Potential Synthetic Lubricants: Diol Ester of C_{18}-Saturated Cyclic Acids[1]

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Abstract

Monoalkyl esters of linseed-oil-derived C_{18}-saturated cyclic acids (HCal), described in earlier work, showed promise as lubricant base stocks for turbine aircraft as set forth in the military specification MIL-L-7808E. These esters, however, did not exhibit the increased oxidative stability and higher viscosity required by the more recent specification MIL-L-23699.

Six diol esters of HCal have now been prepared. Both hindered and unhindered dihydric alcohols were used, including ethylene glycol, 1,4-cyclohexanedimethanol, 1,4-benzenedimethanol, 2,3-dimethyl-1,3-propanediol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (I). The viscosities of these esters at 210F ranged from 10.1 to 19.6 centistokes and the pour points, from −35 to −62F. Oxidative stabilities at 400F were determined with 0.5% each of phenyl-α-napthylamine (PANA) and *p,p′*-dioctyldiphenylamine as inhibitors. The esters of the unhindered diols had poor stability, whereas esters of the hindered diols, in particular I, exhibited excellent resistance to the formation of acidic decomposition products and sludge. Although the HCal ester of I by itself is too viscous to meet specification MIL-L-23699, its ASTM slope (0.650) is excellent. Blends of this material with less viscous hindered esters, commercially available, may find application as lubricants for high-performance turbine engines used in various aircraft.

Introduction

A PREVIOUS PAPER from the Northern Laboratory (6) reported the preparation of 16 monohydric alcohol esters of C_{18}-saturated cyclic acid. A preliminary examination was made of their physical properties as they relate to low-temperature lubricants, particularly gas turbine oils for military aircraft as set forth in the 1963 amendment of specification MIL-L-7808. Concurrently, another specification MIL-L-23699 was adopted. Although it does not supersede the older, much of the military and commercial turbine oil requirements have shifted to the 23699 oil. This specification relaxes the low-temperature requirements but, in turn, calls for a more viscous oil (5–5.5 cs at 210F) with oxidative stability at higher temperatures (400F).

Fluids other than esters e.g., silicones, highly refined petroleum fractions, polynuclear aromatics and others) may meet the high-temperature requirements, but these do not possess the lubricity and load-carrying characteristics of the ester oils. Consequently, esters are still necesasry in primary and secondary power lubricants, as instrument oils and for a base in general-purpose lubricants.

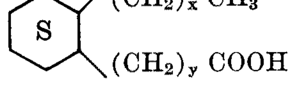
Much of the thermal and oxidative instability of esters has been traced to the degree of substitution on the beta position in the alcohol moiety. If the hydrogens on the beta carbon are replaced by alkyl groups, the stability of the ester is appreciably enhanced (7); however, replacement of only one of these hydrogens (e.g., 2-ethylhexanol) does not increase the stability and may even decrease it as our previously reported data (5) would indicate. Because the oxidative stability of 7808 esters is lower than required by specification MIL-L-23699 and because their instability is explained by the beta hydrogen theory, research in ester lubricants has now shifted to hindered types. In general, the higher viscosities (specified in MIL-L-23699) require higher molecular weights; therefore, esters of trimethylol propane and pentaerythritol (PE) with relatively short-chain carboxylic acids and neo-acids have been extensively investigated (1). When such oils are properly inhibited, some will meet the specifications.

Formulation of an inhibitor system is difficult. No single inhibitor appears adequate, and the more effective systems usually include several components. Of course these components must be compatible with the ester and with one another under all test conditions of the specification. Multicomponent inhibitor systems may produce unexpected oxidative stability with a particular ester because of synergistic effects. Good performance in one system, however, does not ensure the effectiveness of the same inhibitor package in another. One component that appears to be common to most inhibitor systems is an aryl amine, such as phenyl-α-napthylamine or *p,p′*-dioctyldiphenylamine. A mixture of these two was used in this study.

This paper reports the preparation of various diol esters of HCal, an examination of their viscosity characteristics and a preliminary study of their oxidative stability at 400F.

Starting Materials

C_{18}-Saturated cyclic acids (HCal) were prepared by alkaline isomerization of linseed oil in water solution according to the method of Beal et al. (2). Hydrogenation of cyclized monomeric acids was carried out under conditions found to eliminate aromatic contaminants (3,5). The bulk of the straight-chain saturated acids (stearic and palmitic) was removed by crystallization from acetone at −50C followed by centrifugation. The liquid product still contained about 8% of the straight-chain acids, which were removed by the urea-inclusion technique. The hydrogenated cyclic acids contained <1% straight-chain saturates and <1% aromatic acids. The neutralization equivalent was 283 and iodine value <1. As previously reported (4), HCal is composed of a series of isomers with the following general structure:



$x + y = 10$

X varies between 0 and 5, the principal isomer (60%) being 9-(2′-n-propylcyclohexyl) nonanoic acid (x = 2).

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[1] Presented at the AOCS Meeting in Los Angeles, 1966.
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TABLE I
Grade and Source of Diols

Alcohol	Grade	Source
Ethylene glycol	Pure	Union Carbide
2,2,-Dimethyl-1,3-propanediol	Practical	Eastman
1,4-Benzenedimethanol	Research	Aldrich
1,4-Cyclohexanedimethanol	Research sample	Eastman
2,2,4,4-Tetramethyl-1,3-cyclobutanediol	Research sample	Eastman

The diols were used as received, except for 1,4-cyclohexanedimethanol that was furnished in a methanol solution. The methanol was removed under high vacuum at room temperature. The grade and source of the diols are shown in Table I.

Preparation of Esters

The ethylene glycol diester of HCal was prepared by heating together on a steam bath 0.1 mole (6.2 g) of ethylene glycol, 0.4 mole (114 g, 100% excess) HCal and 15 g of BF_3 etherate. After heating the mixture for about 1 hr, the product was diluted with ether, washed several times with water to remove the catalyst and dried. The ether was stripped from the dried product and the residue subjected to high-vacuum distillation to remove excess HCal. Distillation was carried out at 0.035 mm through a short, jacketed Vigreux column. By allowing the pot temperature to reach 260C, all but the last traces of HCal were removed without decomposition of the remaining ester. The pale yellow diester was passed through a mixture of alumina and decolorizing charcoal to remove any traces of acid and color. The yield of purified product was about 92% based on the limiting reagent, ethylene glycol. The theoretical saponification number (190) was obtained and molecular distillation gave only traces of residue.

The 2,2-dimethyl-1,3-propane diol, 1,4-benzenedimethanol and 1,4-cyclohexanedimethanol diesters of HCal were prepared at the same 4:1 molar ratio of acid to alcohol. Esterification was carried out in refluxing toluene containing 1.5% fuming H_2SO_4 (based on the weight of the HCal), and water was removed azeotropically. The products were isolated according to the previous procedure with comparable yields.

The 2,2,4,4-tetramethyl-1,3-cyclobutanediol diester of HCal cannot be prepared in the presence of an acid catalyst because the alcohol dehydrates. This diol was esterified, however, by heating a 4:1 molar ratio of acid to alcohol in toluene solvent and removing the toluene until a pot temperature of about 180C was reached. The mixture was then allowed to reflux and, again, water was removed azeotropically. A small quantity of the alcohol sublimed, or co-distilled, and crystallized in the trap. After no further water was collected (3–4 hr), the crude product was stripped of toluene and excess HCal as previously described. The yield of purified product was about 70% based on starting alcohol.

Physical Tests

Measurement of Viscosities

Viscosities of the esters were determined in Ostwald-Cannon-Fenske pipets immersed in a water bath controlled at 100F and at 210F ± 0.1 degrees. The viscosities were plotted against temperature on ASTM standard viscosity-temperature charts for liquid petroleum products (D341). Extrapolated viscosities at −40F were determined from these plots. From the viscosities at 100 and 210F ASTM slopes were obtained.

Pour Point

Cooling equipment was not available for measuring pour points by the standard ASTM Method D97-47. To get an approximate pour point, a vial (25 mm diameter) containing 15 g of the ester was packed in solid carbon dioxide overnight. The vial was then placed in an air bath, and the air bath in turn was immersed in a Dewar flask containing isopropanol and solid carbon dioxide. The temperature was allowed to rise at the rate of 2C per hr. The temperature at which the surface of the sample would deform in 5 sec when tipped was arbitrarily called the pour point. The pour point of di(2-ethylhexyl) sebacate was determined by this method and found to be approximately 10F higher than that reported by the ASTM method.

Oxidation at 400F

A modification of the standard test had to be made because only small quantities of each ester were available. A 10-g sample of ester containing 50 mg each of phenyl-α-napthylamine and *p,p*-dioctyldiphenylamine was placed in a vial 25 mm in diameter. Through a capillary tube inserted to the bottom of the vial, filtered compressed air was metered at the rate of 500 cc/hr for 72 hr. The sample was heated by immersing the vial in a stirred oil bath maintained at 400F ± 1.0F. After oxidation the sample was filtered to remove ttraces of solid material that had formed. Viscosities and acid values of oxidized esters were run on the filtered samples.

Discussion

Esters of pentaerythritol, dipentaerythritol and trimethylolpropane currently serve as base stocks for jet turbine oils under MIL-L-23699. No pure ester has been accepted as a standard of comparison such as di(2-ethylhexyl) sebacate was for MIL-L-7808. In this study, therefore, a commercial PE ester "Hercolube C" was used for comparative purposes.

From the data given in Table II it can be seen that viscosities of the HCal diesters are too high at

TABLE II
Viscosity Characteristics of HCal[a] Diesters and Control

Diester	Viscosity in cs at			ASTM slope	Pour point, F
	210F	100F	−40F[b]		
1. Hercolube C (control)	3.8	17.7	3.9×10^3	0.715	<−100
2. Ethylene glycol	10.8	73.7	5×10^4	0.630	−62
3. 2,2-Dimethyl-1,3-propanediol	11.7	170	6×10^6	0.758	−44
4. 1,4-Benzenedimethanol	14.1	122	1.5×10^5	0.614	−38
5. 1,4-Cyclohexanedimethanol	19.6	220	7.5×10^5	0.620	−35
6. 2,2,4,4-Tetramethyl-1,3-cyclobutanediol	16.4	169	3.8×10^5	0.629	−36
7. Blend of 24% (6) and 76% (1)	5.23	28.1	1.07×10^4	0.687	−71
Specification MIL-L-23699	5.0–5.5	>25	$<1.3 \times 10^4$	0.619–0.707	<−65

[a] C_{18}-Saturated cyclic acids.
[b] Extrapolated viscosity except for No. 7 which was actually determined.

TABLE III

Oxidative Stability of HCal[a] Diesters and Control at 400F

Diester[b]	% Change in viscosity cs/sec at 100F	Acid value increase	Sludge formation
1. Hercolube C (control)	+36	17.3	None
2. Ethylene glycol	[c]	[c]	Semisolid
3. 2,2-Dimethyl-1,3-propanediol	+216	6.7	None
4. 1,4-Benzenedimethanol	[c]	[c]	Semisolid
5. 1,4-Cyclohexanedimethanol	+70 (Filtrate)	6.7 (Filtrate)	Large amount
6. 2,2,4,4-Tetramethyl-1,3-cyclobutanediol	+377	<1	None
7. Blend of 24% (6) and 76% (1)	+71	14	None
Specification MIL-L-23699	−5 to +25	<3	<1 g/100 ml

[a] C_{18}-Saturated cyclic acids.

[b] Esters inhibited with 1% by weight of an equal mixture of phenyl-α-napthylamine and *p,p'*-dioctyldiphenylamine.

[c] *Sample* decomposed.

both 100 and 210F to meet the specification. The ASTM slopes, however, are quite good for all but the 2,2-dimethyl-1,3-propanediol diester. A mixture of the low viscosity Hercolube C (76%) and the 2,2,4,4-tetramethyl-1,3-cyclobutanediol diester No. 7 (24%) falls within the range of the specification at both temperatures and has an acceptable ASTM slope. The modified pour points and extrapolated low temperature (−40F) viscosities of the pure HCal diesters are also too high to meet sepcifications (Table II); however, the No. 7 mixture again meets the requirements.

Viscosity characteristics are rather rigidly defined in MIL-L-23699. It specifies a minimum viscosity at 100F, a narrow range of viscosities at 210F and a maximum viscosity at −40F. The shaded area in Fig. 1 represents the boundaries allowed by the specification. An ester possessing an ASTM slope <0.619, therefore, could not fall within the range of the specification. The pure HCal diesters lie above the shaded area, as illustrated by the cyclobutanediol diester. The blend of 24% 2,2,4,4-tetramethyl-1,3-cyclobutanediol ester of HCal and 76% Hercolube C, however, falls well within the shading.

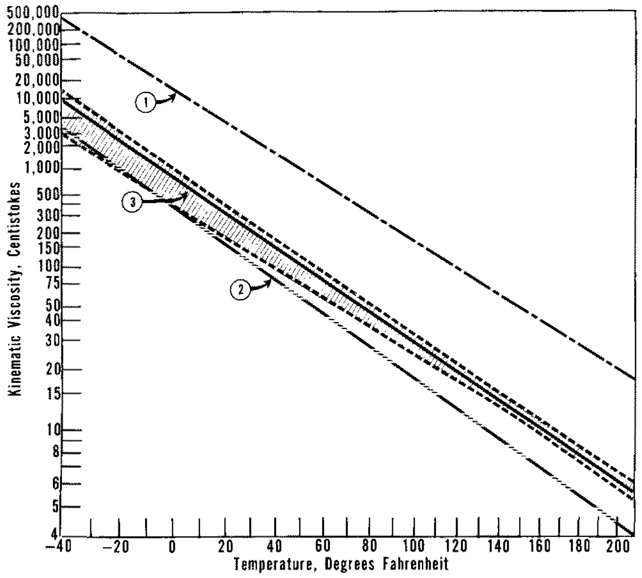

FIG. 1. ASTM D341 Viscosity-temperature charts for: (1) C_{18}-saturated cyclic acid (HCal) diester of 2,2,4,4-tetramethyl-1,3-cyclobutanediol, (2) Hercolube C and (3) blend of 24% (1) and 76% (2). The shaded area represents the limits cited in specification MIL-L-23699.

The comparative data on high-temperature oxidative stability in Table III are significant even though the desired stability was not achieved for either the PE ester or the pure HCal diesters when a mixture of phenyl-α-napthylamine and *p,p'*-dioctyldiphenylamine in 1% concentration was the inhibitor system.

Viewing stability from the aspect of the structural configuration of the alcohol, one could easily explain the marked instability of the ethylene glycol diester No. 2 and the 1,4-cyclohexanedimethanol diester No. 5. The former has four beta hydrogens, whereas the latter has one beta hydrogen, which is also on a tertiary carbon. It is not possible, however, to explain the instability of the 1,4-benzenedimethanol diester No. 4 on this basis. Instability of HCal esters containing aromatic components has been reported previously (6). The 2,2-dimethyl-1,3-propanediol diester No. 3 and the 2,2,4,4-tetramethyl-1,3-cyclobutanediol diester No. 6 have no beta hydrogen in the alcohol moiety and show much greater stability than the others. The unfavorably high ASTM slope of No. 3, however, makes it a much less promising candidate than No. 6. There was no sludge formation with either of these esters nor with the Hercolube control No. 1. The stability of No. 6 toward the formation of free acid is extremely good compared to the control. Conversely, the increase in viscosity at 100F after oxidation is much greater for No. 6 than for the control. As would be expected, Blend No. 7 shows intermediate values.

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