Urethane Foams from Animal Fats. III. Oxypropylated Dihydroxystearic Acids in Rigid Foams[1]

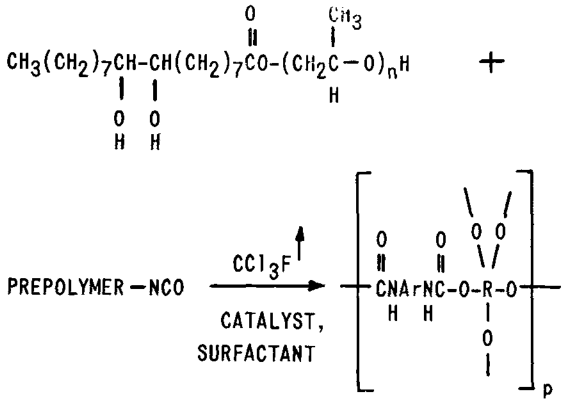
E. J. SAGGESE, FRANK SCHOLNICK, MARTA ZUBILLAGA, WALDO C. AULT and A. N. WRIGLEY,
Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

Abstract

Liquid polyols consisting of *threo*- or *erythro*-9,10-dihydroxystearic acid previously reacted with 1, 2, 4, 6 and 8 moles of propylene oxide were adjusted with triisopropanolamine to equivalent weight 100. Using trichlorofluoromethane as blowing agent and triethylenediamine as catalyst, the adjusted polyols were foamed by reaction with a prepolymer made from oxypropylated sorbitol and tolylene diisocyanate. The resulting rigid foams had densities between 1.6 and 2.0 lb/ft^3, the densities for the *threo* series being parallel to but higher at each stage of oxypropylation than those of the *erythro* series. Compressive strengths in the *erythro* series ranged from 19 psi for the monooxypropylated compound to 38 psi for the octaoxypropylated member; in the *threo* series from 27 to 39 psi. Properties improved in both series as the degree of polyol oxypropylation increased. This contrasted with foams prepared earlier from oxyethylated polyols, whose properties generally reached maxima at intermediate degrees of oxyethylation. Using the tetra- and hexaoxypropylated *threo* polyols, the proportion of blowing agent was varied to relate compressive strength to density of foams between 1.4 and 4 lb/ft^3.

Introduction

The preparation of polyols from *threo*- and *erythro*-9,10-dihydroxystearic acid and propylene oxide has been described (1). The present series of rigid foams were made, like those involving oxyethylated dihydroxystearic acid (2), by reaction of the fat-based polyols with a prepolymer resulting from reaction of excess tolylene diisocyanate with an oxypropylated sorbitol, following the two-step method described by Lyon, Garrett and Goldblatt (3). The overall reaction is outlined in Equation I:



$$CH_3(CH_2)_7\underset{\underset{H}{\underset{|}{O}}}{CH}-\underset{\underset{H}{\underset{|}{O}}}{CH}(CH_2)_7\overset{O}{\overset{\|}{C}}O-(CH_2\overset{CH_3}{\overset{|}{\underset{H}{C}}}-O)_nH \quad + \quad PREPOLYMER-NCO \xrightarrow[\text{CATALYST, SURFACTANT}]{CCl_3F\uparrow} \left[-\overset{O}{\overset{\|}{C}}\underset{H}{N}Ar\underset{H}{N}\overset{O}{\overset{\|}{C}}-O-\underset{\underset{|}{\underset{O}{|}}}{\overset{\overset{\diagdown\ \diagup}{O\ O}}{\overset{\diagdown\diagup}{R}}}-O-\right]_p \qquad [1]$$

The polyols, bearing 1, 2, 4, 6, or 8 oxypropyl units and ranging in hydroxyl equivalent from 131 to 283, were each adjusted to a common equivalent weight of 100 by addition of triisopropanolamine, as recorded in Table I. The reaction with the prepolymer was catalyzed by triethylenediamine; the blowing agent was trichlorofluoromethane; and the cell stabilizing surfactant a silicone.

Experimental

Typical Foam Preparation

To 16.5 g (0.105 equivalents) of the prepolymer (28.0% free NCO, 32,000 cps at 25C) in a paper cup, was added 0.16 g of silicone oil L-520 (Union Carbide Corporation) and 10% more than the desired 4.1 g of trichlorofluoromethane. In a second vessel, 6.2 g of the dioxypropylated *threo*- polyol was first mixed with 3.8 g of triisopropanolamine, resulting in 10.0 g (0.100 equivalents) of adjusted polyol T2, of equivalent weight 100. To this was added 0.45 g of Dabco-33. After the excess blowing agent had evaporated, the adjusted polyol-catalyst mixture was added to the cup containing the prepolymer, and the total mixed by a 4-quadrant stirrer 44-mm in diameter at 1500 rpm for 8 sec. The mixture was then poured into a fresh 9-oz cup and allowed to foam. Creaming was evident 13 sec after the beginning of the mixing; the foam continued to rise until 135 sec had elapsed and was tack-free at 145 sec.

Test Methods

Density, compressive strength (at 10% compression) before and after 7-days' humid aging, and per cent volume change on humid aging were measured by the methods used previously (2).

Percentage of open cells was measured by Tentative ASTM Method D-1940-62, using a Beckman Air Comparison Pycnometer.

Discussion

As noted in the previous paper (1), the present polyols, which were formed by oxypropylation rather than oxyethylation, were liquids or semiliquids conveniently blended in foam formulations. There was also a difference in reactivity toward isocyanate.

TABLE I
Adjustment of Equivalent Weights

Moles PO[a]	Hydroxyl equivalent	Weights taken for OH equiv. = 100: Fatty triol, g	Weights taken for OH equiv. = 100: Triisopropanolamine, g	Adjusted polyol designation
		threo-Polyol		
1.1	130.8	6.9	3.2	T 1
1.9	145.4	6.2	3.8	T 2
3.5	168.6	5.6	4.4	T 4
5.7	220.8	5.2	4.8	T 6
7.8	232.7	4.8	5.2	T 8
		erythro-Polyol		
1.0	173.9	5.4	4.6	E 1
1.9	184.6	5.3	4.7	E 2
4.1	194.3	5.1	4.9	E 4
6.1	242.4	4.8	5.2	E 6
7.9	283.4	4.4	5.6	E 8

[a] Moles of propylene oxide absorbed per mole of dihydroxy acid, measured by weight gain.

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[1] Presented at AOCS Meeting in Cincinnati, October 1965.
[2] E. Utiliz. Res. Dev. Div., ARS, USDA.

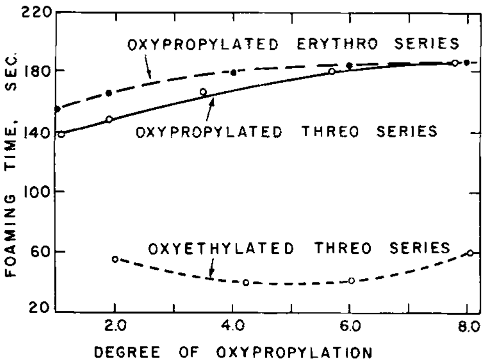

FIG. 1. Duration of foam rise as a function of degree of oxyalkylation of polyol component.

Although with oxyethylated polyols the duration of creaming before rising of foams had been only 8 or 9 sec, the cream time of all the present formulations was 12 or 13 sec. This increased time interval facilitated the transfer of mixture from one cup to another before foam rise, thereby eliminating nonuniformity of product at cup bottom.

The duration of foam rise from the beginning of stirring for three series of formulations is shown in Fig. 1 as a function of kind and degree of oxyalkylation of polyol. It is quite evident that the higher proportion of secondary OH groups in the present two series of oxypropylated polyols leads to longer foaming times, ranging from 138 to 185 sec in the *threo*- and from 155 to 185 in the *erythro*-type. Foaming times of the formulations based on oxyethylated dihydroxystearic acid had ranged from 40 to 60 sec for 2 to 8 units of epoxide fixed. In the two oxypropylated series plateaus were reached near 6 units added. It is interesting that the difference between *erythro* and *threo* also disappeared near this point.

Physical properties and test results on the foams are detailed in Table II. As indicated by Fig. 2, the densities of foams from both oxypropylated dihydroxystearic acids were consistently low (1.59 to 1.83 lb/ft^3) and trended up only gradually with degree of oxyalkylation, in contrast to those from oxyethylated polyols, which were mostly higher and went through a maximum. Densities of the *threo*-series were slightly greater than those of the *erythro*.

TABLE II

Properties of Foams

Adjusted polyol designation	Density[a] lb/ft^3	Open cells, %	Humid aging[b] Δ vol, %	Compressive strength, psi,[c] Before humid aging	Compressive strength, psi,[c] After humid aging
		Oxypropylated *threo* series			
T 1	1.69	16.4	11.0	28.0	14.0
T 2	1.74	15.4	64.4	28.5	13.0
T 4	1.75	14.9	70.8	34.0	12.0
T 6	1.75	18.6	64.5	38.5	15.5
T 8	1.83	14.8	16.6	38.0	9.0
		Oxypropylated *erythro* series			
E 1	1.69	31.0	13.6	21.0	17.0
E 2	1.59	28.4	26.4	21.0	15.0
E 4	1.72	19.5	13.2	32.0	....
E 6	1.74	20.8	38.3	36.0	12.5
E 8	1.77	17.5	76.2	37.6	13.5
		Oxyethylated *threo* series[d]			
T 2	1.83	......	......	43.0	......
T 4	1.97	......	......	67.0	......
T 6	2.01	......	......	45.0	......
T 8	1.77	......	......	26.0	......

[a] Average density of all core samples.

[b] Figures resulting from final evaluation after 1 week; in no case was shrinkage observed from maximum volume reached during this period.

[c] At 10% compression.

[d] Reference 2.

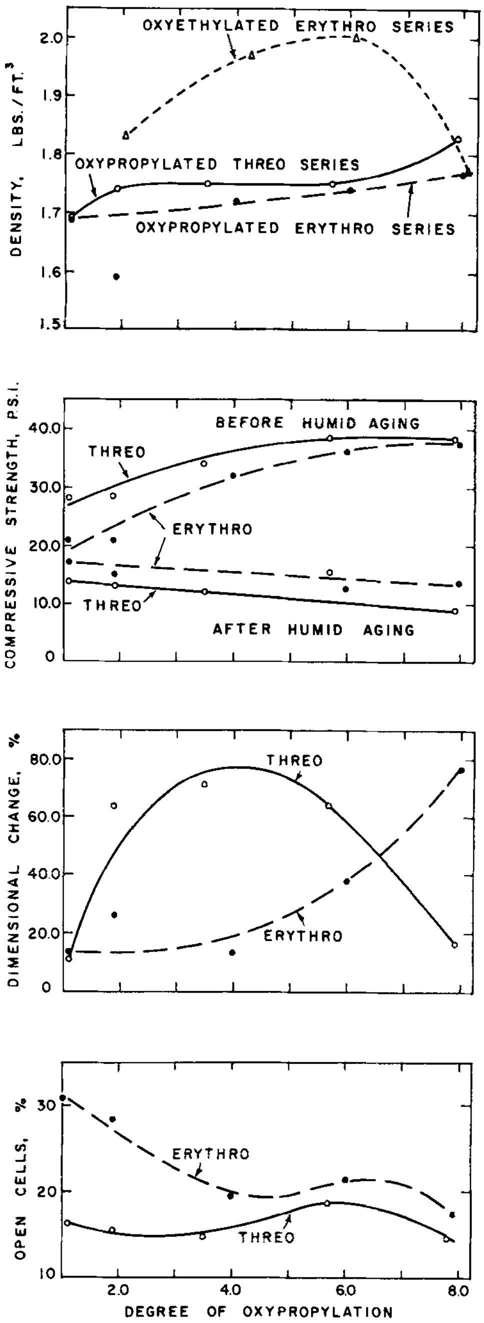

FIG. 2. Foam properties as related to degree of oxypropylation of the polyols.

Compressive strengths before humid aging, paralleling density in the present two series, also increased with degree of oxypropylation, again in contrast to the earlier series, which had had a pronounced maximum at 4 units of oxyethylation. Strengths were lower at oxypropylation degrees of 2 and 4 than those (not shown) for oxyethylates, but densities were desirably lower also. Humid aging moderately impaired the strengths of the present foams.

In two of the *threo*- dihydroxystearic acid-based recipes, density d and compressive strength s were varied systematically by changes in content of blowing agent. The relation noted by Lyon, Garrett and Goldblatt (3) was obeyed:

$$\log s = r \log d + \log C \qquad [2a]$$

or

$$s/s_0 = (d/d_0)^r \qquad [2b]$$

The slope (or exponent) r had the values 1.40 and 1.15 for foams from the tetra- and hexaoxypropylated polyols, respectively. If desired, compressive strengths at other than the observed densities d_0 in modifications of these two formulations can be estimated by Equation 2b.

Dimensional stability to humid aging (Fig. 1) was greatest for foams from monooxypropylated polyols, followed by the di-, tetra-, and hexaoxypropylated *erythro* products. Extensive swelling was shown only by middle members of the *threo* series. None of the present foams suffered shrinkage.

The open cell content of the present *threo* series was in all cases under 20% and was relatively insensitive to degree of oxypropylation. Open cell content of the *erythro* series, almost twice as high as the *threo* at 2 oxypropyl units, fell with higher substitution to nearly the same range.

It is recognized that the foam properties reported here, which were measured on small-scale laboratory samples, may differ from those attainable from commercially available sources.

Use of Free Acid

In the early days of foam technology, the reaction of a free carboxylic acid with isocyanate was sometimes used as a source of carbon dioxide blowing agent as well as some amide linkages. It therefore seemed possible that a dihydroxystearic acid could function in this way without preliminary oxyalkylation. Base-catalyzed mixtures of acetic or stearic acid warmed with tolylene diisocyanate generated substantial amounts of CO_2.

Since the melting points of the dihydroxystearic acids prevented their use at room temperature, a solution of 10% *threo*-9,10-dihydroxystearic acid in the hexaoxypropylated polyol was foamed by the reaction with tolylene diisocyanate. Without added trichlorofluoromethane an excessively dense foam resulted; normal amounts of added blowing agent gave a foam of normal density but greater friability than usual.

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