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3,278,434

LUBRICANT COMPOSITIONS CONTAINING THIODICARBOXYLIC ACID ESTERS

Elaine M. Hoffman, New Brunswick, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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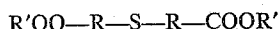
8 Claims. (Cl. 252—48.6)

This invention relates to lubricating compositions containing thiodicarboxylic acid esters. Particularly, the invention relates to synthetic ester lubricants which are inhibited against corrosiveness to magnesium by the incorporation of small amounts of fully esterified esters of thiodicarboxylic acid as an additive.

The use of various ester oil compositions for lubrication of modern day aircraft engines is well known. However, many of these ester oil compositions are corrosive to the magnesium parts of the constant speed drive unit used in conjunction with turbo-fan engines. These constant speed drive units are lubricated with the same oil composition used for lubrication of the turbo-fan engines, and corrosion of magnesium parts of said drive units occurs with the normal type of synthetic ester aircraft engine lubricating oil compositions in present day use.

The present invention resides in the discovery that certain neutral esters of thiodicarboxylic acid are extremely effective additives in inhibiting magnesium corrosion without detracting from other desirable properties of the ester lubricating oil or causing corrosion of other metals present in the lubricating system.

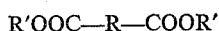
The thiodicarboxylic acid esters used as additives in the invention can be represented by the general formula:



where each R is the same or different hydrocarbon group, which can be aliphatic, aromatic, cycloaliphatic, saturated, unsaturated, branched or straight chain, containing 1 to 12, preferably 1 to 3, carbon atoms. Saturated aliphatic hydrocarbon groups are preferred. Each R' is the same or different hydrocarbon radical of a C₁₂ to C₂₄, preferably a C₁₃ to C₁₈, alcohol. R' is preferably saturated and aliphatic. Examples of such esters are dihexadecyl thiodipropionate; ditiocetyl thiodipropionate; distearyl thiodipropionate; dilauryl thiodipropionate; dilauryl thiodiacetate; lauryl, stearyl thiodipropionate; etc.

The lubricating compositions of the invention will comprise a major amount of synthetic carboxylic acid ester lubricating oil and about 0.001 to 10 wt. percent, preferably 0.1 to 2.0 wt. percent, based upon the total amount of the lubricating composition, of the thiodicarboxylic acid ester additive.

These synthetic ester lubricating oils include diesters represented by the formula:

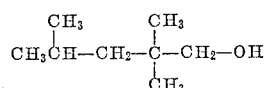
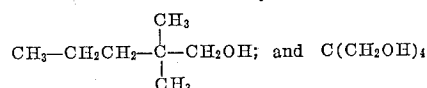


wherein R is a straight or branched chain hydrocarbon radical of a C₆ to C₁₂ alkanedioic acid, R' represents an alkyl radical of a C₆ to C₁₆, branched or straight chain alkanal and the total number of carbon atoms in the molecule is about 20 or more. Specific examples of such diesters include di(2-ethylhexyl) sebacate, di(C₈ Oxo) azelate, di(C₁₀ Oxo) adipate, di-2,2,4-trimethylpentyl sebacate, etc.

Recently, fully esterified hindered esters prepared from alcohols having no β -hydrogen and carboxylic acids having no α -hydrogen have become known for aviation use. These esters are particularly good for high temperature lubrication since they are exceptionally stable because they are completely hindered at the ester linkage, which generally is otherwise the weakest link in an ester molecule from the standpoint of heat stability, oxidation and

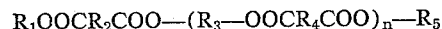
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hydrolysis. The saturated alcohols used to prepare these high temperature esters will generally have 1 to 4 hydroxy groups, and will be free of hydrogen radicals attached to the carbon atoms beta to each of said hydroxy groups, and will generally have a total of 4 to 8 carbon atoms. The acid used to prepare the high temperature esters is usually saturated, preferably has one or two carboxylic acid groups, will be free of hydrogen atoms attached to the carbon atoms alpha to the carboxylic acid group or groups, and will usually contain 7 to 20 carbon atoms. Examples of such no β -hydrogen alcohols include trimethylolethane, trimethylolpropane, and alcohols having the structures:



Examples of such no α -hydrogen acids include α,α -dimethyl valeric; α -ethyl, α -methyl caproic; α,α -dimethyl propionic; α,α -dimethyl octanoic; α,α,α' -tetramethyl pimelic; etc.

The additive of the invention can also be used in compositions containing complex esters which are frequently used as blending agents with other less viscous esters to tailor-make an ester lubricant composition. The more important of the complex esters can be represented by the general formula:



wherein R₁ and R₅ are alkyl radicals of monohydric alcohol, preferably having no beta hydrogen, R₂ and R₄ are hydrocarbon radicals of dicarboxylic acid, and R₃ is the divalent hydrocarbon or hydrocarbonoxy radical of a glycol or polyglycol, which glycol or polyglycol preferably has no beta hydrogen. "n" in the complex ester molecule will range from 1 to 6, usually 1 to 3, depending upon the product viscosity desired which is controlled by the relative molar ratio of the glycol or polyglycol to the dicarboxylic acid. In preparing the complex ester, there will usually be some simple ester formed, i.e. n=0, but this will generally be a minor portion, e.g. 10 to 40 wt. percent of the complex ester esterification reaction product.

Some specific materials used in preparing the above types of complex esters are as follows: Neo alcohols having 6 to 13 carbon atoms such as 2,2,4-trimethylpentanol-1; 2,2-dimethylhexanol-1; 2,2-dimethylpentanol-1; 1-methylcyclohexylmethanol; 2,2-dimethylbutanol-1; 2,2-dimethyldecanol-1; C₆ to C₁₂ dicarboxylic acids such as sebacic, adipic, azelaic and dodecanedioic acid; neo glycols such as 2,2-dimethylpropanediol-1,3; 2-ethyl-2-butyl propanediol-1,3; 2,2-diethylpropanediol-1,3; 2,2-dimethylbutanediol-1,3; etc. In general the complex esters will have a total of 20 to 80, preferably 40 to 65, carbon atoms per molecule. Complex esters and methods for their preparation are known in the art and have been described in various patents. Preferably the complex esters are prepared by reacting 1 mole of glycol, 2 moles of dicarboxylic acid and 2 moles of alcohol. This will result in about 35 wt. percent of diester of the dicarboxylic acid and alcohol, and about 65 wt. percent of complex ester of the formula: Alcohol-Acid-(Glycol-Acid)_x-Alcohol where x averages about 1.8.

Various other additives can also be added to the lubricating compositions of the invention in amounts of about 0.001 to 10.0 wt. percent each, based on the total weight of the composition. Examples of such other additives include: rust preventives such as calcium petro-

leum sulfonate or sorbitan monooleate; V.I. improvers such as the polymethacrylates; oxidation inhibitors such as phenyl - alpha - naphthylamine, para - aminodiphenylamine, 3,7 - dioctylphenothiazine, p,p' - dioctyldiphenylamine and phenothiazine; load carrying agents such as chlorinated biphenyl, tricresyl phosphate and free sebacic acid; etc.

The invention will be further understood by reference to the following examples which include a preferred embodiment of the invention.

EXAMPLE I

Varying amounts of several esters of thiodipropionic acid, as well as the acid per se, were added to 100 parts by weight of aircraft engine lubricating oil to determine their magnesium corrosion inhibiting activity. This lubricating oil contained a base oil consisting of 85 volume percent of di-2,2,4-trimethylpentyl sebacate and 15 volume percent of a complex ester composition. The complex ester composition was prepared by simultaneous reaction of one molar proportion of neopentyl glycol (2,2-dimethylpropanediol - 1,3), two molar proportions of sebacic acid and two molar proportions of 2,2,4-trimethylpentanol-1. The aircraft engine oil was prepared by adding to 100 parts by weight of said base oil, 3 parts by weight of phenyl-alpha-naphthylamine, 2 parts by weight of Acryloid HF-866 and 5 parts by weight of p,p'-dioctyldiphenylamine. Acryloid HF-866 is a concentrate of about 30 wt. percent copolymer of a methacrylate ester and 2-N-vinyl pyrrolidone in about 70 wt. percent di-2-ethylhexyl sebacate, sold by the Rohm & Haas Company as a dispersant V.I. improver.

The test compositions were tested for magnesium corrosion by immersing weighed magnesium strips in the oil composition to be tested, while blowing air for 48 hours through the oil composition while said composition is maintained at a temperature of 450° F. This test is similar to that set forth in Military Specification MIL-L-7808-C, except that it is modified to 450° F., 48 hours instead of the 347° F., 72 hour conditions of MIL-L-7808-C. At the end of the 48 hour test period, the magnesium samples are removed, reweighed, and the weight lost in terms of milligrams per square centimeter of magnesium surface area is calculated.

The test compositions tested and the results obtained are summarized in Table I, which follows:

Table I
MAGNESIUM CORROSION

Parts mg. corr. inh. additive added to 100 parts engine oil:	Mg. corrosion, mg./cm. ²
None -----	Dissolved
0.1 thiodipropionic acid -----	Dissolved
0.1 dilauryl thiodipropionate -----	-21.69
0.25 dilauryl thiodipropionate -----	-34.65
0.5 dilauryl thiodipropionate -----	-24.90
1.0 dilauryl thiodipropionate -----	-0.84
2.0 dilauryl thiodipropionate -----	-1.88
5.0 dilauryl thiodipropionate -----	-3.81
0.25 distearyl thiodipropionate -----	-1.74
0.25 di-n-hexadecyl thiodipropionate -----	-1.72
0.25 ditridecyl thiodipropionate -----	-0.15

As seen by the data of Table I, the aircraft engine lubricating oil, without any magnesium corrosion inhibitor (Mg Corr. Inh.) additive completely dissolved the magnesium test strip. Use of thiodipropionic acid per se also dissolved the test strip. On the other hand, all of the esters of Table I inhibited magnesium corrosion. The most effective ester were those having 13 or more carbon atoms in the alcohol portion of the molecule. Thus, 0.25 parts by weight of ditridecyl thiodipropionate added to 100 parts by weight of the aforesaid aircraft engine lubricating oil gave only 0.15 mg. weight loss per square cm. of magnesium, although without the thiodipropionate, the magnesium test strip completely dissolved.

EXAMPLE II

0.5 wt. percent of dilauryl thiodipropionate was added to 100.0 wt. percent of a lubricating oil composition consisting of 100 parts by weight of 2,2,4-trimethylpentyl sebacate, 3 parts by weight of phenyl-alpha-naphthylamine and 2 parts by weight of p,p'-dioctyldiphenylamine. For comparison, 0.1 wt. percent of dithiopropionic acid was added to 100.0 wt. percent of another sample of said lubricating oil composition.

The resulting compositions, along with the oil composition per se, were subjected to tests for corrosivity to copper, magnesium, iron, aluminum, silver and titanium, according to Oxidation Corrosion Stability (O.C.S.) test described in Military Specification MIL-L-7808-C, with the exception that the test was run at a temperature of 450° F. in place of the 347° F. standard test temperature. This was done in order to accelerate the test. Briefly described, this test involves suspending weighed metal strips of the metals to be tested in the oil sample maintained at 450° F. for 48 hours, while air is bubbled through the sample. The weighed metal strips are reweighed after the test period and the weight change is thereby determined and reported in terms of milligrams per square cm. of metal surface. A weight loss is reported as minus (-), while a weight gained is reported as plus (+).

The results obtained are summarized in the following Table II:

Table II
OXIDATION CORROSION STABILITY—Mg CORR. INHIBIT-
ING ADDITIVE

Metal	0.0%	0.5% Dilauryl thiodipropio- nate	0.1% Thiodi- propionic acid
Mg.-----	Dissolved	-24.90	Dissolved
Cu.-----	-0.46	-2.93	-2.49
Fe.-----	+0.10	+0.04	+0.05
Al.-----	+0.05	+0.03	+0.02
Ag.-----	+0.06	-0.01	+0.06
Ti.-----	+0.06	+0.01	+0.01

As seen by Table II, the lubricating oil composition per se, i.e. with 0.0% Mg corr. inhibiting additive, completely dissolved the magnesium test strip. At the same time the addition of 0.1 part by weight of the thiodipropionic acid to 100.0 parts by weight of said lubricating oil composition was ineffective in preventing the dissolution of the magnesium. On the other hand, the addition of 0.5 part by weight, i.e. 0.5% dilauryl thiodipropionate reduced the amount of dissolution of magnesium to 24.90 milligrams per sq. centimeter of the test strip. While the dilauryl thiodipropionate slightly increased the extent of copper corrosion as compared to the same oil without dilauryl thiodipropionate, this increase was well within established tolerances for the 450° F. test. On the other hand, it is to be noted that the dilauryl thiodipropionate also further inhibited the corrosion of iron, aluminum, silver and titanium.

Use of acid materials such as the thiopropionic acid per se, or even a half ester of thiopropionic acid, will not give results as good as can be obtained with the diesters of the invention. Also, the alcohol portion of the ester of the invention should contain 12 or more carbon atoms. Thus, di-2-ethylhexyl thiodipropionate has been suggested in U.S. Patent 2,947,599 to John L. Ennis, as a vapor phase inhibitor which can be used in an oil carrier to prevent magnesium corrosion. However, the longer chain alcohols are more effective for the purposes of the invention and have a lesser tendency to corrode copper as compared to esters prepared from the shorter chain alcohols.

EXAMPLE III

0.5 part by weight of various thiodipropionates were added to 100 parts by weight of the aircraft engine lubricating oil of Example I and then subjected to a modifica-

tion of the Oxidation Corrosion Stability test described in Example II, wherein the test was run at a temperature of 425° F. instead of the 450° F. temperature used in Example II.

The compositions tested and the results obtained are summarized in Table III which follows:

Table III

Mg Corr. Inh. Additive (parts):						
Monoisooctyl thiodipropionate		0.5				
Di-2-ethylhexyl thiodipropionate			0.5			
Di-n-hexadecyl thiodipropionate				0.5		
Di-tridecyl thiodipropionate					0.5	
Di-lauryl thiodipropionate						0.5
Oxidation Corr. Stability, 425° F., 48 hrs. (mg./sq. cm.):						
Cu	-1.48	-2.22	-2.28	-0.90	-1.23	-1.92
Mg	-6.55	-0.86	-0.46	-0.20	-0.22	-0.15
Fe	0.00	+0.03	+0.03	+0.03	+0.04	+0.02
Al	0.00	+0.02	+0.01	+0.01	+0.01	+0.01
Ag	-0.03	+0.01	-0.01	-0.04	-0.04	-0.04

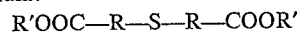
As seen by Table III, monoisooctyl thiodipropionate, and di-2-ethylhexyl thiodipropionate increased copper corrosion as compared to the oil composition with no magnesium corrosion inhibiting additive. On the other hand, the esters formed from hexadecyl, tridecyl and lauryl alcohols gave less copper corrosion, and at the same time, gave considerably less magnesium corrosion. Thus, each of the materials of the present invention have reduced the magnesium corrosion to acceptable limitations, i.e. within the range of ± 0.3 mg./sq. cm., which results were not obtained by any of the other materials subjected to this test.

To further illustrate the invention 0.5 part by weight of di-n-hexadecyl thiodipropionate is added to 100 parts by weight of di-2-ethylhexyl sebacate.

What is claimed is:

1. A lubricating oil composition suitable for aircraft engine lubrication comprising a major amount of carboxylic acid ester lubricating oil and a magnesium corrosion inhibiting amount within the range of about .001

to 10.0 wt. percent, based on the weight of the total composition, of an ester of thiodicarboxylic acid having the general formula:

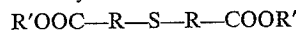


wherein each R is a hydrocarbon group containing 1 to 3 carbon atoms and R' is a C₁₂ to C₂₄ alkyl radical.

2. A lubricating composition according to claim 1, wherein said thiodicarboxylic acid is thiodipropionic acid.

3. A composition according to claim 1, wherein said ester lubricating oil is an ester of a C₆ to C₁₂ aliphatic dicarboxylic acid and a C₆ to C₁₆ aliphatic saturated alcohol.

4. A lubricating oil composition suitable for aircraft engine lubrication, comprising a major proportion of carboxylic acid ester lubricating oil and about 0.1 to 2.0 wt. percent, based on the weight of the total composition, of thiodicarboxylic acid ester of the formula:



wherein R is a C₁ to C₃ saturated hydrocarbon group and R' is a C₁₂ to C₁₈ alkyl group.

5. A composition according to claim 4, wherein said thiodicarboxylic acid ester is dilauryl thiodipropionate.

6. A composition according to claim 4, wherein said thiodicarboxylic acid ester is ditridecyl thiodipropionate.

7. A composition according to claim 4, wherein said thiodicarboxylic acid ester is dihexadecyl thiodipropionate.

8. A composition according to claim 4, wherein said thiodicarboxylic acid ester is distearyl thiodipropionate.

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DANIEL E. WYMAN, *Primary Examiner.*

L. G. XIARHOS, *Assistant Examiner.*