# Urethane Foams from Animal Fats: IX. Polyols Based upon Tallow and Trimethylolpropane; Preparation under Acidic and Basic Catalysis[1]

**A. BILYK, H.A. MONROE, JR., E.J. SAGGESE, M.P. ZUBILLAGA, and A.N. WRIGLEY,**
Eastern Regional Research Center,[2] Philadelphia, Pa 19118

## ABSTRACT

A series of polyols was prepared from epoxidized tallow, by reaction with trimethylolpropane in refluxing toluene, sequentially under basic and acidic catalysis. In preliminary experiments, under catalysis by sodium methoxide alone, the trimethylolpropane reacted rapidly with glyceride linkages and very slowly with oxirane groups. Under catalysis by p-toluenesulfonic acid alone, oxirane was rapidly consumed. Polyols were prepared by the following sequences: (A) reaction under acidic followed by basic catalysis; (B) reaction under basic followed by acidic catalysis; (C) reaction under basic catalysis followed by further treatment with HBr gas to introduce fire retardance; (D) treatment of whole tallow first with trimethylolpropane under basic conditions and secondly with bromine; (E) reaction of epoxidized tallow with diethanolamine under basic catalysis; and (F) treatment of epoxidized tallow first with trimethylolpropane under acidic conditions and then with diethanolamine under basic catalysis. The polyols described were adjusted to equivalent weights of 100 and 120 with added triisopropanolamine and treated with a polymeric isocyanate to give rigid foams. Densities ranged from 1.5-1.8 lb/ft$^3$. Open cell content, for foams made at the equivalent wt of 100, ranged from 14-21%; at the equivalent wt of 120, from 17-27%. Compressive strengths ranged from 14-23 psi, being lower than those of the best previous epoxidized tallow-trimethylolpropane products.

## INTRODUCTION

A recent contribution from this laboratory described the preparation of polyols by reaction of epoxidized tallow with trimethylolpropane (TMP) under catalysis by p-toluenesulfonic acid, as well as a series of fire retardant polyols prepared by reaction of epoxidized tallow with TMP and HBr (1). These polyols gave low-density rigid urethane foams (2) whose properties were superior to those from previous tallow-based polyols (3,4). Although the oxirane and glyceride functions of the epoxidized tallow differ considerably in reactivity, only continuous acidic catalysis had been used in polyol preparation. No attention had been directed to basic catalysis or to a possible change of catalyst type during the course of the reaction. As an alternative to a simple trivalent alcohol such as TMP, an aminoalcohol deserved consideration as a major reactant. Alternate methods of introducing bromine also needed attention. It was desirable, therefore, to examine several other catalytic and preparative treatments, as has been done in the present work.

In the previous study, the hydroxyl content of the polyol products had increased with the functional ratio of reactants employed, that is, the molar ratio of hydroxyl available from TMP to oxirane plus ester function from epoxidized tallow. The best results had been obtained at a functional ratio of 6.6 and a reaction temperature of 120 C. Therefore, these conditions were employed in most of the present work.

In preliminary experiments, under catalysis by sodium methoxide at 120 C, TMP reacted rapidly with the glyceride links of whole tallow to give a mixture of products with polarities appropriate to mono- and diglycerides and esters of TMP. The oxirane groups of epoxidized tallow were attacked very slowly under such conditions. Under catalysis by p-toluenesulfonic acid, oxirane groups were attacked quite rapidly by TMP to give ether-linked triol derivatives; in contrast, glyceride links were attacked less rapidly under acidic than under basic catalysis. The results suggested the investigation of sequential catalysis, under which acidic catalysis would be followed by basic, or the reverse. Reactions of this type are described as Experiments A and B.

The contrasting response of glyceride and oxirane functions to catalytic conditions suggested a new procedure for introducing hydroxyl and fire retardant bromine groups into fatty molecules. Thus epoxidized tallow was treated first with TMP under catalysis by sodium methoxide to produce a mixture of mono- and diglycerides and esters of trimethylolpropane. In a second stage, gaseous hydrogen bromide was used as catalyst reactant to open oxirane rings with formation of hydroxybromides and fatty hydroxyethers of TMP (Experiment C).

Another path examined for the preparation of bromine containing polyols was the treatment of whole tallow, first with TMP under basic catalysis, and secondly with bromine in a double bond addition reaction. This path, exemplified by Experiment D, provides an alternative to an earlier method of preparing hydroxybromides by action of HBr on epoxidized tallow (3,4).

The reaction of epoxidized tallow with the aminoalcohol diethanolamine (DEA) was attempted by two methods. In the first, simple basic catalysis was used (Experiment E). In the second, for more effective opening of the oxirane groups, the epoxidized tallow was first treated with TMP under acid catalysis and then with DEA (and residual TMP) under basic catalysis (Experiment F).

## EXPERIMENTAL PROCEDURES

### Materials

The materials listed below were used as received: tallow, fancy (Mutual-Shoemaker Co., Philadelphia, Pa.), iodine value 52.5 unless otherwise state; TMP (Celanese Corp., New York, N.Y.); DEA, p-toluenesulfonic acid and sodium methoxide (NaOMe) (Fisher Scientific Co., Pittsburgh, Pa.); hydrogen bromide, gaseous (Air Products Co., Allentown, Pa.); bromine, liquid (J.T. Baker Chemical Co., Phillipsburg, N.J.); triisopropanolamine (TIPA), and silicone L530 (Union Carbide Corp., New York, N.Y.); DABCO-33-LV, 33% solution of triethylene diamine in dipropylene glycol (Houdry Process and Chemical Co., Marcus Hook, Pa.); Freon 11, fluorotrichloromethane (Matheson Gas Products, New York, N.Y.); dibutyltin dilaurate (M & T Chemical, Inc., Rahway, N.J.); polymethylene polyphenylisocyanate (PAPI) (Upjohn Co., Kalamazoo, Mich.).

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[2] ARS, USDA.

TABLE I

Properties of Tallow-Based Polyols

| Experiment | Polyol source | Hydroxyl | | Br | N | Viscosity, |
|---|---|---|---|---|---|---|
| | | % | No. | % | % | Stokes, 25 C |
| A | Epoxidized tallow + TMP (acidic; basic catalysis) | 9.9 | 327 | -- | -- | 65 |
| B | Epoxidized tallow + TMP (basic; acidic catalysis) | 9.8 | 323 | -- | -- | 50 |
| C | Epoxidized tallow + TMP (basic, HBr) | 6.3 | 208 | 13.2 | -- | 9 |
| D | Whole tallow (TMP, basic; $Br_2$) | 6.5 | 215 | 18.0 | -- | 5 |
| E | Epoxidized tallow + DEA (basic) | 10.3 | 340 | -- | 3.8 | Solid |
| F | Epoxidized tallow + TMP (acidic); + DEA (basic) | 10.7 | 353 | -- | 3.1 | Semisolid |
| Control 1 | Epoxidized tallow + TMP (acid catalyst)[a] | 10.3 | 340 | -- | -- | -- |
| Control 2 | Epoxidized tallow + TMP, HBr[b] | 7.0 | 231 | 25.0 | -- | -- |

[a,b]Polyols of References 1 and 2.

TABLE II

Typical Urethane Foam Formulation

| Component[a] | Wt, g |
|---|---|
| Epoxidized tallow-TMP polyol (OH No. 323) | 7.3 |
| TIPA (to adjust OH equivalent to 120) | 2.7 |
| DABCO-33-LV | 0.25 |
| Silicone L-530 | 0.15 |
| Fluorotrichloromethane | 4.1 |
| Dibutyltin dilaurate | 0.03 |
| PAPI | 12.3 |

[a]TMP = trimethylolpropane, TIPA = triisopropanolamine, and PAPI = polymethylene polyphenylisocyanate.

### Reaction of Epoxidized Tallow with TMP

*Experiment A:* A 500 ml, three necked flask was fitted with a reflux condenser connected to a Dean-Stark tube to remove any traces of water, a thermometer positioned for immersion in the reaction mixture, magnetic stirrer, and heating mantle. The flask was charged with 75 g epoxidized tallow (oxirane 3% by the Durbetaki method [5], saponification no. 188.8, acid no. 2.7), prepared as described previously (6), 116.7 g TMP (functional ratio of 6.6), 1.5 g p-toluenesulfonic acid (2% based on wt of epoxidized tallow, and 75 ml toluene. The stirred reaction mixture was refluxed, providing a reaction temperature of 120 C. After 1 hr of reaction, no oxirane remained. A sample, water washed, dried, and freed of solvent, had 8.7% OH. At this stage the acidic catalyst was neutralized by addition of 0.5 g NaOMe, and an additional 1.5 g NaOMe (2% on wt of epoxidized tallow) was introduced. The reaction was continued for an additional 3 hr. The toluene solution was then washed with water to neutrality, dried over $MgSO_4$, and the solvent removed by rotary evaporation. In the final product, the hydroxyl content reached 9.9%. The product weighed 32.3% more than the epoxidized tallow starting material.

*Experiment B:* Reactant quantities, solvent, and apparatus were the same as those of Experiment A. After the addition of 1.5 g sodium methoxide, the stirred reaction mixture was refluxed (at a temperature of 120 C). After 3 hr of reaction, a sample of the product contained 2.8% oxirane and 8.2% hydroxyl. At this point the basic catalyst was neutralized by addition of 4.8 g p-toluenesulfonic acid, and an additional 1.5 g p-toluenesulfonic acid (2% on wt of epoxidized tallow) was introduced. After 1 hr more of reaction, oxirane was completely comsumed, and the final product was separated as before. A liquid at room temperature, it contained 9.8% of hydroxyl functionality. The product weighed 37.2% more than the epoxidized tallow starting material.

### Reaction of Epoxidized Tallow with TMP-HBr

*Experiment C:* In a 500 ml flask equipped as before, were placed 60.0 g epoxidized tallow, 93.0 g TMP (functional ratio 6.6), 1.2 g sodium methoxide (2% on wt of epoxidized tallow), and 60 ml toluene. After 4 hr reaction at 120 C, an isolated sample of the product had 2.7% oxirane and 8.5% hydroxyl. Further reaction was carried out at 40 C under acid catalysis provided by gaseous hydrogen bromide, which was bubbled slowly through the reaction mixture. Consumption of oxirane was complete within 2 hr. The brominated polyol contained 6.3% hydroxyl and 13.2% bromine, and the product showed a wt gain of 33.5% over the epoxidized tallow charged.

### Reaction of Whole Tallow with TMP and Bromine

*Experiment D:* In a 500 ml flask equipped as before were placed 80 g fancy tallow (iodine value 55.78, saponification no. 194.2, acid no. 2.5), 81.0 g TMP (resultant functional ratio 6.6), 1.6 g NaOMe, and 80 ml toluene. After 8 hr reaction at 120 C, a product sample had 9.5% hydroxyl and an iodine value of 42.0. The cooled reaction mixture was neutralized with concentrated HCl. The toluene solution was then treated at 25 C, by adaptation of the method of Bornfleth (7), with a solution of 11 ml bromine (1.2 moles/mole of double bonds) in 50 ml methanol, added over a period of 1 hr. After 2 hr additional stirring at room temperature, the product was worked up as in previous experiments and had 6.5% hydroxyl, 18% bromine, and residual iodine number 0.75. The wt of the product had increased by 52.8%.

### Reaction of Epoxidized Tallow with DEA

*Experiment E:* A 500 ml, three necked flask, fitted with condenser, thermometer, and magnetic stirrer, was charged with 140.0 g epoxidized tallow (oxirane 2.7%, saponification no. 197.2, acid no. 3.3), 102.0 g DEA (providing a ratio of active hydrogen to oxirane + ester of 4.0), and 2.8 g NaOMe. The reaction mixture was stirred for 3 hr at 120 C, maintained by a thermostatically controlled oil bath. The reaction mixture then was diluted with 3 volumes of 70% ethanol and the crude reaction product precipitated by storage overnight at -25 C. The precipitated product, separated by filtration, was dissolved in benzene, washed with water to neutrality, dried over $MgSO_4$, and freed of solvent by rotary evaporation. The product, weighing 131 g

TABLE III

Properties of Urethane Foams

| | | At hydroxyl equivalent of 100[c] | | | | | At hydroxyl equivalent of 120[c] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Compressive | | | | | Compressive | | |
| Polyol | OH No. | Density lbs/ft$^3$ | Open cells % | Strength[d] psi | Modulus psi | Instant recovery % | Density lbs/ft$^3$ | Open cells % | Strength[d] psi | Modulus psi | Instant recovery % |
| A | 327 | 1.8 | 17 | 22 | 358 | 95 | 1.6 | 18 | 17 | 287 | 94 |
| B | 323 | 1.8 | 18 | 23 | 413 | 95 | 1.6 | 17 | 17 | 287 | 94 |
| C | 208 | 1.7 | 14 | 21 | 373 | 96 | 1.7 | 21 | 15 | 271 | 95 |
| D | 215 | 1.7 | 16 | 20 | 360 | 96 | 1.6 | 27 | 16 | 274 | 94 |
| E | 340 | 1.7 | 21 | 20 | 324 | 94 | 1.5 | -- | 14 | 258 | 86 |
| F | 353 | 1.7 | 18 | 19 | 289 | 93 | 1.7 | 19 | 17 | 274 | 95 |
| Control 1[a] | 340 | 1.7 | 17 | 40 | 790 | 90 | 1.6 | 17 | 38 | 755 | 90 |
| Control 2[b] | 231 | 1.8 | 20 | 36 | 720 | 85 | 1.8 | 21 | 35 | 770 | 87 |

[a,b] Polyols of References 1 and 2.

[c] Attained by adjustment with triisopropanolamine (TIPA).

[d] At 10% compression.

after losses incurred in washing, had 10.3% hydroxyl, 3.8% nitrogen, and was solid at room temperature. High values for oxirane were obtained by the Durbetaki method (5). NMR examination of model compound 3,4-trans-epoxyhexane (after subjection to similar reaction conditions) indicated no reaction of epoxide with DEA.

### Reaction of Epoxidized Tallow with TMP and DEA

*Experiment F:* A flask equipped as in Experiments A and B was charged with 120.0 g epoxidized tallow (as in Experiment E), 18.3 g TMP (functional ratio 0.66), 2.4 g p-toluenesulfonic acid, and 120 ml toluene. After 3 hr of refluxing (reaction temperature 120 C), all oxirane groups had been consumed, and an isolated product sample contained 4.2% hydroxyl. At this stage the acid catalyst was neutralized by addition of 0.8 g NaOMe; 2.4 g additional NaOMe was added and 86.2 g DEA (ratio of active hydrogen to ester function of 5.9). After 4 hr more refluxing, the product was worked up as in Experiment E. It weighed 107 g, contained 10.7% hydroxyl, 3.1% nitrogen, and was semisolid at room temperature.

*Properties:* Properties of polyols A to F are collected in Table I. Viscosities were measured against Gardner bubble-viscometer standards.

### Foam Preparation and Testing

The polyols prepared were used in the preparation of low-density rigid urethane foams by a procedure previously described (2). The adjustment to an equivalent wt of 100 or 120 was made by incorporation of the adjuvant TIPA. As catalyst, a small amount of dibutyltin dilaurate was used in addition to Dabco. A typical formulation is given in Table II. Foams were aged and their properties measured as by the method of Saggese, et al., (2); results are reported in Table III.

## DISCUSSION

Figures 1 and 2 show graphically the course of the three catalytic sequences employed respectively in Experiments A, B, and C for the reaction of epoxidized tallow with TMP or with TMP and HBr. In sequence A (Fig. 1A), the first, or acidic, stage of catalysis caused the rapid disappearance of oxirane and introduction of substantial hydroxyl functionality through reaction of oxirane and ester links with TMP. The subsequent basic catalysis added only a little more hydroxyl content by TMP reaction mainly at ester linkages.

From Figure 1B it is seen that the basic catalysis of Experiment B introduced substantial OH functionality without corresponding loss of oxirane content. In fact, the lower oxirane content observed after 3 hr treatment was due mostly to the increase in wt of the reaction product. Subsequent acid catalysis led to rapid reaction of the oxirane and the introduction of additional hydroxyl content, presumably by reaction of TMP particularly with oxirane groups.

The course of sequence C, displayed in Figure 2, was the same as sequence B during the first, or base catalyzed treatment of epoxidized tallow with TMP. However, in the subsequent period of joint catalysis by, and reaction with HBr, the rapid introduction of bromine, by attack on oxirane, was necessarily accompanied by a substantial drop in hydroxyl content. This was due mainly to the gain in wt of product.

It is seen from Table I that reaction sequences A, B, C, and D led to liquid polyols in each case. The viscosities of products A and B were in a normal range; but that of product C was lower than usual. Hydroxyl contents of polyols A and B were slightly lower than that of Control 1; and

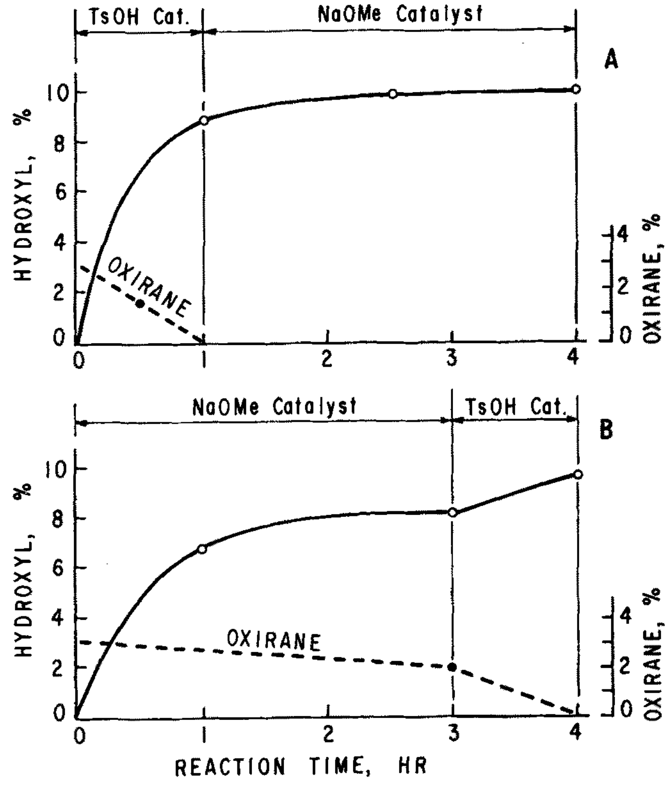

FIG. 1. Reaction of epoxidized tallow with trimethylolpropane (TMP). Hydroxyl and oxirane content of products as a function of reaction time: (A) under acidic catalysis followed by basic; (B) under basic catalysis followed by acidic (Experiments A and B).

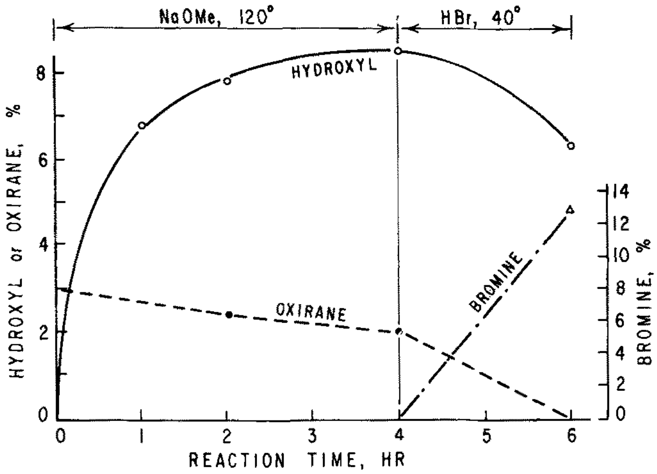

FIG. 2. Reaction of epoxidized tallow with trimethylolpropane (TMP), under catalysis by sodium methoxide (NaOMe) followed by catalysis-reaction with HBr. Hydroxyl, oxirane, and bromine contents of products as functions of reaction time (Experiment C).

brominated polyol C had somewhat lower hydroxyl and considerably lower bromine content than Control 2.

As seen from Table I, sequence D also gave rise to a polyol of particularly low viscosity, with slightly lower hydroxyl and substantially lower bromime content than Control 2. Treatment E, the base-catalyzed reaction of epoxidized tallow with DEA, produced a product with as high a hydroxyl content as Control 1, but which was solid as room temperature. This was not unreasonable for a product considered to be a mixture including fatty ethanolamines and epoxy fatty ethanolamides. Sequence F, which introduced an acid catalyzed reaction with a small amount of TMP before the base catalyzed reaction with DEA (and residual TMP), led to a product having the highest hydroxyl content of the series. It was, however, semisolid, presumably through the influence of the amides present.

## Foam Properties

The major purpose of the work described was to appraise a number of catalytic or reaction sequences in comparison with the simple, acid catalyzed reaction of epoxidized tallow with TMP (or TMP-HBr) previously described (1). It was hoped that one or more of the alternative methods would provide polyols generative of low-density rigid foams superior to those from the former polyols (2).

Table III compares the foam properties realized, at hydroxyl equivalents adjusted to both 100 and 120, using the present polyols and the controls. Densities were just about the same for the new foams as for the controls at both equivalent levels. This was also true for open cell content, although the foams from polyol D were less satisfactory in this respect. At both levels of hydroxyl equivalence, compressive strengths were inferior to those of the foams from the controls. Fire retardance, not tabulated, was lacking in the foams from brominated polyols C and D. In terms of the physical properties of the foams, therefore, the new catalytic or preparative sequences offered no advantage over the simple processes leading to the polyols of Controls 1 and 2. In further examination it was shown that the stiffness (as measured by compressive modulus) was much lower and recovery from deformation a little higher in the present series of foams. This suggested some possible application of these materials in semirigid foams.

Both the earlier polyol syntheses (1) and those described here required a water washing step at the end of the reaction to remove unchanged TMP. Because this step might be troublesome on an inudstrial scale, its elimination is now under study.

## ACKNOWLEDGMENTS

G.R. Riser measured compressive strength, compressive modulus, and instant recovery of foams. L.H. Scroggins provided bromine determinations. E. Beatty cut foam samples. P.E. Pfeffer performed NMR examination of 3,4-trans-epoxyhexane after treatment with DEA.

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