaction product added to the pulp and the time allowed for reaction product and pulp contact before forming mats or handsheets.

In an entirely *in situ* method the xanthate and diepoxide were added directly to the pulp suspension and reaction took place in the fibrous medium. In addition to the variables already mentioned, in this latter method the order of addition of the two reagents to the pulp and the time of contact of the first added, before adding the second, were also manipulated.

Handsheets were tested for strength characteristics by TAPPI Standard Methods — conditioning [16a], burst [16b], breaking length dry [16c], breaking length wet [16d] and MIT folding endurance [16e]. Mats or handsheets were ground in a small laboratory Wiley mill to pass 60 mesh screen and analyzed for sulfur by White's method [17.]

## Results and Discussion

In reactions such as these involving macromolecules, gel formation is a good indicator of crosslinking and reaction progress. Table 1 contains data showing that the gel for-

Table 1. Starch Xanthate and Diepoxide Reaction and Product Nature.

Xanthate D.S. <sup>1)</sup>	Epoxide <sup>2)</sup>	Epoxide/xanthate ratio <sup>3)</sup>	Reaction	
			Time (h)	Product state
0.11—0.13	BDE	1—1.5	0.5—8	Fluid
			0.5—4	Soft gel
		2—3	8	Firm gel
			0.5—8	Firm gel
			0.5	Firm gel
0.31—0.38	BDE	1—1.5	0.5—4	Fluid
			0.5	Soft gel
		2—3	0.5	Firm gel
			0.5	Firm gel
			0.5	Firm gel
0.46—0.48	BDE	1—1.5	0.5—4	Fluid
			0.5	Soft gel
		2—3	0.5	Firm gel
			0.5	Firm gel
			0.5	Firm gel
0.11—0.13	GDE	1—5	0.5—24	Fluid
		12	0.5—24	Fluid
0.31—0.38	GDE	1—1.5	0.5—24	Fluid
		2	0.5—24	Fluid
		5	0.5—24	Fluid
0.46—0.48	GDE	1—5	0.5—24	Fluid
		10	0.5	Fluid
0.24	BD	3	1	Firm gel
0.44		3	1	Firm gel

1 D.S. = degree of substitution.

2 BDE = butandiol diglycidyl ether, GDE = glycerol diglycidyl ether, BD = butadiene diepoxide.

3 A ratio of 1 means 1/2 mole of diepoxide per mole of sodium xanthate group on anhydroglucose.

mation increases with the D.S. of the xanthate, the ratio of epoxide group to xanthate group and the length of the reaction period. For example, solutions of BDE and xanthate whose D.S. is in the 0.11—0.13 range remain fluid over a 0.5—8 h reaction period if the ratio of epoxide group to xanthate group is 1—1.5; but if the ratio is raised to between 2 and 3, a soft gel can be formed in 0.5—4 h and a firm gel in 8 h; and at yet higher ratios the gel formation is still quicker. Also the structure of the diepoxide molecule may be of some import in the gelation because GDE, which has a hydroxyl group that the other epoxides used do not have, does not yield a gel until after several days' reaction. However, the rate of reaction, as indicated by the disappearance of the yellow-orange color of the initial mixtures, does not show much difference between the diepoxides.

Table 2. Viscosity Development in BDE Reaction with Starch Xanthate.

Reactants		Viscosity (cp) after reaction of:			
Na starch xanthate D.S.	Epoxide/xanthate ratio <sup>1)</sup>	4 h	5 h	52 h	76 h
0.11	2	1700	4700	4400	4100
0.27	2	2000	17,000	20,000	
0.48	2	18,000	11,000	10,200	
0.13	5	28,000	29,000		
0.31	5	>100,000			
0.48	5	>100,000			

1 A ratio of 1 means 1/2 mole of diepoxide per mole of sodium xanthate group on anhydroglucose.

Table 2 shows a more definitive progression of the viscosity development in the gels, as determined with a Brookfield viscometer (Model LVF, No. 4 spindle at 6 rpm). When the viscosity is over 10,000 cp, the gels are firm and nonflowing if the vial in which they were formed is inverted. Each value in the table represents a measurement on an individual reaction mixture.

Gels did not form when the reaction was conducted in diluter solution, corresponding to that produced by adding the reaction product at the 2.5 % level to a 2 % pulp suspension. A fine solid material precipitated as reaction progressed. The matter of incorporating the reaction adduct with pulp either by *ex situ* method or by *in situ* method then would reflect one of these two behaviors in the product formation. A combination of *ex situ* and *in situ*, would possibly reflect both.

As examples of the combination, BDE and 0.24 D.S. xanthate were used in each of the three following processes, each involving a reaction ratio of three epoxide groups per xanthate group: (1) an *ex situ* reaction for 1 h in 15 ml water to form a soft, flowable gel which was added to a dilute pulp suspension for 3 h *in situ* reaction; (2) an *ex situ* reaction for 1 h in 250 ml water to form a milky suspension which was added to a dilute pulp suspension for 3 h *in situ* reaction; and (3) an *ex situ* reaction for 3 h in 1400 ml water to form a turbid suspension which was added to a dilute pulp suspension for 3 h *in situ* reaction. Each of these procedures yielded a paper mat whose sulfur content (ca. 0.25 %) indicated about 13 % retention of the added total solids of epoxide and xanthate taken, in these cases equal to an 8.4 % addition level to the dry pulp fiber. The retained solids thus represent a 1 % addition level to the dry fiber. These calculations are based on the assumption that the reaction product is a simple addition product of the two reactants and no sulfur is lost in the combination. If sulfur, or other elements of the xanthate group, were lost, or if less than 100 % of the diepoxide taken were in the product, then the addition level value and retention value would be slightly lower and higher, respectively, but not changed as much as a percentage point because the D.S. of the anhydroglucose unit is so low. When BD was substituted for BDE in procedure (1), the results were very similar to those obtained with BDE, the sulfur content being 0.22 % and the retention, 10 %. The dry mats with additive were of a lighter shade of color and were stiffer to hand bending and more resistant to tearing than control mats of pulp fiber only.

In an *in situ* procedure in the mat-making technique it was noted that the addition of diepoxide first to a more concentrated pulp suspension, 4.5 % rather than 1.5 %, resulted in a higher retention, 21 %; but the addition of xanthate first resulted in lower retention, 7 %. Thus the preferred method in mat making was to add 0.15 g of BDE dropwise to a stirred suspension of 11.25 g of dry pulp fiber in 250 ml of water followed by dropwise addition of 3 g of the xanthate solution, let set overnight (the pulp suspension does not settle much), dilute to 800 ml and form the mat. In this procedure the original dry weight of reactants used is only 4.2 % of the dry weight of pulp.

From the information learned by the paper mat experimentation, three series of handsheet trials were designed. Series 1 utilized a 5-min *ex situ* reaction of epoxide with xanthate solution that had been diluted with water 1/1, followed by a 2-h *in situ* reaction in a 2 % pulp suspension. Series 2 was the same as Series 1 except that the length of the *in situ* reaction was varied. Series 3 involved the same amounts of reactants and pulp as the other series in an 18-h *in situ* reaction only in which the pulp suspension was also at 2 %. In all three series, the ratio of epoxide group to xanthate group was 3 and the addition level of reactants to pulp was 2.5 % (with two exceptions). The results of strength tests of the handsheets are in Tables 3–5.

Table 3. Strength Characteristics of Handsheets of Series 1.<sup>1)</sup>

Xanthate D.S.	Burst factor	MIT fold	Breaking length (m)	
			Wet	Dry
0.10	49.2	1200	200	6930
0.26	56.2	560	620	7700
0.57	56.2	1000	565	6505
Control <sup>2)</sup>	40.1	260	155	6350

1 5-min *ex situ* reaction, 2-h *in situ* reaction, 2.5 % addition level of xanthate-BDE adduct.

2 Pulp only, no additives.

Table 4. Strength Characteristics of Handsheets of Series 2.<sup>1)</sup>

<i>In situ</i> time (h)	Burst factor	MIT fold	Breaking length (m)	
			Wet	Dry
0.5	58.8	780	625	7500
2.0	56.2	560	620	7700
6.0	66.2	980	645	8730
Control <sup>2)</sup>	40.1	260	155	6350

1 5-min *ex situ* reaction, 2.5 % addition level of xanthate-BDE adduct, 0.26 D.S. xanthate.

2 Pulp only, no additives.

Table 5. Strength Characteristics of Handsheets of Series 3.<sup>1)</sup>

Additive	Xanthate D.S.	Addition level %	Burst factor	MIT fold	Breaking length (m)	
					Wet	Dry
Xanthate-BDE	0.57	10	60.6	980	255	7790
Xanthate-BDE	0.26	10	66.3	880	245	7980
Xanthate-BDE	0.57	2.5	54.6	1000	220	7230
Xanthate-BDE	0.26	2.5	56.6	590	225	7390
Xanthate-BDE	0.10	2.5	51.1	500	200	7330
Control <sup>2)</sup>			40.1	260	155	6350
Starch <sup>3)</sup>		2.5	44.9	350	175	6670
Xanthate <sup>4)</sup>	0.10	2.5	42.4	345	180	6480
Cationic starch <sup>5)</sup>		2.5	64.2	715	180	8490

1 18-h *in situ* reaction.

2 Pulp only, no additives.

3 Gelatinized with alkali as when making 0.10 D.S. xanthate.

4 Sodium starch xanthate only.

5 Cato 8, product of the National Starch and Chemical Co., Plainfield, New Jersey 07060, USA.

The xanthate D.S. in the range studied does not seem to be of great importance in governing the strength improvements of the paper. For best improvement in all properties,

it seems that the moderate 0.26 D.S. may be an optimum. The MIT folding endurance has benefited the most, the handsheets with xanthate-BDE adduct having values 1.9–4.6 times those of control pulp. This increase substantiates the observations on bending noted with the pulp mat formations. Concordantly the general wet breaking length increase is notable, the values for sheets with adduct being 1.3–4.2 times those of pulp only sheets. While the burst and dry breaking length characteristics have been improved over the control, the changes are not as great, being only 1.4–1.6 and 1.1–1.4 times the control values, respectively. Thus the xanthate-BDE adduct bettered the performance of a commercial cationic starch which did not improve wet-strength of handsheets. In comparison, starch polyethylenimino thiourethane from starch xanthate-PEI reaction gave the enhancements: MIT folding endurance, 2.9 times; wet breaking length, 5.5 times; burst and dry breaking length each, 1.5 times [6, 7].

It is evident that an *in situ* reaction of several hours will produce the best results. Any *ex situ* reaction should be held to a matter of a half hour or less. This is especially true with xanthates of more than 0.10 D.S. since longer times promote too much crosslinking of starch molecule to starch molecule, as evidenced by the firm gels formed, and less epoxy reagent then remains to effect coupling with cellulose fiber.

#### Acknowledgments

T. R. Naffziger, W. L. Williams and L. D. Miller prepared the starch xanthates. B. R. Heaton, C. E. McGrew and M. D. Swanson conducted analytical work. A. J. Ernst, R. G. Fedt and H. D. Heath formed and tested the handsheets. C. C. Cook, research trainee of the Maize Industry Control Board, Council for Scientific and Industrial Research, Republic of South Africa, Pretoria, South Africa, assisted with early phases of the reaction study.

#### Zusammenfassung

**Papierverstärkung durch Additionsprodukte aus Stärkexanthat und Alkyldiepoxid.** Die Reaktion zwischen Stärkexanthat und Alkyldiepoxid bildete Gele in konzentrierter Lösung (6–8%) oder trübe Suspensionen in verdünnter Lösung (0,1–1,0%); die Gelbildung variierte mit der Natur des Epoxids. Das Gel oder die Suspension wurde dispergiert, einer Holzpulpesuspension zugesetzt, und daraus wurden Papierprodukte mit verbesserter Festigkeitseigenschaften hergestellt. Die Reaktion wurde auch in Gegenwart von Papiermasse durchgeführt. Handgeschöpfte Papiere aus einer Masse, die einen 2,5% auf Fasergehalt bezogenen Zusatz enthielt, zeigten Berstfestigkeits-, Falzfestigkeits- sowie Naß- und Trockendehnfestigkeitswerte, die dem 1,6-, 4,6-, 4,2- und 1,4-fachen der Vergleichspapierproben entsprachen. Die Verbesserung der Eigenschaften war ziemlich unabhängig vom Xanthatsubstitutionsgrad, jedoch abhängig von der Reaktionszeit (entweder getrennt oder in Gegenwart der Faser) und von der Reihenfolge des Zusatzes von Epoxid und Xanthat.

#### Résumé

**Renforcement du papier par addition de xanthate-alcyl-diepoxide d'amidon.** La réaction entre les xanthates d'amidon et l'alcyl diepoxide provoque la formation de gel en solution concentrée (6–8%) ou de suspensions troubles en solution diluée (0,1–1,0%); la gélification varie avec la nature de l'époxide. Le gel ou la suspension sont dispersés et ajoutés à des suspensions de pulpe de bois et de cette façon des papiers ayant des caractéristiques de résistance améliorée sont obtenus. Aussi, la réaction a été mise en œuvre en présence de la pâte à papier. Les feuilles préparées à partir d'une pâte additionnée de 2,5% du produit en question par rapport à la teneur en cellulose, ont des valeurs de résistance à l'éclatement et au pliage et de longueur de déchirement à l'état humide et sec qui sont multipliés respectivement par 1,6, 4,6, 4,2 et 1,4 par rapport au papier témoin. L'amélioration des propriétés est indépendante du degré de substitution des xanthates, mais elle est dépendante du temps de réaction (en absence et en présence de la cellulose) et de l'ordre dans lequel l'époxide et le xanthate sont ajoutés.

#### References

- [1] Russell, C. R., R. A. Buchanan, C. E. Rist, B. T. Hofreiter and A. J. Ernst: Tappi 45 (1962), 557.
- [2] Naffziger, T. R., C. L. Swanson, B. T. Hofreiter, C. R. Russell and C. E. Rist: Tappi 46 (1963), 428.
- [3] Hamerstrand, G. E., M. E. Carr, B. T. Hofreiter and C. E. Rist: Tappi 50 (1967), 98 A.
- [4] Maher, G. G., J. A. Douglas, C. R. Russell and C. E. Rist: J. Polym. Sci. A-1 8 (1970), 1637.
- [5] Maher, G. G., M. L. Junker, J. A. Douglas, C. R. Russell and C. E. Rist: Stärke 22 (1970), 249.
- [6] Maher, G. G., C. R. Russell and C. E. Rist: Stärke 19 (1967), 354.
- [7] Maher, G. G., A. J. Ernst, H. D. Heath, B. T. Hofreiter and C. E. Rist: Tappi 55 (1972), 1378.
- [8] Flodin, P. G. M., and B. G.-A. Ingelman: U.S. Pat. 3,042,667 (1962); Deutsches Pat. 1,292,883 (1969).
- [9] McKelvey, J. B.: Textile Res. J. 34 (1964), 486.
- [10] Commerford, J. D., and I. Ehrental: U.S. Pat. 2,977,356 (1961).
- [11] Sykes, R. L.: J. Soc. Leather Trades Chem. 41 (1957), 199.
- [12] Overberger, C. G., and A. Drucker: J. Org. Chem. 29 (1964), 360.
- [13] Maher, G. G.: U.S. Pat. 3,730,829 (1973).
- [14] Swanson, C. L., T. R. Naffziger, C. R. Russell, B. T. Hofreiter and C. E. Rist: Ind. Eng. Chem., Prod. Res. Develop. 3 (1964), 22.
- [15] Doane, W. M., C. R. Russell and C. E. Rist: Stärke 17 (1965), 77.
- [16] (a) T402 os-70, (b) T403 ts-63, (c) T494 os-70, (d) T456 os-68, (e) T511 su-69; Technical Association of the Pulp and Paper Industry, 360 Lexington Avenue, New York, New York 10017, USA (1970).
- [17] White, D. C.: Mikrochim. Acta (1962), 807.

**Address of the Authors:** G. G. Maher, Ph.D., C. R. Russell, Ph.D., and C. E. Rist, Cereal Products Laboratory, Northern Regional Research Laboratory\*, Peoria, Illinois 61604 (USA).

\* Agricultural Research Service, U.S. Department of Agriculture.

(Received: July 26, 1974)