yield was obtained through the use of catalyst poisons. As reported earlier (25), pyridine was most effective (Table II). In order of decreasing effectiveness, other poisons were: lead acetate, triethyl amine, sodium acetate, and sodium hydroxide. The lead acetate, sodium acetate, and sodium hydroxide were deposited on the catalyst support, in contrast to pyridine and triethyl amine which were used in the solvent medium.

The study on catalytic hydrogenation of ozonolysis products is continuing in this Laboratory, and the effect of using various participating solvents during ozonolysis and hydrogenation will be reported shortly (21).

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Urethane Foams from Animal Fats I. Oxyethylated 9, 10-Dihydroxystearic Acid[1]

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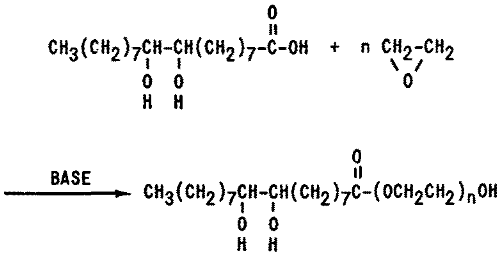
Abstract

Threo- and *erythro-*9,10-dihydroxystearic acids were reacted with 2, 4, 6 and 8 moles of ethylene oxide. The oxyethylated polyols from the *threo* acid, adjusted to equivalent weight 100 with triisopropanolamine, were converted to satisfactory rigid foams by mixing with corresponding amts of isocyanate-terminated oxypropylated sorbitol prepolymers of three viscosities. Typical foam properties had maxima for the tetra- or hexaoxyethylene polyol, and most properties paralleled prepolymer viscosity.

THE STRAIGHTFORWARD preparation of the 9,10-dihydroxystearic acids from oleic acid (1,2), their trifunctionality and hydrocarbon chains suggested study of their value as components of urethane foams. The present report describes the 2-stage preparation of foams based on oxyethylated dihydroxystearic acid as the major "polyol" and the reaction product of oxypropylated sorbitol and excess tolylene diisocyanate as the "prepolymer."

Oxyethylation of Dihydroxystearic Acids

Threo- and *erythro-*9,10-dihydroxystearic acid were converted to triols by base-catalyzed reaction with ethylene oxide at 7 psi and 180C, in an apparatus previously described (3). The reaction is summarized by equation 1, in which *n* has the average values 2, 4, 6 and 8:



$$CH_3(CH_2)_7\underset{\underset{H}{O}}{CH}-\underset{\underset{H}{O}}{CH}(CH_2)_7-\overset{\overset{O}{\|}}{C}-OH + n\ \underset{\diagdown O \diagup}{CH_2-CH_2}$$

$$\xrightarrow{BASE} CH_3(CH_2)_7\underset{\underset{H}{O}}{CH}-\underset{\underset{H}{O}}{CH}(CH_2)_7\overset{\overset{O}{\|}}{C}-(OCH_2CH_2)_nOH \quad (1)$$

As with simple carboxylic acids (4,5), it is considered that the acid group is consumed in the first stages of reaction with ethylene oxide, to form ethylene glycol monoesters. With additional ethylene oxide, reaction presumably continues to a larger extent at the β-oxyethanol and to a smaller extent at the vicinal secondary glycol functions, still disfavored by comparatively low acidities (3). Owing to self-alcoholysis during oxyethylation, the products are more complex than diagrammed and comprise a mixture of monoesters, diesters, and free polyethylene glycol (6,7).

In most of the oxyethylations, 4 mole % KOH based on the dihydroxystearic acid was used as catalyst. Residual catalyst then had to be neutralized (as by concentrated hydrochloric acid) before use of the products in the foaming stage, to avoid overcatalysis of urethane formation. In several preparations, neutralization was avoided by using 2 mole

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[1] Presented at the AOCS meeting in Chicago, 1964.

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TABLE I

Polyols Prepared by Oxyethylation of 9,10-Dihydroxystearic Acids

Dihydroxy acid	Moles EO[a]	Catalyst	Ester equivalent	Hydroxyl equivalent	State	Weight taken for OH Equiv. = 100		Adjusted polyol, designation
						Fatty triol, g	Triiso-propanolamine, g	
Threo								
	2.03	KOH	446.3	133.9	semi-solid	6.7	3.3	T2
	4.19	TEDA[b]	516.2	163.5	liquid	5.7	4.3	T4a
	4.25	KOH	631.8	162.8	liquid	5.8	4.2	T4b
	6.07	KOH	784.7	182.8	liquid	5.4	4.6	T6a
	6.02	TEDA	580.8	180.9	liquid	5.4	4.6	T6b
	8.09	KOH	737.2	221.4	semi-solid	5.0	5.0	T8
Erythro								
	2.00	KOH	444.3	169.4	solid	5.7	4.3	E2
	4.01	KOH	613.8	195.4	solid	5.1	4.9	E4
	6.01	KOH	667.1	229.8	solid	4.8	5.2	E6
	8.04	KOH	759.2	206.3	solid	5.1	4.9	E8

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

% triethylenediamine as oxyethylation catalyst and a complementary amt of the same catalyst for the urethane reaction. This led to foams equal to those from polyols made under KOH catalysis, but KOH was found somewhat preferable, as it gave polyols of better color. Analytical results on the fat-based polyols are given in Table I.

In the *threo* series the di- and octaoxyethylene polyols were soft or semisolids, and the tetra- and hexaoxyethylene products liquid. In the *erythro* series all polyols were waxy solids at room temp. Because of the difficulty of handling firm solids at the foaming stage, investigation of the *erythro* series was discontinued after preparing a limited number of foams.

Prepolymer Preparation

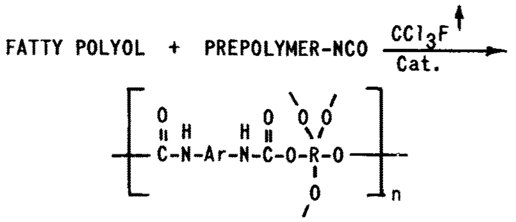
For preparation of prepolymers, polyoxypropylated sorbitol (Atlas G-2408, OH No. 542) was treated at about 80C with excess tolylene diisocyanate (80% 2, 4: 20% 2, 6) following established procedure (8,9). The oxypropylated hexol and the diisocyanate were stirred initially at about 80C for 1 hr. By further heating separate portions at 115C for about 0.5, 1.0, and 1.5 hr, products were obtained of low, medium and high viscosity, respectively. During the heating, some structures other than urethane may be formed, such as isocyanate trimers and allophanates (10), but the isocyanate content suffers very little further decrease.

The prepolymers used in foaming had the following properties:

Designation	Viscosity, cps.	Residual NCO. %	NCO Equivalent
L	17,700	28.3	148.4
M	32,000	28.7	146.3
H	53,000	27.3	153.7

Foam Preparation

The two-step process used for preparing the present foams is shown in principle by Equation 2:



$$\text{FATTY POLYOL} + \text{PREPOLYMER-NCO} \xrightarrow[\text{Cat.}]{CCl_3F\uparrow}$$

(2)

The method of preparation paralleled that described by Lyon, Garrett, and Goldblatt (9). Each 0.1 equivalent of polyol was treated with 0.105 equivalents of isocyanate-terminated prepolymer and with appropriate amts of silicone fluid as surface-active agent, triethylenediamine and dibutyltin dilaurate as catalyst system, and trichlorofluoromethane as blowing agent. Thirty-gram batches were foamed in paper cups.

The equivalent weight of the polyols in terms of hydroxyl function varied from 130 to 220 as the degree of oxyethylation of the dihydroxystearic acid was increased. In initial experiments each polyol was reacted, without modification of its equivalent weight, with the prepolymer. It was hoped that the variation of polyoxyethylene chain length would produce a series of foams ranging from rigid to flexible. Although such a graduation was indeed observed, excessive shrinkage was encountered at each degree of oxyethylation studied.

It was found, however, that good foams resulted from polyols mixed with sufficient lower-molecular-weight triols to give hydroxyl equivalents of about 100. Each polyol was therefore mixed with an appropriate amt of triisopropanolamine to give "adjusted polyols" as indicated at the right of Table I.

TABLE II

Properties of Foams

Adjusted polyol, designation	Prepolymer viscosity cps	Density lb/ft³	Energy rebound, %	Water absorption, %	Open cells, %	Humid aging Δ vol, %	Compressive strength, psi for compression of	
							10%	25%
T2	17,700	1.65	16.0	150	18.8	58.0	27	32
	32,000	1.83	10.0	141	20.4	24.1	43	45
	53,000	1.91	16.0	124	18.5	20.1	45	46
T4b	17,700	1.90	21.0	120	26.8	67.2	68	64
	32,000	1.97	21.0	111	18.7	49.0	67	66
	53,000	2.08	20.0	98	21.5	33.8	48.5	54
T6a	17,700	1.88	22.0	95	9.5	67.4	33	37
	32,000	2.01	22.0	83	19.4	61.0	45	50
	53,000	2.08	16.0	64	15.3	7.4	41	43.5
T8	17,700	1.64	3.0	152	....	72.8	31	35
	32,000	1.77	12.0	130	11.0	62.8	26	29.5
	53,000	1.82	17.0	89	18.5	21.7	30	34.5

The use of the adjusted polyols in the foaming reaction with prepolymer and Freon eliminated the shrinkage problem, but limited the foam series to the rigid category. It is hoped at a later time to develop systems leading to nonshrinkage flexible foams.

Typical Foam Preparation. A typical foam preparation was that reacting the *threo*-polyol containing 4.25 oxyethylene units (hydroxyl equivalent 162.8), after equivalent weight adjustment, with a prepolymer of 32,000 cps viscosity (isocyanate equivalent 146.3).

In vessel A, 5.8 g of the polyol were mixed at 80C with 4.2 g of triisopropanolamine, resulting in 10.0 g (0.100 equivalents) of adjusted polyol T 4b of equivalent weight 100. After cooling to room temp this was mixed with 0.45 g of Dabco-33 (Triethylenediamine 33% solution in 1,2,6-hexanetroil, Houdry), and 0.10 g dibutyltin dilaurate.

In vessel B, a 9-oz waxed paper cup tared together with a light spatula, were hand mixed 15.4 g (0.105 equivalents) of prepolymer M, 0.16 g silicone oil L-520 (Union Carbide Corporation), and about 10% more than the desired 4.1 g of trichlorofluoromethane. When the excess Freon had evaporated, the solution in vessel A was poured into cup B and the total mixed by a 4-quadrant stirrer, 44 mm in diameter (Conn and Co., Warren, Pa.), at 1500 rpm. When creaming began, after 6 sec, mixing was discontinued. Creaming continued for 2 sec more, when definite foaming was evident, and the foam rose to a height of 7.5 in. in 40 sec, measured from beginning of mixing. The top surface was tack-free at 60 sec.

In other members of the series, creaming was evident after 6 to 8 sec, foam rise was complete after 40 to 70 sec, and the foams were tack-free after 50 to 130 sec.

Although, in the *threo*-9,10-dihydroxystearic acid series, blends of the tetra- and hexaethylenoxy fatty triols with triisopropanolamine were conveniently liquid at room temp, blends made from the di- or octaoxyethylene derivatives deposited some solid if allowed to fully cool and had to be used while still slightly warm. This made it somewhat more difficult to achieve consistent results with the latter two. As noted earlier, this problem was more acute for each of the triols made from *erythro*-9,10-dihydroxystearic acid.

Test Methods

In general tests were run on blocks 1 in. high × 1.5 in. square, cut from the core of 30-g batches of foam. Specific methods are as cited below, but subject to the sample size noted:

Density. Procedure ASTM D 1622-59T.

Compressive Strength. Procedure ASTM D 1621-59T, using an Instron Tensile Tester with reversed cage attachment (8), operated at a cross-head speed of 0.1 in./min.

Percent Water Absorption. Weighed samples were immersed beneath a 10-ft. head of water for 24 hr. The samples were then blown free of surface water (8) and weighed. Weight gain as a percent of original sample weight was reported.

Humid Aging, Percent Volume Change. Following Atlas Physical Test Method 413-12-2823, samples were conditioned for 1 wk in a lagged tank at 70C and 100% relative humidity. After removal from the tank and standing 48 hr under ambient conditions, sample volumes were measured, and percent change from original volume was reported.

Energy Rebound. Using a Bayshore Resiliometer, a 28.5-g steel bushing was mechanically dropped

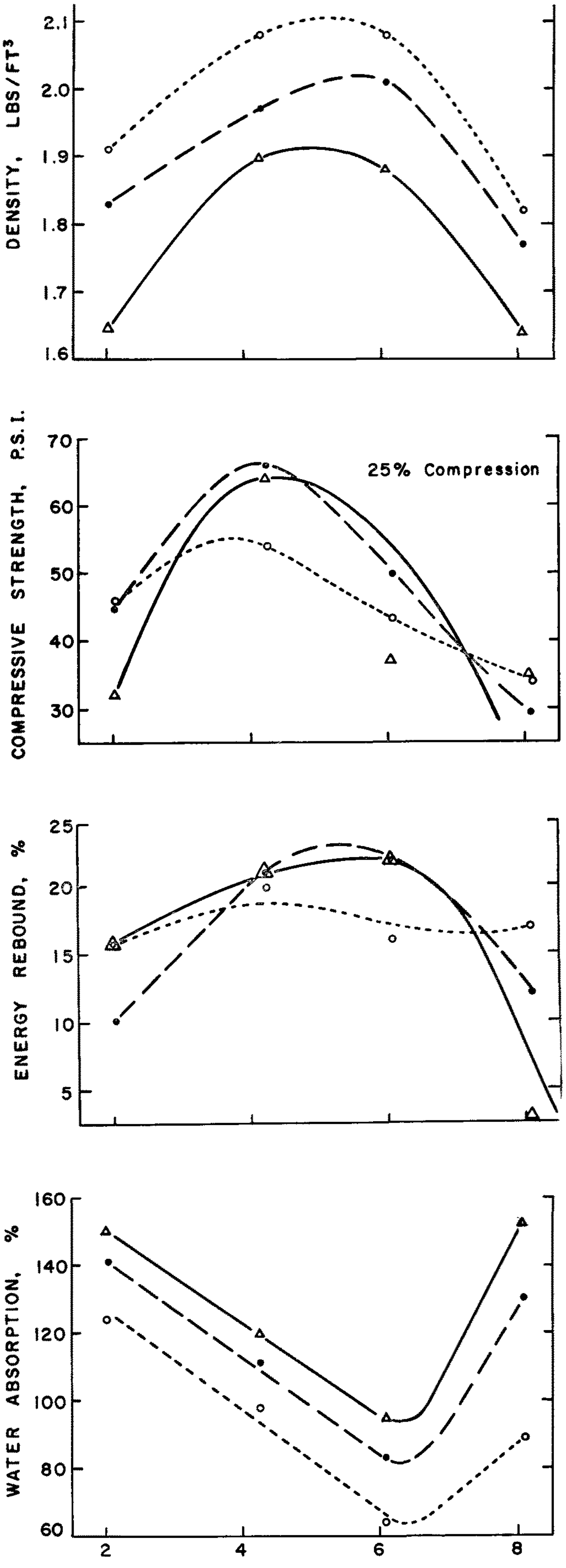


FIG. 1. Effect of degree of oxyethylation on foam properties. Prepolymer viscosities: —△— 17,700; — — ● — — 32,000; - - - - - ○ - - - - - 53,000 cps.

16 in. onto the sample. The rebound percent was read on the height scale.

Percent Open Cells. The method and apparatus of Remington and Pariser (11) were employed, and duplicate determinations were performed following ASTM D 1940-62T, except that the sample for each determination consisted of two 7-cm^3 specimens.

Discussion

Physical properties and test results on the foams are listed in Table II. Dimensional stability after humid aging was greatest for foams from the dioxyethylene polyols. Stability increased, however, with prepolymer viscosity, since dimensional change was least at each degree of polyol oxyethylation for the 53,000 cps-viscosity prepolymer.

Trends of density, compressive strength, energy rebound, and water absorption are compared graphically in Figure 1, as functions of polyol oxyethylation, n, for the three prepolymer viscosities. Average densities ranged from 1.64 to 2.08 lb/ft^3. The curves were convex, being higher at 4 and 6, and lower at 2 and 8 oxyethylene units. Densities also paralleled the viscosities of the prepolymers used.

Average compressive strengths at 25% compression ranged from 29 to 65 lb/in^2, with a maximum in each prepolymer series at 4.25 polyol oxyethylene units. In general highest values were obtained from the 32,000 cps prepolymer. Compressive strengths appear to be in a satisfactory range for rigid foams. Since the densities of most of these foams were below 2 lb/ft^3, the use of somewhat less Freon would presumably lead to foams of still acceptable density and even higher compressive strengths.

Energy rebound varied with *n* in the same fashion as density. For each viscosity, water absorption decreased linearly to a striking minimum at 6 oxyethylene units. The inverse of these curves, measuring resistance to water absorption would be more comparable to the curves for the positive properties. Increase in prepolymer viscosity caused less water to be absorbed.

The results reported show that rigid foams of satisfactory low density and good compressive strength can be made from oxyethylated *threo*-9,10-dihydroxystearic acid, triisopropanolamine, and prepolymers based on oxypropylated sorbital and tolylene diisocyanate. A moderate range of properties was obtained by varying degree of polyol oxyethylation and prepolymer viscosity.

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Cutting of foams by R. R. Bram and R. R. Calhoun, Jr. of the Instrument Shop; compression evaluations by G. R. Riser and W. E. Palm of the Animal Fat Properties Laboratory; and helpful discussions with A. F. Talbot and A. Farkas, Houdry Process and Chemical Company, and T. H. Applewhite, Western Util. Res. & Dev. Division.

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Hydrogenation of Cottonseed Oil With Reused Catalyst

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Abstract

Cottonseed oil was hydrogenated using both new (Rufert catalyst flakes) and reused (up to five uses) catalysts at 130–169C, at a pressure of 45 psig, and with high degrees of agitation.

The activity of the catalyst increased initially with use, especially at 130C, but with continued use the activity decreased. The selectivity of the hydrogenation decreased with reuse of the catalyst, especially at lower temp. Isomerization decreased slightly as the catalyst was used only at higher temps. The induction period found with fresh catalyst at 130C was eliminated in runs with second- and third-use catalyst. A small induction period was noted with fifth-use catalyst.

Treatment of once-use catalyst with air severely reduced the catalyst activity. Steam- and vacuum-treatment of the catalyst resulted in a slightly less active catalyst than a hydrogen-treated catalyst. None of these treatments significantly affected selectivity or isomerization.

Results of this investigation can be explained in large part by the concn of hydrogen absorbed on the catalyst surface.

Introduction

NICKEL CATALYSTS for the hydrogenation of triglycerides are commonly used industrially at least several times. With oils that have been carefully refined and bleached to remove catalyst poisons, the catalyst is often used 10, 20 or even more times. Hence, 90% or more of the hydrogenations are made with used catalyst. Yet the literature pertaining to used catalysts is meagre.

Factors which are of importance when the catalyst is reused include the amt and type of poison in the oil or hydrogen. Poisons which are sometimes present in the oil include free fatty acids, cartenoid-type compounds, alkali salts and sulfur compounds (4). Modern refining and bleaching techniques are generally effective in removing most, but not necessarily all, of the poisons from the raw oils. Besides catalyst poisons, used catalysts probably lose their activity because of just repeated uses, i.e., they just get "tired" with continued use. The activity of the used catalyst (ability of the catalyst to add hydrogen to the oil at a rapid rate) and the type of hydrogenation obtained (degree of selectivity and of isomerization) probably vary to a considerable extent with the past history of the catalyst.

Bailey (4) defines selectivity as applied to cata-

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