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.

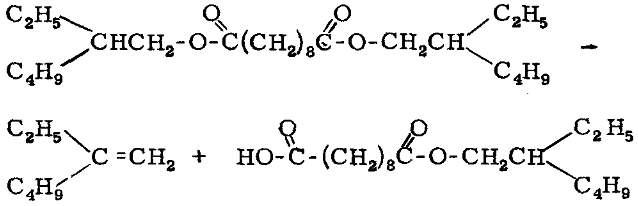
[Received June 2, 1958]

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):



$$(C_2H_5)(C_4H_9)CHCH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2CH(C_2H_5)(C_4H_9) \rightarrow$$

$$(C_2H_5)(C_4H_9)C{=}CH_2 + HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_8\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2CH(C_2H_5)(C_4H_9)$$

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

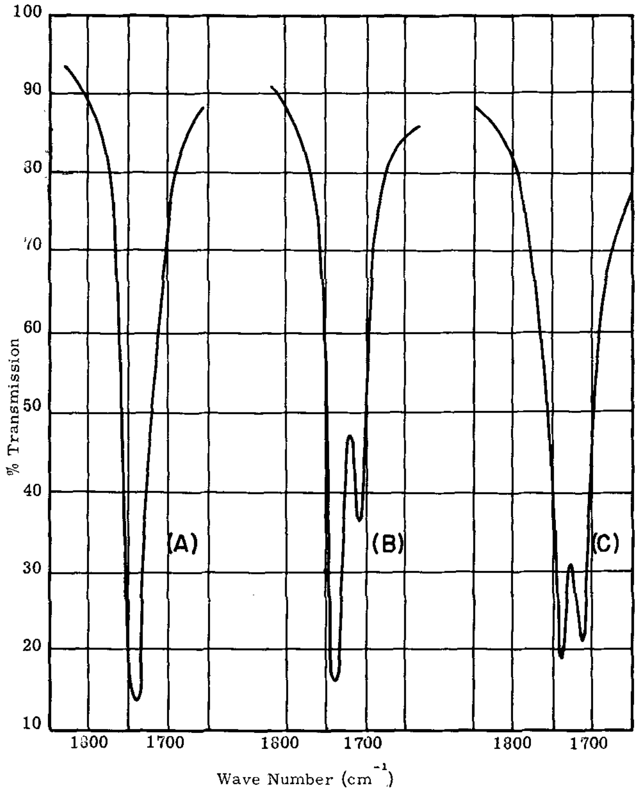


FIG. 1. Infrared spectra of Skellysolve C solutions of (A) a degraded oil and (B), (C), concentrates of the monoester obtained by solvent extraction of the oil.

that contained approximately 0.1 g./ml. of (A) a degraded oil sample, (B) the monoester concentrate obtained by one extraction, and (C) the monoester concentrate obtained by two extractions. Spectrum (A) shows that the monoester absorption at 1,710 cm.$^{-1}$ is obscured by intense diester absorption at 1,740 cm.$^{-1}$ when the concentration of monoester is only about 5 mole-percentage. But spectrum (B) shows that one extraction sufficiently concentrates the monoester with respect to the diester that the 1,710 cm.$^{-1}$ band is partially resolved from the 1,740 cm.$^{-1}$ band. Finally it is shown by spectrum (C) that the second extraction leaves behind relatively pure monoester, inasmuch as the 1,710 and 1,740 cm.$^{-1}$ bands are nearly equal in intensity, as they are for pure monoester.

Spectra similar to (C) have been obtained for the oil residues that remain after two extraction steps, and these spectra have been accepted as positive identification of the monoester. If the principal acid in the oil were not the acid monoester but some other compound—in particular, if the acid were some compound that contained no ester linkage—a spectrum such as (C) could not be obtained, that is, there could be only very slight absorption at 1,740 cm.$^{-1}$ on account of the virtual absence of ester from the sample.

Distribution Coefficients. Coefficients for the distribution of bis(2-ethylhexyl) sebacate and 2-ethylhexyl hydrogen sebacate between acetonitrile-methanol and Skellysolve C were determined by distributing from 0.1 to 1.2 g. of each compound between 20-ml. portions of the two solvents. The volume of each phase at equilibrium and the amount of solute contained in it were determined, and distribution coefficients were calculated as the ratio of concentration in acetonitrile-methanol to concentration in Skellysolve C. (The two solvents were partially miscible, as shown by the fact that the volume of the acetonitrile-methanol phase at equilibrium was approximately 24 ml. and the volume of the Skellysolve C phase was only about 16 ml.) Results of these measurements are summarized as follows:

Diester —0.117 g. distributed $D=0.16_8$
1.168 g. distributed $D=0.16_4$
Average value $\overline{D=0.16_6}$

Monoester—0.098 g. distributed $D=6.3_8$
0.575 g. distributed $D=6.7_2$
0.980 g. distributed $D=7.1_6$
Average value $\overline{D=6.8}$

For the diester the distribution coefficient was approximately constant over a ten-fold concentration range. For the monoester the distribution coefficient apparently increased as the concentration increased. Such an effect could be caused by association or dissociation of monoester molecules in one of the phases.

These distribution constants are of interest to indicate only semiquantitatively the degree of separation that can be effected by extraction. The constants are not strictly appropriate for the procedure detailed above, principally because the relatively large sample of oil appreciably changes the composition of the two solvents in reaching equilibrium.

Summary

The acid monoester 2-ethylhexyl hydrogen sebacate has been identified in bis(2-ethylhexyl) sebacate oils by carrying out a partial separation of components with the solvents Skellysolve C and acetonitrile-methanol and by examining the infrared spectrum of the fraction contained in the acetonitrile-methanol phase for the characteristic 1,710- and 1,740-cm.$^{-1}$ absorption peaks of the monoester.

Acknowledgment

This work was carried out in connection with Contract No. AF 33(616)-5006 for the Propulsion Laboratory at Wright Air Development Center of the U. S. Air Force.

REFERENCES

1. Murphy, C. M., and Ravner, H., Ind. Eng. Chem., *44*, 1607–1612 (1952).
2. Cole, J. W. Jr., WADC Technical Report 53-293, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, 1953.
3. Dismukes, E. B., WADC Technical Report 58-125, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, 1958.
4. Ahrens, E. H. Jr., and Craig, L. C., J. Biol. Chem., *195*, 299–310 (1952).

[Received September 12, 1958]