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3,124,533

FLUORINE CONTAINING ESTERS OF POLY-CARBOXYLIC ACIDS

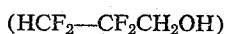
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8 Claims. (Cl. 252—54.6)

This invention relates to esters of fluoro alcohol and aliphatic polycarboxylic acids and to lubricating oil compositions containing said esters. Particularly, the invention relates to partial esters which are useful as load-carrying agents and as lead corrosion inhibitors, said esters being prepared from fluorine substituted alkanols with aliphatic tri- and tetra-carboxy acids, wherein said acids have a total of 6 to 8 carbon atoms.

The use of various aliphatic diesters and complex synthetic esters as lubricating oils is well known to the art and have been described in numerous patents, e.g. U.S. 2,723,286; 2,743,234; and 2,575,196. In general, these prior aliphatic synthetic ester lubricating oils are prepared from dicarboxylic acids and have viscosity properties that are outstanding at both low and high temperatures, especially when compared to mineral oils. Because of these characteristics, synthetic ester oils have become of increasing importance in the field of lubrication and one of the most important current application of such compounds is in the lubrication of aviation gas-turbine systems such as are used in the "turbo-jet" and "turbo-prop" type of aircraft. However, in general, the load-carrying ability of the aliphatic ester oils prepared from dicarboxylic acids is not particularly high. Because of the increasing severity of the conditions prevailing in the lubrication of aviation gas-turbine systems, it is highly desirable to form synthetic ester lubricating compositions having higher load-carrying ability than is now generally available and yet at the same time being non-corrosive. It has now been found that partial esters of certain tri- and tetra-carboxy acids are useful as load-carrying agents in lubricating oils, particularly diester and complex ester lubricating oils. While many prior load-carrying agents greatly increase lead corrosion, these partial esters of tri- and tetra-carboxy acids do not corrode lead, and in fact inhibit lead corrosion. This is particularly important because of the lead-containing bearings frequently used in aircraft engines.

The esters of the invention include mono- and diesters of C_6 to C_8 alkanetricarboxylic acids, and mono-, di- and triesters of C_6 to C_8 alkanetetracarboxylic acids with C_3 to C_{20} alkanols having fluorine substituents. The preferred acids are 1,2,3-tricarboxy propane (tricarballic acid), 1,2,4-tricarboxy butane and 1,2,3,4-tetracarboxy butane.

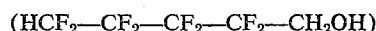
Preferred alcohols for forming the ester are those fluorinated alkanols with about 3 to 20, preferably 5 to 13 carbon atoms and having the formula $X(CF_2)_nCH_2OH$, wherein n is an integer of 2 to 19 and where X is either hydrogen or fluorine. Examples of such alcohols are: 1H, 1H, 3H, tetrafluoro-1-propanol



1H, 1H, pentafluoro-1-propanol ($CF_3-CH_2-CH_2OH$);

2

1H, 1H, 5H-octafluoro-1-pentanol



1H, 1H, 7H-dodecafluoro-1-heptanol



1H, 1H, 9H-hexadecafluoro-1-nonanol



10 1H, 1H, 11H, eicosafluoro-1-undecanol

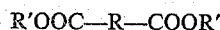


Fluoroalcohols of the above type where X is hydrogen have recently become commercially available and may be prepared by the free radical telomerization of tetrafluoroethylene with methanol as described in U.S. Patent 2,559,628 to R.M. Joyce.

The partial esters of the invention are prepared by conventional esterification techniques. The esterification is carried out by reacting 1 to 3 molar proportions of alcohol (depending upon whether the acid is tri-carboxy or tetracarboxy), per one molar proportion of the acid, under reflux conditions. Generally, a water-entraining agent, e.g. heptane, toluene, etc., is used, and the reaction is carried out until the calculated amount of water is removed overhead. Generally, no catalyst is employed because the reaction proceeds well enough without catalyst and this eliminates the necessity for filtering and washing to remove the catalyst. After the desired amount of water is removed, the remaining reaction product may be distilled under vacuum in order to remove the entraining agent and any unreacted alcohol.

The resulting ester product can be used by blending with other oils, particularly other ester oils. Thus, such blends may contain for example, about 0.1 to 10.0, preferably 0.25 to 2.0, weight percent of the partial ester in lubricating oil.

The lubricating oil used with the esters of the invention may be a mineral lubricating oil, a synthetic lubricating oil or any mixtures thereof. Particularly, preferred synthetic oils for blending with the partial ester materials are the saturated aliphatic diesters represented by the formula:



45 wherein R is a straight or branched chain hydrocarbon radical of a C_6 to C_{12} alkanedioic acid, R' represents an alkyl radical of a C_6 to C_{16} branched or straight chain alkanol and the total number of carbon atoms in the molecule is about 20 or more. Specific examples of such diesters include di(2-ethylhexyl) sebacate and di(C_{10} Oxo) adipate, etc. Another useful class of synthetic esters are the C_5 to C_9 alkyl full esters of C_4 to C_7 tri- and tetrahydric alcohols such as trimethylol propane, trimethylol ethane, neopentyl glycol and pentaerythritol. One example of such esters that was used in the working examples of this invention is trimethylol propane tri-n-heptate. Still other synthetic oils which may be used will include esters of monobasic acids (e.g. C_{10} Oxo alcohol ester of C_8 Oxo acid), esters of glycols (e.g. C_{13} Oxo acid diester of tetraethylene glycol), complex esters, esters of phosphoric acid, halocarbon oils, sulfite esters, silicone oils, carbonates, formals, polyglycol-type synthetic oils, etc.

Various other additives may also be added to the lubri-

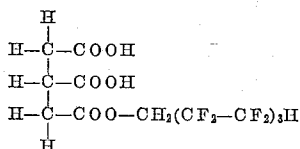
3

cating compositions of the invention in amounts of about 0.1 to 10.0 weight percent, based on the total weight of the composition. For example, oxidation inhibitors such as phenylalpha-naphthylamine, para-amino diphenylamine or phenothiazine; corrosion inhibitors such as sorbitan monooleate, antifoamants; auxiliary load carrying agents; dyes; grease thickeners; and the like may be added.

The invention will be further understood by the following examples:

EXAMPLE

(A) A monoester of tricarballic acid and C₇ fluoro alcohol was prepared which has the formula:

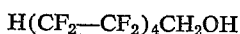


The monoester was prepared as follows: Into a 1,000 ml. round bottom three-necked flask equipped with a stirrer, thermometer, reflux condenser and water trap, was placed 332 grams (1 mole) of a C₇ fluoro alcohol having the formula:



and 176 grams (1 mole) of tricarballic acid. 50 ml. of heptane as a water entraining agent were next introduced. The mixture was then refluxed at atmospheric pressure and stirred vigorously for 3 hours. During this time the calculated amount of water (1 mole) collected in the trap. The resulting oil residue was stripped of volatiles at 220° C. at atmospheric pressure (760 mm. of Hg). The residue was filtered through Hiflo filter aid (diatomaceous earth) and the filtered product was a soft waxy material, solid at room temperature.

(B) A mono C₉ fluoro alcohol ester of tricarballic acid was prepared by following the procedure of A above, but using C₉ fluoro alcohol of the formula:



in place of the C₇ fluoro alcohol. The product was also a soft waxy solid.

Compositions 1 to 3

Several lubricating oil compositions were prepared by simply mixing the components. Two compositions were prepared consisting of trimethylolpropane tri-n-heptate, 0.5 wt. percent of phenothiazine as an antioxidant and 1 wt. percent of the products of A or B above, said weight percents being based upon the weight of tri-n-heptate ester. A third composition was made up in a similar manner but containing 0.85 wt. percent of the product of A. The resulting compositions were then subjected to the following tests:

Lead (Pb) Corrosion Test

Compositions 1 to 3 were each tested by rapidly rotating a bi-metallic strip consisting of a lead strip and a copper strip bound together in the oil sample maintained at 325° C. while air was bubbled through the sample. The weight loss of the lead strip was then determined, and reported in terms of milligram weight loss per square inch of lead surface (mg./in.²). Measurements were made after one hour and after 12 hours. Lubricants giving very low lead corrosion are desired for aircraft engine lubrication. Low lead corrosion at the 12 hour period is an indication of good storage stability.

Oxidation-Corrosion Stability (500° F. O.C.S.) Test

The ester compositions were also tested for corrosiveness to copper, titanium, iron, aluminum and silver and for change in acidity and viscosity. These tests were carried out by immersing weighed strips of the metal to be tested in 100 cc. of the sample maintained at 500° F. for

4

48 hours while bubbling 5.0 liter per hour of air through the sample. The metal strip is then reweighed to determine the weight change as mg./cm.². The viscosity (cs, at 100° F.) and the increase in total neutralization number in terms of mg. KOH/gm., of the oxidized composition is also determined.

Ryder-Gear Load Carrying Test

The load carrying ability of the synthetic ester composition was determined by the Ryder Gear Test in accordance with the MIL-L-7808C specification procedures.

SAE-SOD Load Carrying Test

This is a modified SAE test using the standard SAE Lubricant Tester except that a gear ratio of 3.4 to 1 was used in place of the conventional ratio of 14.6 to 1. The test was carried out by running the machine for two minutes under a 50 pound load, and then manually increasing the load 50 pounds every ten seconds until scuffing occurred. The total load at which scuffing occurs is then reported.

In addition to the above tests, the usual determination of viscosities, flash point, fire point, and other standard measurements were made.

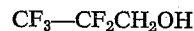
The compositions tested, along with a sample (Sample A) containing no fluorine-containing additive, and the results obtained are summarized in Table I which follows:

TABLE I

	Examples			
	I	II	III	Sample A
Composition:				
Vol. Percent Trimethylol propane tri-n-heptate	100	100	100	100
Wt. Percent Phenothiazine	0.5	0.5	0.5	0.5
Wt. Percent C ₇ Fluoroester of tricarballic acid	1.0		0.85	
Wt. Percent C ₉ Fluoroester of tricarballic acid		1.0		
Properties:				
Total Acid No. (mg. KOH/gm.)	1.89	2.34	1.31	0.04
Pb Corr. (mg./sq. in.)—				
1 hr.	0	0	0	-1.2
12 hrs.	0	0.75	0	-620
Oxidation Corrosion Stability 500° F., 48 hours (mg./sq. cm.):				
Cu	+0.22	0.0	-0.24	-0.038
Ti	+0.07	+0.07	+0.07	+0.04
Fe	-2.04	-16.64	-10.88	-16.73
Al	+0.05	+0.04	+0.07	+0.06
Ag	+0.07	+0.03	+0.07	+0.05
Increase in total acid number	18	27.6	28	28
Visc. @ 100° F. (cs.)	78.6	98	40.5	136
Ryder Gear Load, lbs./in.			2,295	1,495
SAE-SOD Load, lbs.			1,000	625

As seen by Table I, the partial esters of the invention drastically inhibit lead corrosion of the synthetic ester base oil, while at the same time showing good oxidation and corrosion stability. In addition, the additives of the invention were effective in increasing the load-carrying ability of the composition.

Other esters of the invention may be readily prepared as previously illustrated. For example, a triester can be prepared by esterifying one mole of 1,2,3,4 tetracarboxy butane with three moles of alcohol of the formula



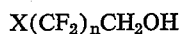
by following the procedure used in the previously described Example A. The resulting triester can be used in a lubricating oil by simple blending. To illustrate, 2 parts by weight of the triester can be mixed into 98 parts by weight of di(2-ethylhexyl) sebacate.

What is claimed is:

1. A lubricating oil composition comprising a major amount of a synthetic ester lubricating oil and about 0.1 to 10.0 wt. percent, based upon the weight of said synthetic ester lubricating oil, of a partial ester of a C₆ to C₈

5

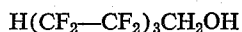
saturated aliphatic hydrocarbon polycarboxylic acid having 3 to 4 carboxy groups and an alcohol of the formula:



wherein X is selected from the group consisting of hydrogen and fluorine and n is an integer of 2 to 19.

2. A lubricating oil composition according to claim 1, wherein the amount of said partial ester is about .25 to 2.0 wt. percent, based on the weight of said synthetic ester lubricating oil.

3. A lubricating oil composition according to claim 2, wherein said partial ester is a monoester of tricarballic acid and a C_7 fluoro alcohol of the formula:



4. A composition according to claim 1, wherein said partial ester is a monoester of tricarballic acid and a C_9 fluoro alcohol of the formula:



5. A lubricating oil composition according to claim 1,

6

wherein said synthetic ester lubricating oil is a C_5 to C_9 alkyl full ester of C_4 to C_7 polyhydric alcohol containing 3 to 4 hydroxy groups.

6. A lubricating oil composition according to claim 1, wherein said alcohol contains a total of 5 to 13 carbon atoms.

7. A lubricating oil composition according to claim 1, wherein said polycarboxylic acid has 3 carboxy groups.

8. A lubricating oil composition according to claim 1, wherein said partial ester is a monoester of a polycarboxylic acid having 3 carboxy groups.

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