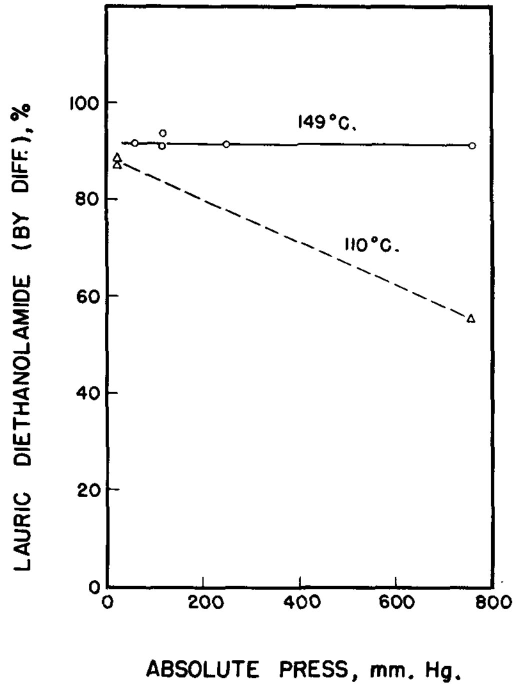

FIG. 3. Effect of temperature and pressure on yield of alkylolamides.

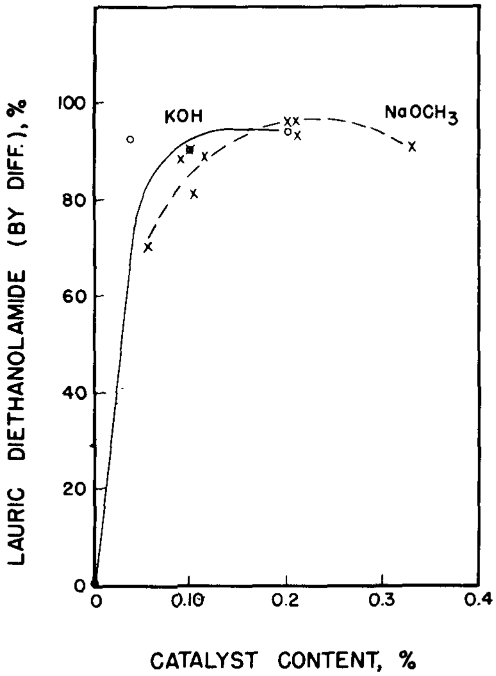

FIG. 4. Effect of catalyst content on yield of alkylolamides.

Figure 4 depicts the effect of catalyst quantity on yield. Similar results were obtained with KOH and sodium methylate, each giving a high yield at 0.2% catalyst content. The small catalyst usage plus the efficient removal of methanol and diethanolamine from the thin reaction zone both contributed to the high product purity. Therefore, it has been demonstrated that alylolamides can be made continuously at high temperatures (149C) while achieving a purity of 95–97%.

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Preparation of Foams from Vegetable Oil Derivatives

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Abstract

Dimer acid was hydroxyethylated at 110–240C in the presence of alkaline catalysts. Products having ethylene oxide: dimer acid mole ratios of 0.8 to 1.4 were transformed into flexible urethane foams of density 2.0 to 4.4 lb/ft^3. Hydrogenated "aldehyde oil" gave a rigid foam which had a density of 1.2 lb/ft^3.

IN THE SEARCH for inexpensive ingredients for commercial production of urethane foams, polyether types of polyols have largely taken over from the more expensive polyester types derived from polyols and polybasic acids. However, certain polyester polyols are still used in the clothing industry because of superior drape and feel. These polyols are from dimer acid and polyols such as diethylene glycol and trimethylolethane. Dimer acids are commercially available and are produced by the polymerization of polyunsaturated fatty acids derived from soybean, cottonseed, and linseed oils (1). Less expensive polyols should result from the condensation of ethylene oxide with dimer acid. The purpose of this paper is to describe the preparation of such polyols and to evaluate in a preliminary way urethane foams prepared from them.

In connection with a program now in progress at the Northern Laboratory, it became desirable to prepare foams from the polyol from an "aldehyde oil." These oils have been prepared by the ozonization of soybean or other vegetable oil followed by reductive decomposition of the ozonolysis solution to form aldehydic materials. After removal of solvent and volatile aldehydes, the residue, "aldehyde oil," should have the structure of a triglyceride of azelaic semialdehyde (2). The product obtained by the catalytic hydrogenation of this oil should have the structure of a triglyceride of 9-hydroxynonanoic acid. Departure from the ideal structures results from the presence of palmitic and stearic acids in the original soybean oil.

Experimental

Hydroxyethylated Dimer Acid. Polymerized fatty acid (Emery 3065-S) was the starting material. This brown liquid, consisting of three parts C_{36}-dibasic acid and one part C_{54}-tribasic acid, had an acid value of 188.5, a saponification value of 198.5, a neutralization equivalent of 297, a viscosity at 25C of 99 poises, and a Karl Fischer water content of 0.0%.

The condensation of ethylene oxide with dimer acid

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under pressure at 140C in 28 molar proportions has been described (3). In the present work, the condensation was conveniently carried out at approximately atmospheric pressure in an apparatus similar to that used by Wrigley for stearic acid (4). Up to 350 g of dimer acid were charged for each batch. The catalyst was 0.5% potassium carbonate, or sodium methoxide, either as a solid or in methanol solution. Ethylene oxide was continuously bubbled through the reaction mixture. A reasonable excess was maintained even when there was strong absorption of the gas at lower reaction temperatures. The reaction was followed by periodic determinations of acid number. The apparatus was flushed with nitrogen at the beginning, before sampling, and at the end of an experiment. Foaming of the mixture was avoided by proper stirring. The products were brown liquids. Usually a two-layer condensate containing ethylene glycol accumulated in an ice trap which was placed after the reaction flask, and was discarded. Table I shows data on typical reactions. Analyses of products are shown in Table II.

TABLE I

Hydroxyethylation of Dimer Acid

Reaction conditions		Product characteristics				
Time, hr	Temp, °C min–max	Acid value[a]	Viscosity at 25C, poises	Hydroxyl value	Sapon. value	n[b]
7¾	100–155	0.5	36	110	183	1.1
5	141–161	1	62	110	......	......
5¾	135–155	1	63	98	175	1.8
5½	140–153	3	66	101	......	......
10¼	140–177	0	790	54	184	1.1
8¼	203–210	0	900	59	180	1.4[c]
10½	192–253	3	1500	24	184	1.1[c]
6¼	165–230	0	2200	50	......	......

[a] The low acid values, even with less than stoichiometric amounts of ethylene oxide, resulted from polyesterification reactions.

[b] $n = \frac{\text{moles ethylene oxide}}{\text{mole dimer acid}}$, as calculated from saponification values.

[c] K_2CO_3 catalyst was used for these experiments; $NaOCH_3$ for others.

TABLE II

Analyses of Hydroxyethylated Dimer Acid

Analysis	Hydroxyethylated dimer acid nos.				
	1	2	3	4	5
Acid value	16	0	0	0	0.5
Hydroxy value	55	113	122	99	110
Saponification value	179.7	......	......	180	183
Moles ethylene oxide/mole dimer acid	1.1	......	......	1.4	1.1
Viscosity at 25C, poises	90	132	112	79	36
Molecular weight	886	......	......	797	757
Water content (Karl Fischer), wt %	0.03	......	......	0.4	0.2

Hydroxy Oils. Aldehyde oil having an aldehyde content of 3.7 mmole/g was hydrogenated in dioxane for 5 hr at 100C and 1,000 psi to give a product having an acid number of 3 and a hydroxyl number of 231. Another aldehyde oil having an aldehyde content of 2.6 mmole/g was hydrogenated for 8 hr. in alcohol in the presence of triethylamine at 100C and 2,100 psi to give a product having an acid number of 42 and a hydroxyl number of 114. W-6 Raney nickel catalyst was used in both preparations.

Preparation of Foams. A one-shot technique was used to prepare several foams as indicated in Table III. A reversed mixing order was employed in other experiments described in Table IV. Ingredients were mixed and allowed to foam in waxed paper cups, and the foams were cured overnight at 70C. To prepare foam from a hydroxy oil having an acid number of 42 and a hydroxyl number of 114, 3.15 g of the oil were stirred to mix with 0.5 g triethylene diamine, 0.5 g water, 0.05 g ethanol, and 1.25 g silicone (L520, Union Carbide and Carbon, New York, N. Y.). Then 2.5 ml toluenediisocyanate were added, and the mixture was stirred 0.3 min. A rigid foam with density of 1.2 lb/ft^3 was obtained.

TABLE III

Foams Prepared with the One-Shot Technique

Formula	Foam nos.		
	6	7	8
Triethylenediamine, g[a]	0.1	0.2	0.2
H_2O, ml	0.5	1.0	1.0
Polyoxyethylated vegetable oil, g[b]	2	5	5
	Mixed to clear solution		
Then added hydroxyethylated dimer acid, sample no. (Table II)	2	3	4
Weight, g	17.2	32	39.3
Stirred, min	2	....	2
Then added toluene diisocyanate, ml[c]	8	16	16
	Stirred until foaming began (about 2 sec)		

[a] DABCO, a catalyst from Houdry Process Company, Philadelphia, Pa.

[b] Emulphor El-719, an emulsifier of Antara Chemicals, New York, N.Y.

[c] Nacconate 80 of Allied Chemical Corporation, New York, N.Y.

TABLE IV

Foams Prepared with Reversed Mixing Order

Formula	Foam nos.				
	9	10–12	13	14–16	17–18
Hydroxyethylated dimer acid, sample no. (Table II)	5	1	1	1	1
Weight, g	16.9	6.9	6.9	6.9	6.9
Nacconate 80, ml	8	2.5	2.5	2.0	2.0
Stirred 5,900 rpm, min	......	0.3	0.25	0.15–0.25	0.2
Then added DABCO, g	0.05	0.1	0.12	0.08–0.09	0.1–0.12
In H_2O g	0.25	0.18–0.22	0.27	0.15–0.20	0.18–0.21
Stirred, min	......	0.15–0.20	0.15	0.15	0.15

Test Methods. Area shrinkage was measured in terms of the percentage reduction in cross-sectional area of the cured foam in comparison to the corresponding container dimension. Density was determined by weighing a regularly cut piece of foam on an analytical balance. Compression modulus (5) and load required for 25% compression was calculated from results obtained with a Hinde and Dauch crush tester (Testing Machines, Inc., Mineola, Long Island, N. Y.). Compression set test was performed following essentially ASTM D 1564-58T, 18 to 23. The results of these tests are given in Table V.

Discussion of Results

Hydroxyethylation of Dimer Acid. The alkali-catalyzed reaction of ethylene oxide with fatty acids is complex (6). In the reaction of ethylene oxide with available reactive hydrogen atoms, the more acidic hydrogen atoms of the carboxyl group tend to react before the less acidic hydrogen atoms of the hydroxyl group. With pure dimer acid HOOC-R-R-COOH (I) the first increment of ethylene oxide to react gives the compound $\mathrm{HOOC{-}R{-}R{-}COO.CH_2.CH_2.OH}$ (II). The next increment of ethylene oxide either yields more of II or reacts with II to produce $\mathrm{HO.CH_2.CH_2.OOC{-}R{-}R{-}COO.CH_2.CH_2.OH}$ (III). When hydroxyethylation of the carboxyl groups is substantially complete polyester-ethers such as $\mathrm{HO.CH_2.CH_2.OOC{-}R{-}R{-}COO.CH_2.CH_2.O.CH_2.CH_2.OH}$ will be produced. In addition, alkaline conditions favor alcoholysis in which $\mathrm{{-}R{-}COO.CH_2.CH_2.O^-}$ reacts with $\mathrm{{-}R{-}COO.CH_2.CH_2.OH}$ to give $\mathrm{{-}R{-}COO.CH_2.CH_2.OOC{-}R{-}}$ and $\mathrm{HO.CH_2{-}CH_2.O^-}$. The relative amounts of the different products depend on the velocity constants of the different reactions possible at the temperature prevailing, on the concentrations of the reactants, on the treatment of the reaction mixture, and on the manner in which the ethylene oxide is introduced into it. Thus, the reaction products are mixtures of condensates containing different molecular proportions of ethylene oxide.

TABLE V

Polyurethane Foams from Hydroxyethylated Dimer Acids

Foam nos.	Premix			Catalyst	Water	Physical properties				
	Hydroxyethylated dimer acids		Mole ratio, OH/NCO	Triethylene, diamine, wt. % of polyester	Wt, % of polyester	Area shrinkage, %	Density lb./ft^3	Compression modulus, psi	Load required for 25% compression, psi	Compression set test test % of original height
	Sample no.	Wt %								
6	2[a]	64	0.32	0.6	2.9	3	2.7	1.2	0.6	50
7	3[a]	82	0.32	0.6	3.1	....	2.2	1.0	0.4	50
8	4[a]	67	0.32	0.5	2.5	8	2.3	0.7	0.15	50
9	5	63	0.33	0.3	1.5	16	4.4	13.4	3.5	50
10–12	1	69	0.20	1.4	2.9	0	2.1–2.2	3.1	1.2	44–45
13	1	69	0.20	1.7	3.9	0	2.2	3.1	1.1	......
14–16	1	74	0.25	1.3	2.6	0	2.3–2.5	2.0–2.3	0.9	46–50
17–18	1	74	0.25	1.6	2.8	0	2.0	......	......	......

[a] One-shot procedure was used.

In the hydroxyethylation of dimer acid, short reaction time and low temperature led to low viscosity and high hydroxyl number. Longer reaction time and high temperature gave high viscosity and low hydroxyl number (Table I).

Foam Nos. 6 to 8 (Table V) (7) showed an average density of 2.4 lb/ft^3 and did not recover after 22 hr compression at 70C (compression set test = 50). Accordingly, the mixing order was reversed (Table IV) to give polymerization an opportunity to begin before the evolution of CO_2. Also, some residual acidity of the starting material (Table II, No. 1) was expected to be more favorable for crosslinking. Foams prepared with reversed mixing order Nos. 10 to 18 (Table IV) gave no area shrinkage, had an average density of 2.2 lb/ft^3, and showed somewhat improved compression set tests. Foams made with 2.0 ml of Nacconate were more flexible than those made with 2.5 ml.

Foam No. 9 with compression modulus 12.4 had properties like those of a tennis ball.

The preparation of polyurethane foams depends on the starting materials used and on how the ingredients are mixed together to obtain the proper ratio of polymerization to evolution of carbon dioxide. Although results obtained from small-scale experiments may not duplicate those with large-scale mixing machines, because of the large number of variables involved (8) our small-scale exploratory experiments have shown that low-density, flexible, polyurethane foams can be prepared by a very direct route from dimer acid.

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Infrared Spectra and Gas Chromatography of Some Oxygenated Fatty Acid Derivatives[1]

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Abstract

Infrared spectra of hydroxy-, acetoxy-, oxo-, and unsaturated oxo-stearic acid derivatives were studied, and their purities were checked by gas-liquid chromatography.

INFRARED spectral studies of oxygenated fatty acids and their derivatives have been carried out by a number of workers (1). These studies included the saturated fatty acid derivatives (2,3,4,5,6), unsaturated fatty acid derivatives (7,8), *trans*-acids (9,10), linoleate (11), fatty alcohols (4), oxostearic acid derivatives (12), unsaturated oxostearic acids (13), hydroxy fatty acids (8,14,15), ricinoleate (16), ricinelaidate (17), branched chain fatty acids (18), epoxy fatty acids (14,19), glycerides (9,20), hydroperoxides (21), oxidation products of methyl oleates (22), methyl linoleate (23,24), and fats (25). In this report, the infrared spectra of some of the oxygenated fatty acids will be given. Their purity was checked by gas-liquid chromatographic analysis.

The infrared spectra of the oxygenated fatty acids were obtained at 24 ± 1C with a Beckman Model IR-7 spectrophotometer equipped with sodium chloride optics. They were studied as Nujol pastes unless otherwise indicated. Although perfect cancellation of Nujol absorption may occur with this instrument, results at ν C–H (about 3000 cm^{-1}) and δ C–H (about 1350–1500 cm^{-1}) were not conclusive. Therefore, these regions will not be discussed in detail (Table I).

Materials and Methods

Methyl 2-acetoxystearate. This compound was synthesized from stearic acid by the method of Mendel and Coops (26). The stearic acid was purified through methylation and repeated distillation under vacuum; mp 69.6C. The methyl 2-acetoxystearate of 90% purity was subjected to gas-liquid chromatography on a 10-ft silicone rubber column at 235C. It was purified by gas chromatography on a 5-ft preparatory silicone rubber column at 228C and 18 psi helium flow, 200 mA, sensitivity ×8. A 50 λ melted sample was in-

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