Bench-Scale Evaluation of Nonvolatile *alpha*-Branched Chain Fatty Esters as Potential Lubricants[1]

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Abstract

Several nonvolatile esters of α-branched fatty acids have been prepared in a highly purified state and examined by bench-scale tests of the sort usually used in the preliminary evaluation of lubricants. Viscosity characteristics and Shell-Boerlage wear-test results for these compounds are comparable with those of compounds used in the manufacture of modern synthetic lubricants. These esters are substantially superior to one such compound in thermal stability and resistance to acid hydrolysis.

Introduction

IMPROVING JET ENGINE DESIGNS are continually demanding lubricants which are capable of resisting increasingly higher bulk-lubricant temperatures. Although the dicarboxylic acid esters have supplied most synthetic lubricant requirements in recent years, it has been suggested that it may be necessary to turn to other classes of compounds to find the temperature stability desired (1–3). Esters of carboxylic acids however have valuable properties, such as low volatility and good lubricity, i.e., great capacity for lubricating metal surfaces. Therefore it is not surprising that several investigators (4,5) have conducted studies of esters with structural modification which might improve the thermal and oxidative stabilities of these compounds. Considerable progress has been made in meeting the difficult requirements of military specifications by new formulations, derived from polyol esters of trimethylol propane, pentaaerythritol, and dipentaerythritol (6).

This paper is concerned with the properties of high-molecular-weight esters prepared from fatty acids having a branch in the 2- or *alpha*-position. These compounds were selected for investigation for a number of reasons. The long-chain fatty acids and the olefins essential for their preparation are readily available, and it is relatively easy to add a fatty acid or ester to a terminal olefin under free radical conditions (7,8). Moreover branching at the *alpha*-position greatly improves stability to acid hydrolysis (4).

[1] Presented at AOCS Meeting, Philadelphia, October 1966.
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TABLE I
Analytical Properties

Samples	M.P. °C	n_D^{60}	Mol. Wt. Calc.	Mol. Wt. Found
Methyl 2-decyl-octadecanoate	37	1.4372	438	438[a]
Methyl 2-dodecyl-octadecanoate	39	1.4412	466	466[a]
2-Ethylhexyl 2-dodecyl-octadecanoate	13	1.4420	565	571
Neopentyl 2-decyl-octadecanoate	22	1.4375	495	495[a]
Benzyl 2-decyl-octadecanoate	27	1.4612	515	515[a]
Isobutyl 2-decyl-octadecanoate	27	1.4382	480	480[a]

[a] Molecular weight by mass spectrometry, otherwise by isothermal distillation.

TABLE II
Viscosity Data

Sample	Kinematic Viscosity (Cs) 25C	37.8C	54.5C	98.8C	Viscosity index	A.S.T.M. slope
Methyl 2-dodecyl-octadecanoate	Solid	28.2	16.0	5.70	161	0.665
2-Ethylhexyl 2-dodecyl-octadecanoate	53.1	32.1	18.3	6.34	166	0.647
Isobutyl 2-decyl-octadecanoate	38.4	22.7	13.7	5.00	166	0.665
Neopentyl 2-decyl-octadecanoate	45.3	27.1	15.4	5.40	151	0.683
Benzyl 2-decyl-octadecanoate		24.5	14.2	5.21	163	0.699
100 Paraffin oil	92.6	45.2	21.7	5.94	76	0.782
Di-2-ethylhexyl sebacate	19.9	12.9	8.13	3.40	158	0.692

Experimental Section

Starting Materials

Esters of the *alpha*-branched acids were prepared by the addition of terminal olefins to methyl stearate under free radical conditions. Details of their preparation and purification are given in a separate paper (9). The α-branched esters showed properties reported in Table I. Di-2-ethylhexyl sebacate was obtained from commercial sources, as was the engine oil supplement (EOS), which was used as an additive in some tests.

Methods

Kinematic Viscosity, Viscosity Index, and ASTM Slope. The viscosity, viscosity index, and ASTM slope were determined according to the procedures given in ASTM D-445-60, ASTM D-567-53, and ASTM D-341-43 respectively. Where possible, the viscosities were determined at four temperatures. The results are given in Table II.

Precision Shell Four-Ball Wear Test

The samples were run at 120C under 50-kg load for one hour as described by Peale (10). The rotation of the upper ball was 600 rpm. DOS (di-2-ethylhexyl sebacate) and a refined Pennsylvania petroleum paraffin base oil were used as reference materials. The data obtained are shown in Table III.

Thermal Stability. The determination of thermal stability was done by thermogravimetry (TGA) by using an Aminco Thermo-grav instrument. The method for determining thermal stability has been described previously (5). In some cases the samples were dried 2 to 8 hrs at a temperature of 100–130C and pressures of 2 to 15-mm Hg; the principal object of the drying was to remove trace residues of solvent or other volatile materials. Data are shown in Table IV.

TABLE III
Shell-Boerlage Wear-Test Results

Sample	Scar diameter (mm)
Methyl 2-decyloctadecanoate	0.562
Methyl 2-decyloctadecanoate + 5% EOS[a]	0.485
2-Ethylhexyl 2-dodecyloctadecanoate	0.510
Neopentyl 2-decyloctadecanoate	0.598
Benzyl 2-decyloctadecanoate	0.835
Di-2-ethylhexyl sebacate	0.872
Di-2-ethylhexyl sebacate + 5% EOS[a]	0.378
100 Paraffin oil	0.803
100 Paraffin oil + 5% EOS[a]	0.563

[a] EOS = engine oil supplement containing zinc dialkyl dithiophosphate.

TABLE IV
Thermal Stability of Esters

Sample	Decomposition °C				
	Onset	1%	2%	5%	10%
Methyl 2-decyl-octadecanoate	340	365	380	402	418
2-Ethylhexyl 2-dodecyl-octadecanoate	345	365	375	390	403
Isobutyl 2-decyl-octadecanoate	345	365	375	393	407
Neopentyl 2-decyl-octadecanoate	350	377	393	412	426
Benzyl 2-decyl-octadecanoate	355	373	382	394	406
Methyl palmitate	300	340	350	370	386
Methyl stearate	302	320	349	390	410
100 Paraffin oil	235	278	307	405	435
Di-2-ethylhexyl sebacate	289	325	349	374	387

Hydrolytic Stability. Hydrolytic stability was studied by heating a sample of the material on the steam bath in the presence of H_2O and of dilute 0.1N H_2SO_4 for varied periods of time, after which the acid number was determined. Data are shown in Table V.

Discussion

The melting points for the esters discussed here are related to the length of the branch and also to the degree of branching in the alcohol moiety. Most of these esters melt at or near room temperature, a point requiring consideration in connection with any practical use as lubricants.

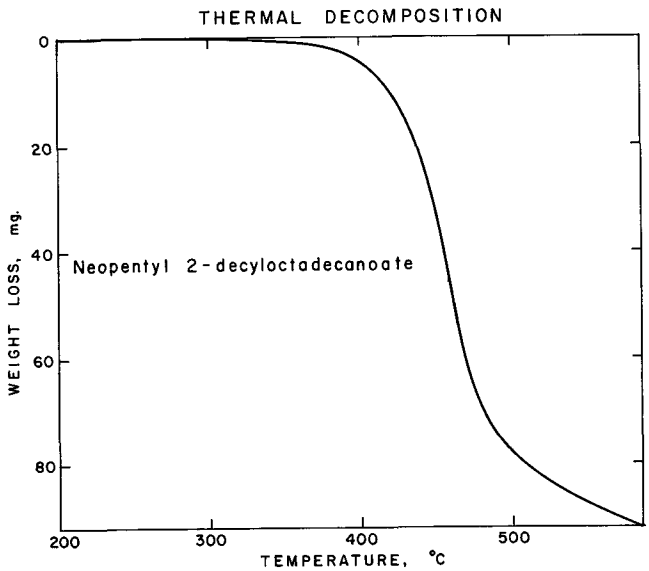
The viscosity characteristics of the *alpha*-branched esters are quite good over the range tested. They are considerably better than those of mineral oils. They compare favorably with di-2-ethylhexyl sebacate in several important respects; the viscosity indices and slopes are comparatively good. Almost without exception these branched-chain esters give smaller wear-scar diameters by the Shell-Boerlage test than does either di-2-ethylhexyl sebacate or a paraffin-base mineral oil lubricant. They tend to be comparable with a mineral oil base, to which has been added 5% engine oil supplement, and only slightly inferior in this respect to DOS (di-2-ethylhexyl sebacate), to which the supplement has been added.

It has been pointed out by Coats and Redfern (11) that there may be little agreement between thermal decomposition values obtained by isothermal and non-isothermal methods. Variation in values obtained by TGA results from a lack of uniformity in experimental procedure and from lack of an adequate definition for locating the decomposition temperature. The "onset" of decomposition is defined for the purposes of this paper as the point where a) the material shows the first detectable weight-loss, as determined by a deviation from a blank run, and/or b) the slope (dw/dT) shows a sharp change from some minimum value. A typical curve is shown in Figure 1.

TABLE V
Ester Hydrolysis

Sample	Acid Number (mg KOH/g)			
	Initial	H_2O[a] 6 hr	Acid[a] 1 hr	Acid[a] 6 hr
Methyl 2-decyl-octadecanoate	0			0
2-Ethylhexyl 2-dodecyl-octadecanoate	0			0
Neopentyl 2-decyl-octadecanoate	0			0
Benzyl 2-decyl-octadecanoate	1.1			3.9
Methyl oleate	0	0	15.4	35.2
Di-2-ethylhexyl sebacate	0	0	5.7	15.5
Di-2-ethylhexyl azelate	0	0		16.5
Lubricant B (DOS type)	1.5	1.0		20.6

[a] Heated on steam bath for time indicated; acid was 0.1 N H_2SO_4.



In order to facilitate interpretation of the data in Table IV, temperatures have been listed at which various degrees of decomposition are shown. The decomposition temperatures observed for di-(2-ethylhexyl) sebacate and for a paraffin oil are included for purposes of comparison. In their study of the thermal stability of more than 100 organic compounds, Blake and coworkers (3) reported a decomposition point of 284C for the sebacate ester, 5 degrees lower than our findings. A much better comparison perhaps is with methyl palmitate and methyl stearate, which decompose (onset) at 300C and 302C respectively.

Substitution at the position *alpha* to the carboxyl group appears to stabilize the compounds against thermal decomposition to a rather considerable degree when compared with DOS. At 5% and higher levels of decomposition the stability of the branched esters appear to be comparable with that of the paraffin oils but substantially better than that of di-2-ethylhexyl sebacate. Outstanding resistance to hydrolysis, as evidenced by the lack of formation of acid, is shown for the α-branched chain fatty esters in the presence of water alone and in the presence of 0.1N sulfuric acid. After six hours in the presence of 0.1N sulfuric acid, the methyl oleate, di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, and Lubricant B (a commercial dioctyl sebacate lubricant containing additives) gave significant acid numbers whereas the α-substituted esters, with the exception of the benzyl ester, showed zero acid number. This resistance to hydrolysis is probably owing to steric hindrance created by the alkyl group in the α-position.

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[Received September 8, 1967]