REFERENCES

1. Audrieth, L. F., and Kleinberg, J., "Non-aqueous Solvents," p. 210, New York, John Wiley and Sons Inc., 1953.
2. Bailey, A. E., "Melting and Solidification of Fats," p. 281, New York, Interscience Publishers Inc., 1950.
3. Brown, J. B., and Stoner, G. G., J. Am. Chem. Soc., *59*, 3 (1937).
4. Brown, J. B., and Kolb, D. K., in "Progress in the Chemistry of Fats and Other Lipids," vol. *III*, p. *58*, edited by Holman, R. T., Lundberg, W. O., and Malkin, T., Pergamon Press, London, 1955.
5. Cox, W. M., and Reid, E. E., J. Am. Chem. Soc., *54*, 220 (1932); Reid, R. E., U. S. 2,004,131 (1935).
6. DeCarli, F., Gazz. chim. ital., *57*, 347 (1927).
7. Earle, F. R., and Milner, R. T., Oil & Soap, *17*, 106 (1940).
8. Edeleanu Ges., French Pat. 775,700 (1935); Voogt, G., and Seeles, H., U. S. 2,228,040 (1941); Brandt R. L., U. S. 2,308,431 (1943).
9. Edeleanu, L., J. Inst. Petroleum Tech., *18*, 900 (1932); Hall, F. C., "The Science of Petroleum," vol. III, p. 1888, Oxford University Press, New York, 1938.
10. Grillo, W., and Schröder, M., D.R.P. 50,360 (1889); see Chem. Zentr., *61, I*, 703 (1890).
11. Kolb, D. K., dissertation, The Ohio State University, 1953, see ref. (4); Privett, O. S., Breault, E., Covell, J. B., Norcia, L. N., and Lundberg, W. O., *J. Am. Oil Chemists' Soc., 35, 366 (1958)*.
12. Lutton, E. S., Oil & Soap, *23*, 265 (1946); Hoerr, C. W., and Harwood, H. J., J. Phys. Chem., *56*, 1068 (1952).
13. Mangold, H. K., and Schlenk, H., J. Biol. Chem., *229*, 731 (1957).
14. Official and Tentative Methods of the Am. Oil Chemists' Soc., Cd 1–25, revised April *1956*, edited by Mehlenbacher, V. C., and Hopper, T. H., Chicago, *1946*.
15. Ralston, A. W., "Fatty Acids and Their Derivatives," p. 380, New York, John Wiley and Sons Inc., 1948.
16. Schlenk, H., Gellerman, J. L., Tillotson, J. A., and Mangold, H. K., J. Am. Oil Chemists' Soc., *34*, 377 (1957).
17. Sedgwick, R. S., Hoerr, C. W., and Harwood, H. J., J. Org. Chem., *17*, 327 (1952).
18. Seyer, W. F., and Ball, R. W., Trans. Roy. Soc. Can., (3) *19*, 149 (1926).
19. Singleton, W. S., J. Am. Oil Chemists' Soc., *25*, 15 (1948); *ibid.*, *26*, 332 (1949).
20. Smith, F. A., and Brown, J. B., Oil & Soap, *22*, 277, 321 (1945).
21. Zerner, E., Weiss, H., and Opalski, H., Z. angew. Chem., *35*, 253(1922).

[Received April 14, 1958]

Castor Polyols for Urethane Foams[1]

A. EHRLICH, M. K. SMITH, T. C. PATTON, The Baker Castor Oil Company, Bayonne, New Jersey

THE CHARACTERISTIC REACTION of the isocyanate group is that of addition with compounds containing reactive hydrogen groups. In a typical reaction the reactive hydrogen atom migrates to the nitrogen of the isocyanate group, and the remainder of the reacting molecule attaches itself to the carbon atom of the isocyanate group. For example, an isocyanate compound and the reactive hydrogen of an alcohol react to give a urethane.

$$\mathrm{R{-}OH + R'{-}NCO \longrightarrow R'{-}NH{-}COOR}$$

Similarly a di-isocyanate and a polyol react to give a polymeric urethane or a polyurethane; the terminal groups of the end-product are determined by the relative proportions of the reacting components.

$$\mathrm{n\ HO{-}R{-}OH + n\ OCN{-}R'{-}NCO \longrightarrow (-OCNH{-}R'{-}NH{-}COO{-}R{-}O{-})_n}$$

A polyurethane, under the influence of such a catalyst as an alkylamine and in the presence of excess isocyanate groups, can be caused to react at the urethane linkages to give a polymeric material.

In the production of a urethane foam, advantage is taken of the above reactions as well as the reaction of an isocyanate with water. Water reacts with an isocyanate to form an intermediate unstable carbamic acid which breaks down into carbon dioxide gas and an amine.

$$\mathrm{RNCO + H_2O \rightarrow (R{-}NH{-}COOH) \rightarrow CO_2\uparrow + RNH_2}$$

The gas expands the viscous polymer to form the urethane foam while the amine reacts with more isocyanate to form ureas which further cross-link the expanding urethane.

$$\mathrm{RNH_2 + R'NCO \longrightarrow R'{-}NH{-}CO{-}NH{-}R}$$

A recent commercial technical bulletin (1) has listed some 25 castor-based polyols as suitable for study in preparing urethane products. The present article reports on the investigation of some of these castor products as base materials for preparing urethane foams. A listing of the castor polyols selected for evaluation, together with associated properties of interest to workers in the field of urethane chemistry, is presented in Table I.

Ninety per cent of the combined fatty acids of commercial castor oil is ricinoleic acid (12-hydroxyoleic acid). This high percentage of a single fatty acid type is unusual in a naturally-occurring oil. Because of its triol structure, castor oil is a most satisfactory raw material for urethane reactions even though its three secondary hydroxyl groups, located on the 12th carbon atom of 18 carbon acid chains, are relatively slow to react. The trifunctionality of castor oil contributes toughness to polymer structures, and the long chain fatty acid chain imparts flexibility and water-resistance. From this castor oil base-product there can be obtained innumerable derivatives to give a wealth of polyols for further investigation. The castor polyols being evaluated serve to explore some of these possibilities. All products used in this investigation were sampled from commercial or pilot-plant material and have been processed during manufacture to give the maximum amount of desired structure.

Since all of the polyols embraced by this study contained one or more secondary (slow-reacting) hydroxyl groups in their molecule, the prepolymer method, rather than a one-shot method, was chosen as the most suitable for the preparation of the foams. In the first phase of this study (a preliminary screening) an isocyanate to hydroxyl equivalent ratio of 2.5/1 was tentatively selected for formulation of these prepolymers. This ratio was subsequently adopted for all remaining work as being the most satisfactory.

Prepolymer Preparation

The following preparation method, which gives a nonshrinking, semirigid, light-weight urethane foam, is typical of the methods used to prepare all the prepolymers used in this evaluation study. Some 305 g. of anhydrous castor oil and 53 g. of epoxidized castor

---

[1] Presented at the Spring Meeting, American Oil Chemists' Society, Memphis, Tenn., April 20–23, 1958.

TABLE I
Typical Properties of Castor-Based Polyols

	Color (Gardner)	Viscosity CP/25°C.	Specific gravity 25°C./25°C.	Acid value	Volatile (%)	Hydroxyl value	Mol. wt. (mean)	Number and nature of hydroxyls	Isocyanate equivalent
Propylene glycol monoricinoleate (Flexricin 9)	2	290	.959	6.8	.37	297	360	2–2°	185
Propylene glycol mono-12-hydroxystearate (Paricin 9)	4	MP 51°C.	1.00	8.9	.3	275	362	2–2°	197
Neopentyl glycol diricinoleate (Flexricin 30)	7	250	.938	3.8	.41	164	664	2–2°	334
Ricinoleyl ricinoleate (Flexricin 31)	6	200	.910	1	.2	193	562	2–2°	289
Dehydrated castor oil[a] (Flexricin 32)	4	390	.948	4	.2	101	910	2–2°	535
Dehydrated castor wax[a] (Paricin 32)	3	MP 60°C.	.957	3	.3	100	915	2–2°	540
Acetylated castor oil[a] (Flexricin 83)	1	430	.962	1	.1	105	950	2–2°	525
Ethylene glycol monoricinoleate (Flexricin 15)	2+	380	.969	5	.5	273	380	1–1°, 1–2°	204
Ethylene glycol mono-12-hydroxystearate (Paricin 15)	3	MP 62°C.	1.01	4.4	.4	263	382	1–1°, 1–2°	210
Polyethylene glycol-200 monoricinoleate (Flexricin 20)	7	152	.996	7.6	.2	233	480	1–1°, 1–2°	234
Triglyceride of ricinoleic acid [DB oil (anhydrous type)]	1	680	.959	1	.02	163	926	3–2°	342
Triglyceride of ricinoleic acid (AA oil)	1	680	.959	2	.2	163	926	3–2°	340
Triglyceride of ricinoleic acid (Castor oil No. 3)	6	660	.957	12	.3	154	900	3–2°	338
Triglyceride of 12-hydroxystearic acid (Castor wax)	1+	MP 86°C.	.990	2	.1	158	932	3–2°	350
Triglyceride of 12-hydroxystearic acid (Castor wax MP-70)	3	MP 70°C.	.973	2	.1	160	930	3–2°	346
Epoxidized castor oil[a] (Estynox 300[b])	2	2000	.988	1.8	.3	225	945	3–2°	246
Glyceryl monoricinoleate (Flexiricin 13)	4	900	.985	5.4	.2	345	490	1–1°, 2–2°	159
Glyceryl mono-12-hydroxystearate (Paricin 13)	6	MP 66°C.	1.03	5.5	.5	311	493	1–1°, 2–2°	177
Pentaerythritol tetraricinoleate (Flexricin 19)	10	2700	.967	2	.3	172	1190	4–2°	324
Hydroxylated castor oil[a] (Estynox 350[c])	2	Paste	1.0	2	.1	235	980	4–2°	238
Pentaerythritol monoricinoleate (Flexricin 17)	8	3600	.995	2.9	.2	391	660	3–1°, 1–2°	143

[a] Partially. [b] Oxirane oxygen, % = 2.0. [c] Formerly Estynox 500.
AA, Castorwax, DB, Estynox, Flexricin and Paricin are all trade-marksof the Baker Castor Oil Company.

oil were charged into a three-neck, one-liter glass flask fitted with a stirrer, thermometer, and condenser with attached drying tube. Then 242 g. of tolylene di-isocyanate (80/20)[2], as five equal portions, were gradually added over a 15-min. period with moderate stirrer agitation until the 2.5 equivalents of tolylene di-isocyanate corresponding to each equivalent of charged castor polyol were introduced. After completion of the initial exotherm (15–30 min.) the reactants were heated for an hour at 110°C. The prepolymer which formed was cooled to 65°C. and packaged in a sealed container (1-quart tin can).

In the case of solid castor polyols the material was first heated to its melting point, after which the tolylene di-isocyanate was added and the reaction started at that temperature. In those cases where the exotherm started to exceed 100°C., the reaction products were cooled by immersing the flask and contents in cold water until no further exotherm was noted. The reaction mass was then heated to 110°C. for an hour. This cooling treatment permitted the preparation of prepolymers which otherwise could not be prepared.

As a result of the above work it became apparent that some of the polyols could not be used alone in the preparation of the prepolymer. Hence the study was extended to include combination of anhydrous castor oil (85%) with each of the castor-based polyols (15%) in turn, with the conditions of prepolymer preparation unchanged. This gave a second series of prepolymers which were also tested for foam-producing ability.

During the progress of the work it was further discovered that aged (stored) prepolymers in which a viscosity increase had occurred gave foams with altered physical properties. Hence it was decided to determine whether preparation of the prepolymer at a higher temperature might not duplicate, to some extent, the effect of room-temperature aging on end-properties. This led to a repeat, with selected castor polyols, of the first two series of preparations at 130°C. (as opposed to 110°C.) to check on the effect of temperature of polymer preparation on polymer and foam properties.

Thus four sets of prepolymers in all were finally scheduled and used to prepare foams under standardized conditions. After some preliminary experimentation the following conditions for foam preparation were specified.

Foam Preparation

One-half gram of dimethyl siloxane fluid[3] was

---

[2] Du Pont-Hylene TM, Mobay-Mondur TD-80, National Aniline-Nacconate 80.

[3] Dow Corning DC 200 (50 cp.) or equivalent silicones.

TABLE II
Properties of Prepolymers and Foams Obtained With Castor Polyols Prepared at 110°C. Using a 2.5 NCO/1 OH Ratio

	Viscosity of prepolymer	Foam density	Area shrinkage	Compression modulus	
				Original	Humid aging[b]
	(poises at 25°C.)	(lb./ft.^{3})	(%)	(p.s.i.)	(p.s.i.)
Propylene glycol monoricinoleate	682	2.0	0.0	5.0[c]	....
Propylene glycol mono-12-hydroxystearate	3,000	........[e]	........[e]	........[e]	........[e]
Neopentyl glycol diricinoleate	7	........[e]	........[e]	........[e]	........[e]
Ricinoleyl ricinoleate	13	........[e]	........[e]	........[e]	........[e]
Dehydrated castor oil[a]	29	4.0	10.0	1.5	1.5
Dehydrated hydrogenated castor oil[a]	159	4.0+	30.0	6.5	3.5
Acetylated castor oil[a]	31	2.9	7.0	3.0	2.0
Ethylene glycol monoricinoleate	146	2.5	10.0	26.0	21.5[c]
Ethylene glycol mono-12-hydroxystearate	Foaming	........[d]	.. ..[d]	........[d]	........[d]
Polyethylene glycol-200 monoricinoleate	24	........[e]	........[e]	........[e]	........[e]
Triglyceride of ricinoleic acid-anhydrous	80	2.9	10.0	19.0	10.0
Triglyceride of ricinoleic acid (AA)	85	2.5	19.0	22.0	....
Triglyceride of ricinoleic acid (No. 3)	120	4.4	29.0	18.5	....
Triglyceride of 12-hydroxystearic acid	720	2.5	15.0	18.0	18.0
Triglyceride of 12-hydroxystearic acid (MP-70)	550	2.4	20.0	18.5	12.8
Epoxidized castor oil[a]	Gelation	........[d]	........[d]	........[d]	........[d]
Glyceryl monoricinoleate	3,000	1.6	10.0	26.0	16.0[c]
Glyceryl mono-12-hydroxystearate	Foaming	........[d]	........[d]	........[d]	........[d]
Pentaerythritol tetraricinoleate	Foaming	........[d]	........[d]	........[d]	........[d]
Hydroxylated castor oil[a]	Gelation	........[d]	........[d]	........[d]	........[d]
Pentaerythritol monoricinoleate	10,000+	........[f]	........[f]	........[f]	........[f]

[a] Partially. [b] Three weeks at 70°C./100% R.H. [c] Very brittle foams. [d] Foaming or gelation during prepolymer preparation prevented obtaining physical data. [e] Foam collapses. [f] Viscosity prevented foam preparation.

TABLE III

Properties of Prepolymers and Foams Obtained from 85% DB Castor Oil and 15% of Castor Polyol Prepared at 110°C., Using a 2.5 NCO/1 OH Ratio

	Viscosity of polymer	Foam density	Area shrinkage	Compression modulus	
				Original	Humid aged[b]
	(poises at 25°C.)	(lb./ft.^{3})	(%)	(p.s.i.)	(p.s.i.)
Propylene glycol monoricinoleate	198	5.6	25.0	18.5	10.5
Propylene glycol mono-12-hydroxystearate	196	3.0	8.0	21.5	16.5
Neopentyl glycol diricinoleate	110	........[c]	........[c]	........[c]	........[c]
Ricinoleyl ricinoleate	96	2.9	17.5	14.2	11.0
Dehydrated castor oil[a]	119	....	78.0	....	....
Dehydrated castor wax[a]	134	........[c]	........[c]	........[c]	........[c]
Acetylated castor oil[a]	178	....	31.5	....	....
Ethylene glycol monoricinoleate	179	....	48.5	....	....
Ethylene glycol mono-12-hydroxystearate	260	3.2	3.5	22.0	17.5
Triglyceride of ricinoleic acid	80	2.9	10.0	19.0	10.0
Triglyceride of 12-hydroxystearic acid	221	2.7	25.0	16.5	10.0
Epoxidized castor oil[a]	331	3.0	0.0	21.5	21.5
Glyceryl monoricinoleate	297	5.5	20.0	21.0	20.0
Glyceryl mono-12-hydroxystearate	1,300	3.5	3.5	26.0	23.0
Pentaerythritol tetraricinoleate	198	3.5	7.8	20.0	20.0
Hydroxylated castor oil[a]	........[d]	........[d]	........[d]	........[d]	........[d]
Pentaerythritol monoricinoleate	340	3.2	17.8	22.0	18.5

[a] Partially. [b] Three weeks at 70°C./100% R.H. [c] Foam collapses. [d] Foaming prevented prepolymer preparation.

hand-mixed into 100 g. of the prepolymer. To this mixture were added 4.4 g. of buffered diethylethanolamine[4] together with sufficient additional water to react stoichiometrically with the remaining excess of tolylene di-isocyanate. The blend was manually mixed to a point where incipient foaming became observable (about 45 seconds), after which it was poured into a waxed paper container (3.5 × 6.5 × 4 in.) to foam.

In each case the prepolymer viscosity was measured, and the foams prepared therefrom were tested for density, area shrinkage, and compression modulus (the latter both before and after humid aging).

Results and Discussion

Table II gives the properties obtained when each castor polyol in turn was used as the sole polyol (prepolymer preparation at 110°C.). Table III gives these same properties when anhydrous castor oil was modified in turn with 15% of each of the castor polyol derivatives (prepolymer preparation at 110°C.). Tables IV and V list the results obtained for these same series, but with the prepolymer prepared at a temperature of 130°C.

At 110°C. several of the 100% castor polyols gave prepolymers which either set to a brittle mass on cooling or foamed and/or gelled during the preparation stage (epoxidized castor oils, pentaerythritol tetraricinoleate, glycerol, and propylene glycol 12-hydroxy monostearates). On occasion the same difficulty was encountered with ethylene glycol monoricinoleate and neopentyl glycol diricinoleate. Pentaerythritol monoricinoleate gave a prepolymer of such high viscosity that no foam at all could be prepared. Of the prepolymers prepared at 130°C. hydrogenated castor oil alone gave a product that set to a gel on cooling and from which no foam could be prepared. In a side experiment where a less refined grade of castor oil (AA or No. 3) was used, having significant moisture and acid contents, in place of anhydrous castor oil in preparing the prepolymer at 130°C., it was found that extreme caution was necessary to prevent the reaction mass from foaming out of the kettle.

Prepolymer Viscosity. Castor-based prepolymers, when prepared from a single polyol at 110°C., varied in viscosity from 7 to 10,000 poises (viscosities measured at 25°C. with Brookfield Viscometer, Model RVF). When prepared at 130°, the viscosities were correspondingly higher. In some cases the increase was almost ten-fold. The use of castor polyols as modifiers for the anhydrous castor oil prepolymer resulted in an increase in viscosity over the corresponding straight anhydrous castor oil system. Modified polyol systems prepared at 130°C. were also higher in viscosity than their prepolymer counterparts prepared at 110°C. In some cases the increase was three-fold.

In general, the viscosity of the prepolymer was found to increase with the number of primary and/or secondary hydroxyl groups present in the base polyol. The order of viscosities for the modified anhydrous castor oil series was found to be quite similar to that obtained with the straight castor polyols. It was also possible to prepare prepolymers by using castor polyols which, although unsatisfactory by themselves, made acceptable modifiers for anhydrous castor oil.

The ability of several of the highly functional castor polyols drastically to raise the initial viscosity of the castor oil prepolymer suggests their use in systems where difficulty is normally encountered in obtaining a desirable high viscosity.

It is interesting that a foam made from a polyethylene glycol monoricinoleate prepolymer collapsed when prepared at 110°C.; but, when prepared at 130°C., the foam showed no significant shrinkage

TABLE IV

Properties of Prepolymers and Foams Obtained with Castor Polyols Prepared at 130°C. Using a 2.5 NCO/1 OH Ratio

	Viscosity of prepolymer	Foam density	Area shrinkage	Compression modulus
	(poises at 25°C.)	(lb./ft.^{3})	(%)	(p.s.i.)
Propylene glycol monoricinoleate	2,088	2.3	0.0	22.0[b]
Dehydrated castor oil[a]	135	4.5	0.0	2.2
Acetylated castor oil[a]	142	4.3	0.0	1.2
Ethylene glycol monoricinoleate	1,800	2.6	0.0	23.0[b]
Polyethylene glycol 200-monoricinoleate	366	2.3	0.0	22.0
Triglyceride of ricinoleic acid (anhydrous)	816	3.7	16.0	19.0
Triglyceride of ricinoleic acid (AA)	1,200	4.2	21.0	17.0
Triglyceride of ricinoleic acid (No. 3)	6,000	5.1	16.0	20.0
Triglyceride of 12-hydroxystearic acid	........[c]	........[c]	........[c]	........[c]

[a] Partially.
[b] Very brittle foam.
[c] Gelation prevented prepolymer preparation.

---

[4] Du Pont Isofoam I: diethylethanolamine 42 g., 36.5% HCl 24 g., distilled H_2O 34 g. (mixture adjusted to a pH of 9.8 ± .1; H_2O content 49.1%).

TABLE V

Properties of Prepolymers and Foams Obtained from 85% DB Castor Oil and 15% of Castor Polyol, Prepared at 130°C. Using a 2.5 NCO/1 OH Ratio

	Viscosity prepolymer	Foam density	Area shringage	Compression modulus
	(poises at 25°C.)	*(lb./ft.^{3})*	*(%)*	*(p.s.i.)*
Propylene glycol monoricinoleate	434	3.5	30.0	18.0[c]
Propylene glycol mono-12-hydroxystearate	504	3.1	21.0	21.5
Dehydrated castor wax[a]	415	........[d]	........[d]	........[d]
Ethylene glycol mono-12-hydroxystearate	819	3.3	21.0	22.0
Triglyceride of ricinoleic acid	816	3.7	16.0	19.0
Triglyceride of 12-hydroxystearic acid	1,033	3.9	21.0	22.0
Epoxidized castor oil	5,920	........[b]	0.0	........[b]
Glyceryl monoricinoleate	1,224	3.5	16.0	22.0[c]
Pentaerythritol tetraricinoleate	1,210	3.6	21.0	24.0
Pentaerythritol monoricinoleate	1,672	3.2	16.0	24.0

[a] Partially.

[b] Very poor mix and very low rise of foam prevented testing for physical data.

[c] Very brittle foam.

[d] Foam collapses.

and exhibited good physical properties. Foams prepared at 130°C. from propylene and ethylene glycol monoricinoleates also showed no shrinkage, but these foams tended to be brittle and extremely friable when abraded. This tendency toward embrittlement was lost on aging the foams for two weeks at room temperature.

As a second side experiment a number of anhydrous castor oil prepolymers were prepared in which the time and temperature of the reaction were varied to determine their effect on viscosity (Figure 1). As expected, a more or less direct relationship was found, relating the viscosity of the prepolymer to these two variables.

Industrial experience has indicated that most of the useful foams are prepared from prepolymers which have a viscosity falling in the range from 10 to 500 poises. This finding was confirmed by our laboratory experience. It also points up the fact that caution should be exercised when increasing the temperature of prepolymer preparation for the higher temperature may well give a finished polymer having excessive viscosity for proper foam preparation.

For example, in the formulation in which the epoxidized castor oil was used to modify the anhydrous castor oil system, it was found that, whereas a useful prepolymer could be formed at 110°C. (viscosity of 330 poises), raising the temperature of prepolymer preparation to 130°C. produced a prepolymer so viscous (5,920 poises) that it could not be successfully foamed by the released carbon dioxide.

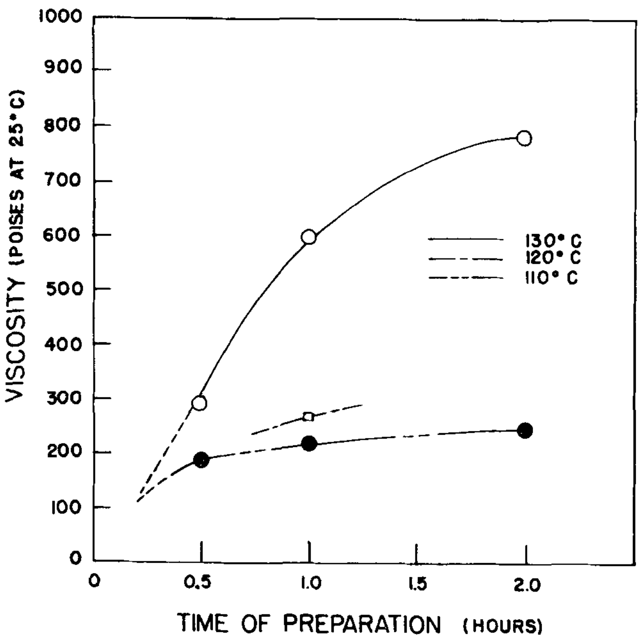


FIG. 1. Effect of time and temperature of prepolymer preparation on the viscosity of the resulting anhydrous castor oil/tolylene di-isocyanate prepolymer.

Foam Time. Using the buffered diethylethanolamine as catalyst, foam times for the major portion of the prepolymers were found to vary from 25–40 min., with tack-free time usually 30 min. longer. The use of the following catalysts (1.85 g./100 g. prepolymer) appeared to cause increased shrinkage in castor oil-based systems although they did considerably decrease foam time: dimethylamino ethanol, triethylamine, N-methyl morpholine, trimethanolamine, and diethanolamine.

Density. Foam density ranged from 2 to 5 lb. /ft.^{3} with most foams falling in the lower range.

Area Shrinkage. Most of the foams prepared from prepolymers based on a single castor polyol exhibited excessive shrinkage. Foams prepared from anhydrous castor oil prepolymers varied in area shrinkage between 5 and 35%, depending on mechanical variables. However, by careful attention to manual techniques (fast incorporation, thorough mixing, minimum air entrapment), it was possible to obtain foams with a reproducible shrinkage of 9%. Greater shrinkage was invariably obtained when AA or No. 3 Castor Oil were used, presumably because of their significant acidity and volatile content. Excess water, over stoichiometric proportions, also caused increased shrinkage. The incorporation of fine silica (such as Cabot's Cab-O-Sil) to the castor oil prepolymer (1.5% on weight of prepolymer) greatly reduced shrinkage.

The modified castor oil prepolymers (85% anhydrous castor oil/15% castor polyol) gave foams with significantly reduced shrinkage. Most promising were pentaerythritol tetraricinoleate, propylene glycol-, glyceryl-, and ethylene glycol 12-hydroxy monostearates; epoxidized castor oil was outstanding.

Since the area shrinkage of the formulation with epoxidized castor oil was nil, it was decided to study the effect of variations from the original conditions. Ratio of NCO/OH and effect of excess water were checked. In those cases where the catalyst system by itself furnished more than the percentage of water called for, a reduction in catalyst with its associated water content was made to meet this condition. As can be seen from Figure 2, variations to either side of the original conditions led to a shrinkage condition so that the original 85% anhydrous castor oil/15% epoxidized castor oil blend and the use of theoretical water was evidently optimum.

Compression Modulus and Humid Aging. All the castor polyol foams except partially dehydrated and partially acetylated castor oils gave foams with modulus values corresponding to semi-rigid foams. The latter two gave modulus values corresponding to flexible foams. A retest of compression modulus after aging for three weeks at 70°C. and 100% relative

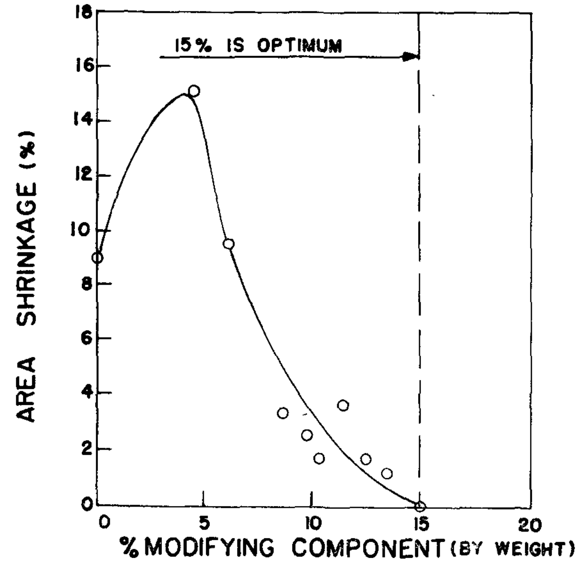


Fig. 2. Effect on foam shrinkage because of partially substituting epoxidized castor oil (Estynox 300) for castor oil in the anhydrous castor oil/tolylene di-isocyanate prepolymer from which the foam was prepared.

humidity showed, with two notable exceptions, a 10–80% loss of compression modulus. The exceptions were the two modified castor oil systems containing pentaerythritol tetraricinoleate and epoxidized castor oil, respectively, which showed little or no loss of compression modulus. There were no significant differences noted in the compression modulus of foams prepared from prepolymers made at either 110° or 130°C.

Compression Set. All foams exhibited compression set values that were disturbingly high. While this factor is not too significant for semi-rigid foams, it is important for flexible foams. For this reason the foams given by partially dehydrated and partially acetylated castor oils would undoubtedly have to be reformulated to provide better compression set before their flexible properties could be utilized.

Commercial Application of Castor Polyols to Industrial Foams

The ability of an 85% anhydrous castor oil/15% epoxidized castor oil prepolymer to give a lightweight semi-rigid foam with no shrinkage is of utmost interest. Such interblending of castor polyols in the field of polyurethane foams to achieve optimum results suggests that the use of castor-based materials can be greatly expanded. The specific combination given here is believed to be quite satisfactory in itself and deserves investigation by urethane chemists. It should be realized however that different laboratories use different techniques, and the formulation as it stands may need adjustment to achieve an end-product satisfactory for the particular equipment being used.

Control of prepolymer viscosity is of considerable industrial importance. From the findings reported in this paper, it is evident that castor polyols can be used as modifiers readily to increase prepolymer viscosity to any required degree, or alternately to reduce processing time to achieve a given viscosity. The slight loss in compression modulus given by foams modified with pentaerythritol tetraricinoleate and epoxidized castor oil suggest their evaluation in systems where minimum loss of modulus on humid aging is required. Also, if moderate shrinkage of the foam can be tolerated, hydrogenated castor oil can be used as the base polyol to give a foam with excellent resistance to humid aging.

The ability to prepare a satisfactory foam from polyethylene glycol monoricinoleate by preparing the prepolymer at 130°C. rather than 110°C. is of more than passing interest, and this technique appears to be applicable to other castor polyols.

The fast reactions given by several of the castor polyols (leading to gelation when used alone) suggest that these same materials be used as modifiers for more sluggish systems where slow increase in viscosity is a problem. The larger-molecular-weight castor polyols could probably be substituted for polyols, such as trimethylol propane, to increase crosslinking in flexible foams, without adversely affecting physical properties. Pentaerythritol mono- and tetraricinoleates and glyceryl- and ethylene-glycol 12-hydroxy monostearates and the epoxidized products are recommended for investigation in this field.

Test Methods

Foam Time. The time of mixing the materials to an almost imperceptible collapse is noted at the top of the rising foam.

Tack-Free Time. The time of mixing the materials to the expanded foam can be removed from the mold without distortion.

Density. Density was obtained by taking the average of four samples weighed to the nearest thousandth of a gram on an analytical balance. The foam samples were cylindrical, measuring 1.00 in. in height by 2.00 in. in diameter, and were cut from cured foam (aged 7 days at 28°C.).

Area Shrinkage. Shrinkage was measured in terms of the percentage reduction in cross-sectional area of the formed foam referred to the container dimensions. The foam cross-sectional area was calculated from the foam dimensions as measured across the bottom (length and width distances were taken across the bottom where shrinkage was most evident). In cases of low shrinkage the foam overflow was cut off across the top, and confirming length and width measurements were made across this top area.

Compression Modulus. A cylindrical sample of foam (1 × 2 in. in diameter) was compressed between the pan of a triple-beam laboratory balance and an immovable upper plate. Compression of the sample was plotted against the weight applied to the balance pan over a compression range of 5% to 6%. The average modulus in lb./in.^{3} was taken as the compression modulus. For humid aging, the samples were kept at 70°C. for 21 days at 100% R.H. in a desiccator.

Compression Set. The set was measured according to A.S.T.M. D395-55 Method B.

Summary

A systematic investigation of some 21 castor polyols as base materials for preparing urethane foams was carried out. Prepolymers were prepared both from individual castor polyols and from mixtures of them with an anhydrous castor oil. Foams formed from these prepolymers were checked for shrinkage on cure, density, and modulus.

From the wide range of results obtained it is evi-

dent that castor polyols can serve as effective urethane components. Aside from serving as major polyols for reaction with di-isocyanates, they can also be used as modifying polyols a) to speed up prepolymer preparation, b) to adjust prepolymer viscosity to any required degree, c) to minimize loss of modulus on humid aging, and as cross-linking centers with negligible loss of foam modulus. Details covering the preparation of a nonshrinking, semi-rigid, lightweight urethane foam based on an 85% anhydrous castor oil/15% epoxidized castor oil mix are outlined in the article.

REFERENCES

1. "Castor Oil Products for Urethane Polymers," Technical Bulletin, No. 31, The Baker Castor Oil Company.

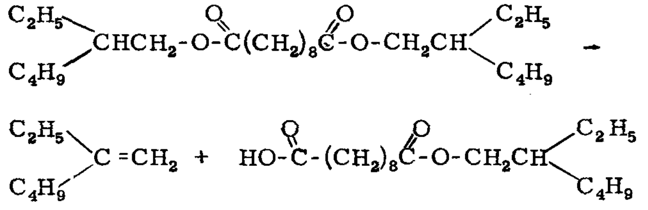
[Received June 2, 1958]

Identification of 2-Ethylhexyl Hydrogen Sebacate in Bis(2-Ethylhexyl) Sebacate Synthetic Oils

EDWARD B. DISMUKES, Southern Research Institute, Birmingham, Alabama

ESTERS of dibasic carboxylic acids are now used as the primary component in many synthetic oils. One such ester that is encountered frequently is bis(2-ethylhexyl) sebacate. This compound is acceptably stable at temperatures below 200°C. if protected against oxidation with a small amount of phenothiazine or some other material. However, at temperatures above 200°C. that are reached in gas-turbine lubrication, this sebacate diester is subject to appreciable oxidative attack and also pyrolytic attack.

Various products including unspecified acid compounds are produced when bis(2-ethylhexyl) sebacate is oxidized (1, 2). When the diester is pyrolyzed, the reaction follows this principal course (2, 3):



That is, pyrolysis products are an olefin, 2-ethyl-1-hexene, and an acid monoester, 2-ethylhexyl hydrogen sebacate. The acid monoester may undergo subsequent decomposition to sebacic acid and olefin.

Recently it was necessary to determine whether the acid monoester was present in samples of degraded bis(2-ethylhexyl) sebacate oils. Titration of acid was not a satisfactory method of identification inasmuch as acids other than the acid monoester were present. Therefore it was necessary to effect a separation of the acid monoester from other components of the oil.

The simplest means of separating acids from the other components seemed at first to be extraction with aqueous sodium hydroxide or other alkali. However the sodium salt of the long-chain acid, 2-ethylhexyl hydrogen sebacate, caused a very stable emulsion to form, and no satisfactory means of separating the water and oil phases could be found. Other separation methods were investigated therefore, and a useful procedure was developed by use of organic solvent-extraction.

Procedure

In their work on the separation of various fatty acids Ahrens and Craig (4) successfully used as solvents *n*-heptane and a mixture of acetonitrile, methanol, and acetic acid. In the present work the solvent pair Skellysolve C (principally *n*-heptane) and acetonitrile-methanol (a mixture of two volumes of acetonitrile and one volume of methanol) was found to be useful as a means of separating bis(2-ethylhexyl) sebacate and its acid monoester. If a mixture of the monoester and diester is distributed between Skellysolve C and acetonitrile-methanol, the monoester is contained primarily in the acetonitrile-methanol phase and the diester is contained primarily in the Skellysolve C phase.

Based on this difference in distribution properties, the following procedure was adopted for separating monoester and diester:

a) A 15-g. sample of oil is dissolved in 45 ml. of acetonitrile-methanol and extracted with 180 ml. of Skellysolve C. The Skellysolve C phase is then discarded.

b) The acetonitrile-methanol phase is again extracted with a four-fold excess of Skellysolve C, and the hydrocarbon phase is discarded as before.

c) The portion of the original oil sample remaining in the acetonitrile-methanol phase after the second extraction is recovered by evaporating the solvent. Then this residue is dissolved in Skellysolve C at the approximate concentration of 0.1 g./ml. For this solution the infrared absorption spectrum between 1,600 and 2,000 cm.$^{-1}$ is recorded to permit the monoester to be identified. (See the following section, Spectral Interpretation.)

This procedure has proved satisfactory for isolating an appreciable portion of the monoester when it is present in the original oil at a concentration of approximately 5 mole-percentage. In order to obtain isolation when the concentration is much less, one or more additional extraction steps should be added to the procedure.

Discussion

Spectral Interpretation. In the infrared spectral region, mixtures of the monoester and diester absorb at 1,710 cm.$^{-1}$ because of the carboxyl group in the monoester and at 1,740 cm.$^{-1}$ because of the ester groups in both the monoester and diester. Spectra are shown in Figure 1 for Skellysolve C solutions