

# Preparations and Properties of Castor Oil Urethane Foams<sup>1</sup>

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EXPANDED FOAMS now constitute a large volume outlet for plastic materials, and greatly increased applications during the next few years are predicted. Urethane foams are expected to contribute significantly to this increase. Recent articles (1-4) review the background and history of urethane foams and elaborate on their potential future utility. Polyurethanes are obtained by reaction of organic polyhydroxy compounds with excess polyisocyanates, a reaction known more than a century ago. Subsequent reaction of the urethane polymers with water in the presence of an alkaline catalyst, usually tertiary amines, causes crosslinking accompanied by evolution of carbon dioxide which expands the plastic material into a foam. Figure 1 shows some typical

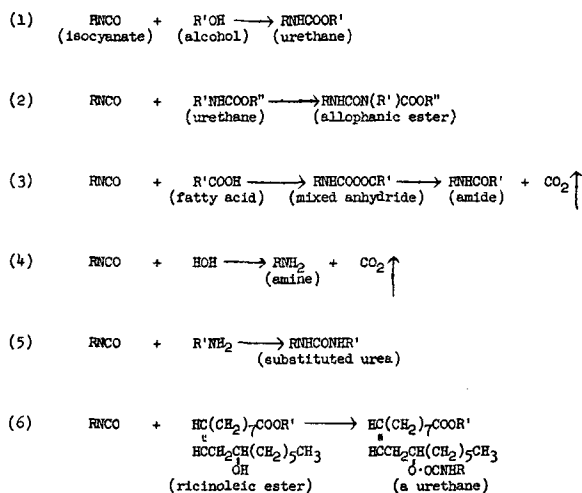


FIG. 1. Typical isocyanate reactions related to preparation of urethane foams.

reactions involved. By varying the ingredients, foaming conditions, and additives, foams can be obtained which are flexible or semirigid in nature (as low in density as 1 to 2 lbs./cu. ft.) and possess many other desirable properties.

Most commercial applications have utilized polyesters to produce urethane polymers (2). Castor oil, essentially a trihydroxy compound, *i.e.*, an ester of glycerol with ricinoleic acid, has been found useful in urethane applications. An ester of ricinoleic acid will react with isocyanate as shown in equation 6 of Figure 1. The reaction product of one mole of castor oil and three moles of tolylene diisocyanate may be visualized as in Figure 2. This shows that it is necessary to have an excess of isocyanate groups over hydroxyl groups so that the prepolymer will contain residual unreacted isocyanate necessary for the foaming stage. Also, if the number of isocyanate groups is less than twice the number of hydroxyl groups, crosslinking will occur. Although some crosslinking

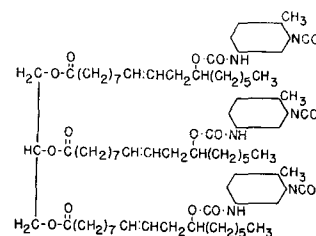


FIG. 2. A reaction product of castor oil with tolylene diisocyanate.

is desirable to build up the molecular weight of the prepolymer, too much crosslinking leads to excessive viscosity.

Most information in the literature on castor oil polyurethane foams is somewhat scattered, limited in scope, and generally confined to special applications. Since a favorable price differential exists for castor oil over most polyesters, information concerning the properties of various castor urethane foams should be useful to manufacturers and consumers of expanded plastic foams. It was the purpose of this investigation to evaluate the utility of castor oil and to determine the effect, on properties of the foams obtained, of varying the proportions of castor oil over the range of 50 to 80%. The effect of modification of the double bonds in castor oil on foam properties was also investigated. Evaluations were obtained on foams prepared from hydrogenated castor oil, elaidinized castor oil (containing *trans* double bonds), and a formulation in which a portion of the castor oil had been replaced with an epoxidized castor oil. In the interest of simplicity these investigations were confined to readily available commercial materials. Thus a commercial grade of dry castor oil, an 80/20 TDI (80% 2,4- and 20% 2,6-tolylene diisocyanate), and a commercial preparation of buffered 2-diethylaminoethanol catalyst were employed.

Generally from two to five tests were made on specimens from about five separate batches of each foam formulation studied. Properties tested were: foaming time, density, shrinkage, tensile-elongation, compression-deflection, compression set, accelerated aging, energy absorption, and water absorption.

## Experimental

**Prepolymer Preparation.** Castor oil urethane foams are prepared by the prepolymer or two-stage method rather than a one-step method as used with most polyesters. The use of elevated temperatures for the preparation of a castor oil prepolymer is necessary to obtain a workable viscosity range of about 10,000 to 30,000 centipoises at room temperature. This is because of the presence in castor oil of secondary hydroxyl groups which are slow to react with the isocyanate. The general procedure used to prepare the prepolymer (in batches of 400 to 800 g.) was as follows:

The required amount of 80/20 tolylene diisocyanate was added at room temperature to castor oil contained

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in a 1-quart fruit jar fitted through the top with a stirrer, thermometer, reflux condenser, and dry nitrogen inlet tube. After the initial exothermic reaction reached its maximum of about 80°C., the jar was lowered into a hot oil bath, allowed to reach the desired temperature, and then heated for the time required. In preliminary tests it was found that in making the 60% castor oil prepolymer at 130°C. a viscosity of 60,000–100,000 centipoises was usually reached after heating 1 hr. Since this viscosity was greater than that desired, a lower reaction temperature of 110°C. was generally used thereafter. However, to prepare a 50% castor oil prepolymer, it was found that a heating period of about 16 hrs. at 110°C. would be required to attain the desired viscosity. Further tests showed that even at 130°C., the temperature chosen for preparing the 50% castor oil prepolymer, about 4 hrs. of heating were necessary to reach the desired viscosity. The changes in viscosity of the 50% castor oil prepolymers on heating at 110°C. and 130°C. are shown in Figure 3. The changes in isocyanate content, as determined by the method of Tazuma and Latourette (5), are also shown in this figure.

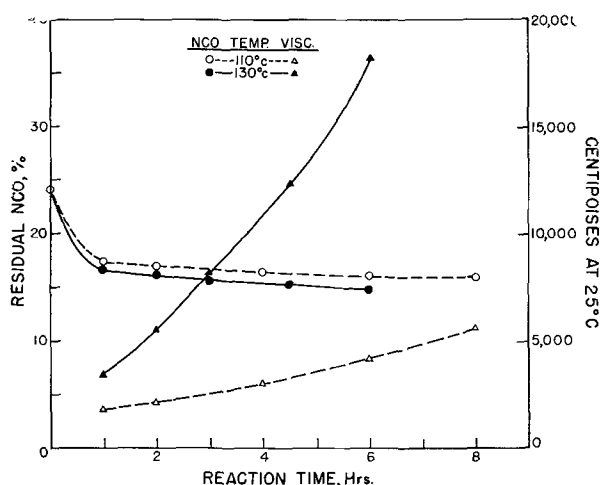


Fig. 3. Effect of time and temperature of preparation on residual NCO content and viscosity of prepolymers made with 50% of castor oil.

Attempts to prepare prepolymers of high castor oil content by this procedure were unsuccessful; the products were hard, rubbery to solid resins. With large proportions of castor oil the ratio of NCO to OH groups falls below 2:1 and is approximately 1:1 at the 80% level. The preparation by this method of an 80% castor oil prepolymer was not practical since the prepolymer would not possess free isocyanate groups necessary to produce foaming and would be excessively crosslinked. Consequently the procedure employed in preparing foams with 70% and 80% castor oil was to mix appropriate quantities of 60% castor oil prepolymer with additional dry castor oil just before the foaming operation. This technique is similar to that described for the preparation of foams made with 68% castor oil (6).

To determine the effect of modification of the double bond in the fatty acid portion of castor oil, prepolymers were prepared from hydrogenated, elaidinized, and partially epoxidized castor oils. The hydrogenated oil was substantially saturated, the elaidinized

oil contained approximately 75% of its double bonds in the *trans* configuration (7), and the partially epoxidized oil was used with about five parts of normal oil to make a comparable prepolymer. In the preparation of these prepolymers the requisite amount of diisocyanate was added to the modified castor oil at room temperature and mixed manually while increasing the temperature until fluid enough to be mechanically stirred, then the usual procedure for the preparation of prepolymers was followed.

Table I presents some properties for the various oils used. The viscosity and NCO content of the prepolymers are listed in Table II.

**Foam Preparation.** In order to minimize variations produced by the foaming step, a uniform formulation and foaming procedure was adopted. This procedure

TABLE I  
Properties of Castor Oil and Modifications

Tests	Normal (dry)	Hydrogenated	Elaidinized	Partially epoxidized <sup>a</sup>
Molecular weight (mean) <sup>b</sup> .....	926	932	926 (theory)	945
Viscosity, cps. at 25°C. <sup>b</sup> .....	680	....	....	2000
Melting point, °C.....	....	86 <sup>b</sup>	40–50	....
Isocyanate equivalent <sup>b</sup> .....	342	350	340 (theory)	280 (max.)
Moisture, % <sup>c, d</sup> .....	0.05	0.05	0.13	0.20
Hydroxyl, % <sup>d</sup> .....	4.98	4.73	4.85	6.23
Acid value <sup>d</sup> .....	0.67	2.6	1.8	0.76
Iodine value <sup>d</sup> .....	85.2	1.92	83.1	43.3
Saponification value <sup>d</sup> .....	179	179	182	181

<sup>a</sup> Oxirane oxygen, 1.71%.  
<sup>b</sup> "Castor Oil Products for Urethane Polymers," Baker Castor Oil Company, Tech. Bull. No. 31, p. 22 (1957).  
<sup>c</sup> Karl-Fischer method.  
<sup>d</sup> A.O.C.S. methods.

was to mix 100 g. of prepolymer with 0.5 g. of a dispersing agent,<sup>3, 4</sup> add 4.4 g. of a commercial 2-diethylaminoethanol catalyst<sup>5</sup> and additional water necessary to reach a minimum of 100% of the amount theoretically required to react with the ex-

TABLE II  
Isocyanate Content and Viscosity of Prepolymers

Castor oil (%)	Molar ratio NCO/OH	Residual NCO, % (calculated)	Viscosity (cps. at 25°C.)
50.....	3.93	18.0	11,100
60.....	2.63	11.9	15,000
70.....	1.68	8.9	.....
80.....	0.98	6.0	.....
60 (H).....	2.63	11.9	22,800
60 (El).....	2.63	11.9	29,700
58 (Ep).....	2.75	13.0	17,600

(H), hydrogenated; (El), elaidinized; (Ep), approximately 9% partially epoxidized castor oil + 49% normal castor oil.

cess isocyanate. For the preparation of the foams using 70 and 80% castor oil no additional water over that present in the catalyst was required. The reactants were then rapidly mixed with a flat-tipped spatula for 45 seconds, scraping the sides and bottom of the cup, and poured into a heavily waxed 1/2-gal.

<sup>3</sup> Dow Corning's DC 200 fluid—50 centistokes viscosity.  
<sup>4</sup> Mention of names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.  
<sup>5</sup> Isofoam Catalyst No. 1, Isocyanate Products' buffered catalyst, pH 10.6.

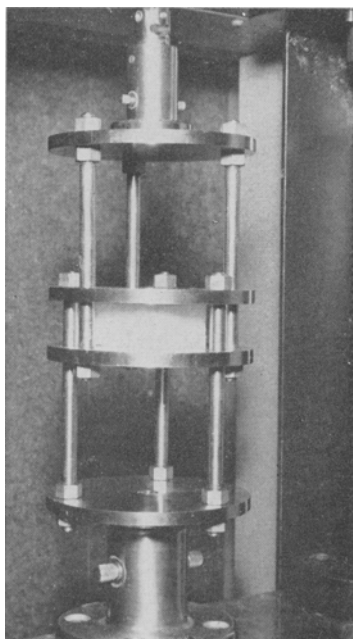


FIG. 4. Reverse cage attachment for Instron Tensile Tester.

paper carton (12 × 17 cm. at the base and 8.5 cm. in height) and allowed to foam freely. The height of the foam was observed periodically.

**Sample Preparation.** After the initial standing period of two to three days the sides of the foams were trimmed. Inch slices were cut horizontally from the bottom of the foam. The test specimens were cut from these slices. The specimens used for determination of tensile strength, elongation, and compression-deflection characteristics were conditioned in a constant temperature and humidity room (21°C. and 65% relative humidity) for at least three days before testing.

**Test Methods.** Foaming time was taken as the time required for the foam to reach maximum height. Density was determined by weighing 2 × 2 × 1-in. blocks of foam. Values for the percentage area and linear shrinkage of the foams, referred to container dimensions, were determined by use of the following equations.

$$\% \text{ Area shrinkage} = \frac{A_0 B_0 - \frac{(AB + XY)}{2}}{A_0 B_0} \times 100$$

$$\% \text{ Linear shrinkage} = \frac{(A_0 + B_0) - (x + y)}{A_0 + B_0} \times 100$$

where

- $A_0$  = shorter edge of mold at the base
- $B_0$  = longer edge of mold at the base
- $A$  = shorter edge of foam at the base
- $B$  = longer edge of foam at the base
- $h$  = height of foam
- $X$  = shortest edge of foam at 0.5 h
- $Y$  = longest edge of foam at 0.5 h
- $x$  = shortest axis through foam at 0.5 h
- $y$  = longest axis through foam at 0.5 h

Tensile-elongation was determined by means of an Instron Tensile Tester (Model TT3), fitted with modified clamps to hold  $\frac{1}{2} \times \frac{1}{2} \times 2\frac{1}{2}$ -in. foam strips. The testing procedures used were based upon the test methods of the Society of the Plastics Industry Inc.

(8). Gage lengths of the specimens were 1 in. and the rates of elongations were 0.05–0.10 in./min. for the semirigid foams and 20 in./min. for the flexible soft foams.

A reverse cage attachment (Figure 4) was made for use with the Instron Tensile Tester to permit measurement of compression resistance of a sample of foam placed between the suspended plates as the cross-head moves away from the tension cell. The procedures outlined in the SPI methods were used to measure the forces required to compress 2 × 2 × 1-in. samples more than 50% of their original height at a compression rate of 0.1 in./min.

Compression set was determined by a constant deflection procedure, as outlined in Method A of the SPI methods previously mentioned. Test specimens were about 1 in. high and had a cross section of 1 sq. in. (cubes or cylinders). The specimens were accurately measured, then compressed to 0.5 in., and placed in a forced draft oven at 70°C. for 22 hrs. They were then removed, and after 30 min. at room conditions the heights of the specimens were measured. The compression set was calculated by the formula:

$$\% \text{ Compression set} = \frac{T_0 - T_1}{T_0} \times 100$$

where

$T_0$  = original thickness

$T_1$  = final thickness

Since the samples were compressed to 0.5 in., even though they were not all exactly 1 in. high originally, they were not always compressed exactly 50%. In such cases the compression set was corrected for the small deviations.

The samples were aged by placing them on wire screens over water in a closed container at 70°C. for three weeks. Tensile compression strength and compression set were determined on the aged samples.

Energy absorption tests were made by using a simple procedure employed for determination of the "bounce" from cellular foams. A small steel ball bearing ( $\frac{3}{16}$  in.) was dropped from a height of 70 cm. by means of an electromagnet onto a 1-in. thick foam sample, inclined at a 45° angle. The distance the ball bounced was measured by allowing it to fall on graph paper covered with carbon paper, and this was compared to the distance noted for a control foam rubber sample. The percentage of energy absorbed (as compared to foam rubber) was calculated by the equation:

$$\% \text{ Energy absorption} = \frac{D_r - D_s}{D_r} \times 100$$

where

$D_r$  = distance ball bounced from foam rubber

$D_s$  = distance ball bounced from foam sample

Water absorption was determined by immersion of the weighed samples, contained in a screen cage, beneath 8 ft. of water for 24 hrs. After removal from the water the samples were blown free of surface water (not blotted) and weighed. The percentage of water absorbed was calculated from the increase in weight.

### Results and Discussion

Inspection of the data in Table III shows that foaming time increased from about 20 to 45 min., that foam density increased from 1.7 to 6.4 lbs./cu. ft., and shrinkage values decreased from 21% to about 1% as the proportion of castor oil was increased from

TABLE III  
Properties of Foams

Castor oil (%)	Type and characteristics					Tensile strength and elongation						
	Foaming time	Type	Density lbs./cu. ft.	Shrinkage		Original			Aged			
				Area	Linear	Ultimate elongation		100% elongation		Ultimate elongation		100% elongation
						(%)	(%)	(%)	(p.s.i.)	(p.s.i.)	(%)	(p.s.i.)
50.....	20-25	Semirigid	1.7	21	31	27	13.5	.....	20	10.3	.....	
60.....	30-40	Semirigid	2.8	11	20	42	27.9	.....	54	23.7	.....	
70.....	30-45	Soft	3.5	4	3	121	20.6	18.4	136	19.5	15.8	
80.....	35-45	Soft	6.4	1	0.6	103	6.3	6.1	109	6.6	6.4	
60 (H).....	30-35	Semirigid	3.0	6	19	37	28.1	.....	45	28.8	.....	
60 (El).....	30-35	Semirigid	2.6	4	10	43	24.9	.....	51	23.6	.....	
58 (Ep).....	20-25	Semirigid	2.6	8	22	42	22.0	.....	42	25.5	.....	

Castor oil (%)	Compression-deflection modulus						Compression set, energy and water absorption			
	Original			Aged			Compression set		Energy absorption	Water absorption
	10%	25%	50%	10%	25%	50%	Original	Aged		
	(p.s.i.)	(p.s.i.)	(p.s.i.)	(p.s.i.)	(p.s.i.)	(p.s.i.)	(%)	(%)	(%) <sup>a</sup>	(%)
50.....	4.9	5.5	7.6	5.6	6.1	8.3	50	49	19	515
60.....	5.3	6.5	10.4	4.8	6.4	11.3	47	44	23	323
70.....	0.55	0.71	1.19	0.43	0.55	0.94	30	22	50	230
80.....	0.20	0.30	0.52	0.16	0.23	0.41	16	10	47	170
60 (H).....	4.9	7.7	13.7	3.4	4.9	8.7	48	43	41	198
60 (El).....	5.6	6.9	10.9	4.0	5.0	8.6	45	42	30	234
58 (Ep).....	5.3	7.1	11.3	4.3	5.0	7.7	49	48	28	286

<sup>a</sup>Percentage of value for control foam rubber having the following properties: density, 7.2 lbs./cu. ft.; 50% compression modulus, 1.0 p.s.i.; and ultimate tensile strength, 16.6 p.s.i. at 218% elongation.

50% to 80%. The data also show that foams made with elaidinized or partially epoxidized castor oil have slightly lower densities than those made with normal or hydrogenated castor oil and that the foams made by using modified oils all showed improved shrinkage characteristics.

Results of tests of tensile strength and elongation (Table III) show that foams made by using 60% castor oil have the highest tensile strength. Neither modification of the castor oil, as by hydrogenation or elaidinization, nor aging greatly affected the tensile strength or elongation.

Results of compression-deflection tests (Table III) again point to the greater strength of the foams made by using 60% of castor oil. As anticipated, the foams made by using 70 and 80% of castor oil were weaker but more flexible. Aging had only slight effect on compression resistance. Foams made with larger proportions of castor oil showed a slight decrease in compression resistance. Foams made with smaller proportions of castor oil were greatly distorted on aging so that compression-deflection was hard to measure accurately, but the compression resistance of these foams appeared actually to increase on aging. Typical compression-recovery curves are shown in Figure

5. Rates of compression and recovery were the same and relatively slow, 0.1 in. per min. The foam made by using 80% of castor oil was resilient, and reminiscent of soft foam rubber; it is noted from Figure 5 that the recovery curve resembles the compression curve. On the other hand, the recovery curve of the foam made with 70% of castor oil is very different from its compression curve. Such a foam is slow to recover its initial shape and is useful to absorb shock without abrupt recoil, as in automotive crash pads.

Results of tests of compression set and energy and water absorption are shown in Table III. As expected, the softer foams resulting from the use of larger proportions of castor oil exhibited less compression set than did the semirigid foams. The values in this table indicate the percentage of the original height which the foam lost during the test; thus a value of 50% indicates that the foam did not recover at all after compression. Aging did not significantly affect the compression set of the semirigid foams but markedly decreased the values obtained for the soft foams. Hydrogenation, elaidinization, or replacement of part of the castor oil with partially epoxidized castor oil did not significantly affect the compression set. On the other hand, such modification did markedly affect both the energy absorption and the water absorption. Hydrogenation of the castor oil greatly increased the energy absorption and greatly decreased the water absorption. The corresponding values for the foams made with elaidinized castor oil and with partially epoxidized castor oil were intermediate between those made with natural castor oil and those made with the hydrogenated oil.

**Summary**

The preparations and properties of urethane foams made from tolylene diisocyanate and 50, 60, 70, and 80% castor oil were investigated. Foams of 50 and 60% castor content were prepared by the prepolymer technique; those of 70 and 80% castor content were prepared by mixing a 60% castor oil prepolymer with additional castor oil just before foaming. Foam density increased from 1.7 to 6.4 lbs./cu. ft., and shrinkage decreased from 21 to about 1% as the proportion of castor oil was increased. Tensile strength

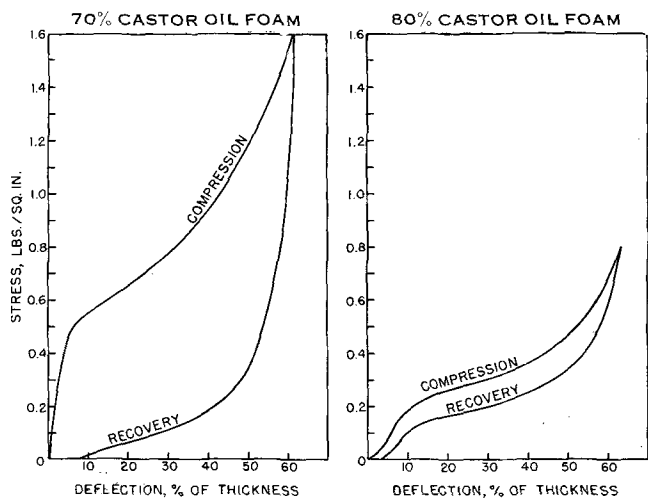


Fig. 5. Compression-recovery curves of foams.

ranged from 6.3 to 27.9 p.s.i., ultimate elongation from 27 to 121%, and 50% compression modulus from 0.5 to 10.4 p.s.i. Neither modification of the unsaturation of castor oil, as by hydrogenation, elaidinization, or partial epoxidation, nor aging at elevated temperature and humidity greatly affected the density, tensile strength, or elongation, but water resistance and shrinkage of the foams were improved by such modification.

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#### REFERENCES

1. Bjorksten, J., Tovey, H., and Dollard, H. L. Jr., *Modern Plastics*, 31, No. 8, 143-44, 146, 228-30, 233 (1954).
2. Hirschbeck, R. D., *Plastics Technol.*, 1, 95-99 (1955).
3. Kenline, W. E., and Hirschbeck, R. D., *Plastics Technol.*, 2, 168-174, 178-179 (1956).
4. "Urethane Plastics," a staff report, *Ind. Eng. Chem.*, 48, 1383-1391 (1956).
5. Tazuma, J. J., and Latourette, H. K., *Am. Chem. Soc., Div. Paint, Plastics, and Printing Ink Chem. Papers*, 16, No. 3, 22-31 (1956).
6. Bailey, M. E., Khawam, A., and Toone, G. C., *Am. Chem. Soc., Div. Paint, Plastics, and Printing Ink Chem. Papers*, 17, No. 2, 50-56 (1957).
7. McCutcheon, M. A., O'Connor, R. T., DuPré, E. F., Goldblatt, L. A., and Bickford, W. G., in press.
8. Society of Plastics Industry Inc., New York, "Tentative Methods of Test for Rigid Cellular Materials" (January 28, 1957); and "Tentative Methods of Test for Flexible Urethane Foam" (May 24, 1957).

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## Gas-Liquid Chromatography of Fatty Derivatives. I. Separation of Homologous Series of $\alpha$ -Olefins, n-Hydrocarbons, n-Nitriles, and n-Alcohols<sup>1,2</sup>

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SINCE THE FIRST application of gas-liquid chromatography by James and Martin (3) to the separation of long-chain fatty acids, the technique has been extended by other investigators (8) to fatty acids through C<sub>22</sub>, as their methyl esters, and to the fatty alcohols (1, 6) up to C<sub>18</sub>. James and Martin and their co-workers have shown that gas-liquid chromatography can be applied to the separation of the methyl esters of saturated and unsaturated fatty acids (2, 4) and have studied the structure of unsaturated fatty acids (5) through chromatography of their oxidation products. Very recently Orr and Callen (7), screening various partitioning agents, have found that polyester columns will resolve unsaturated acids, giving good, quantitative separations in reasonable times.

In this laboratory conditions have been established for the separation and identification of  $\alpha$ -olefins from C<sub>8</sub> to C<sub>24</sub>, saturated n-hydrocarbons from C<sub>8</sub> to C<sub>24</sub>, and fatty nitriles from C<sub>6</sub> to C<sub>20</sub>. The separation of the saturated higher fatty methyl esters and fatty alcohols has been improved so that the useful range has been extended through ricinoleic for the fatty acids and through behenyl for the fatty alcohols. Through the use of pure standards the accuracy has been established for the olefin and nitrile separations and subsequent analyses.

#### Experimental

**Gas Chromatography.** The chromatographic separations were carried out on a Beckman GC-2 gas chromatograph. The columns had as the stationary phase, Apiezon L (Burrell No. 341-117) for hydrocarbons, Carbowax 4000 monostearate (Beckman No. 70006), and Carbowax (Wilkins No. 3),<sup>3</sup> for alcohols and

nitriles, and silicone (Wilkins No. 1)<sup>3</sup> for alcohols and castor derivatives. The support for the stationary phase was 30-60 mesh C-22 firebrick (Johns-Manville). The column packing contained 31-38% by weight of the partitioning agent. Packing of the columns was done as previously described (3). Columns were prepared from stainless steel tubing 0.25 in. o.d. by 0.020 in. wall thickness.

Helium was used as the carrier gas. The column and detector were operated at the same temperature in the range of 220-260°C. The detector was maintained at atmospheric pressure. The recorder was a strip-chart type with a 1-mv. full-scale deflection. Other variables are defined in the results following. Samples were injected with a Beckman liquid sampler, a precision hypodermic syringe. Solid samples were easily handled by their previous melting. This required heating the barrel and the needle of the sampler with an infrared lamp. Peaks were identified by their retention volumes and by the method of internal standards; peak areas were measured with a compensating planimeter.

**1-Olefins.** Through the chromatography of standard samples of 1-decene, 1-dodecene, 1-tetradecene, and 1-hexadecene, obtained from the American Petroleum Institute, the relationship between chain length and retention time was established for three sets of operating conditions. The results shown in Figure 1 were obtained by chromatographing these pure olefins and a commercial olefin containing both odd and even chain lengths from C<sub>10</sub> to C<sub>18</sub>. A typical curve, Figure 2, and the data derived from the curve, Table I, revealed that the method was suitable for the quantitative analysis of long chain  $\alpha$ -olefin mixtures since peak areas were directly proportional to weight percentage. A statistical evaluation of a limited set of data shows that the standard deviation for this analysis is 0.47.

<sup>1</sup> Presented at annual meeting, American Oil Chemists' Society, Memphis, Tenn., April 21-23, 1958.

<sup>2</sup> Technical Paper No. 160, Archer-Daniels-Midland Company.

<sup>3</sup> Wilkins Instrument and Research Inc.