United States Patent Office 3,090,753 Patented May 21, 1963

3,090,753

ESTER OIL COMPOSITIONS CONTAINING ACID ANHYDRIDE

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No Drawing. Filed Aug. 2, 1960, Ser. No. 46,878
3 Claims. (Cl. 252—42.7)

This invention relates to lubricating oil compositions containing acid anhydrides. Particularly, the invention relates to synthetic ester lubricating oil compositions containing a minor amount of organic acid anhydride as a lead corrosion inhibitor.

The use of various diesters, polyesters and complex esters as lubricating oils is well known to the art and has been described in various patents, e.g. U.S. 2,723,286; 2,743,234 and 2,575,196. These ester oils are characterized by viscosity properties that are outstanding at both low and high temperatures, and in this respect are superior to the mineral oils. Because of their utility over extremely wide temperature ranges, the synthetic ester lubricating oils are widely used in the formation of lubricants for aircraft engines such as "turbo-jet," turbo-prop" and "pure-jet" aircraft. In such engines, lead-containing bearings are used and unfortunately, the synthetic esters per se are corrosive to such bearings. The present invention resides in the discovery that acid anhydrides may be directly added to ester oils in order to inhibit lead corrosion. At the same time, the anhydrides do not detract from the other desirable properties of the ester oil. In fact, the anhydrides tend to enhance other important properties of the composition, particularly the load-carrying ability of the oil.

The acid anhydrides of the invention include mono- or dianhydrides of carboxylic acids, particularly of hydrocarbon acids, i.e. where the entire molecule is made up of carbon and hydrogen except for the oxygen of the anhydride portions, containing about 8 to 50, preferably 8 to 30 carbon atoms per molecule. Such anhydrides will include those of aromatic, alicyclic, aliphatic, alkaryl, and other acids. Examples of these anhydrides include pyromellitic dianhydride, alkenyl succinic anhydride, phthalic anhydride, dialkyl pyromellitic monoanhydride, hemimellitic anhydride, trimellitic anhydride, naphthalic anhydride (1,8), prehnitic dianhydride, diphenic anhydride, and mellitic dianhydride.

The lubricants of the invention will comprise a major amount of an ester oil and dissolved therein, about 0.001 to 5.0 wt. percent, preferably 0.01 to 2.0 wt. percent, based upon the total amount of the lubricant, of anhydride.

The ester oils operable as base oils in the compositions of this invention comprise hydrocarbon chains interruped with 2 to 10 ester linkages, and which can be further interrupted with ether or thioether linkages. Included are diesters, polyesters, and complex esters.

The diesters are generally prepared from dicarboxylic acids fully esterified with monohydric alcohols, or from glycols fully esterified with monocarboxylic acids. The total number of carbon atoms in the diester molecule is generally about 18 to 36, preferably 20 to 28. Preferred dicarboxylic diesters are those of the formula:

ROOCR'COOR

wherein each R may be the same or different and represents the straight or branched chain alkyl radical of a monohydric alcohol having about 6 to 13 carbon atoms, while R' is a straight or branched chain C_2 to C_8 divalent saturated aliphatic hydrocarbon radical. Examples of such diesters include: di-2-ethylhexyl sebacate, di-C_{10} Oxo sebacate, di-nonyl sebacate, di-2,2,4-trimethylpentyl

sebacate, di-2-ethylhexyl azelate, di-2,2,4-trimethylpentyl azelate, di-C_8 Oxo azelate, di-n-heptyl isosebacate, di-C_{10} Oxo adipate, di-nonyl adipate, di-C_8 Oxo adipate, di-2-ethylhexyl adipate, mono C_8 Oxo, mono C_{10} Oxo adipate, di-C_7 Oxo adipate, di-C_8 trimethyl adipate, di-C_{13} Oxo pimelate, etc. Other operable diesters are those prepared from glycols and monocarboxylic acids such as dipropylene glycol dipelargonate and polyethylene glycol 200 dicaproate. Diesters prepared from the Oxo alcohols, which are isomeric mixtures of branched chain aliphatic primary alcohols, are particularly desirable. The Oxo alcohols have a very high degree of branching in the hydrocarbon chain, which results in diester oils having low pour points and low viscosities at low temperatures. These alcohols are prepared from olefins, such as polymers and copolymers of C_3 and C_4 monoolefins, which are reacted with carbon monoxide and hydrogen in the presence of a cobalt-containing catalyst such as a cobalt carbonyl, at temperatures of about 300° to 400° F., and under pressures of about 1000 to 3000 p.s.i. to form aldehydes. The resulting aldehyde product is then hydrogenated to form the Oxo alcohol which is then recovered by distillation from the hydrogenation product.

Operable polyesters are prepared by reacting polyhydric alcohols such as trimethylolpropane and pentaerythritol with monocarboxylic acids such as butyric acid, caproic acid, caprylic acid, pelargonic acid, etc. to give the corresponding tri- or tetraesters.

The complex esters which may be used as the base oils are formed by esterification reactions between a dicarboxylic acid, a glycol, and an alcohol and/or a monocarboxylic acid. These esters may be represented by the following formulas:

$$R_1COO—R_3—(OOCR_2COO—R_6)_n—OOCR_5$$
$$R_1—OOCR_2COO—(R_3—OOCR_4COO)_n—R_5$$
$$R_1—(OOCR_2COO—R_3)_n—OOCR_5$$

wherein: R_1 and R_5 are alkyl radicals of a monohydric alcohol or a monocarboxylic acid; R_2 and R_4 are hydrogen radicals of dicarboxylic acids, e.g. alkandioic acids; and R_3 and R_6 are divalent hydrocarbon or hydrocarbon-oxy radicals, such as $—CH_2(CH_2)_n—$, or

$$—CH_2CH_2(OCH_2CH_2)_n—$$

or

$$—CH_2CH(CH_3)OCH_2CH(CH_3)—$$

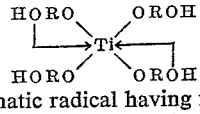
derived from an alkylene glycol or polyalkylene glycol. "n" in the complex ester molecule will usually range from 1 to 6 depending upon the product viscosity desired which is controlled by the relative molar ratio of the glycol or polyglycol to the dicarboxylic acid. In preparing the complex ester, there will always be some simple ester formed, i.e. $n=0$, but this will generally be a minor portion.

Some specific materials used in preparing the above types of complex esters are as follows: alcohols having 6 to 13 carbon atoms such as n-butyl alcohol, 2-ethylbutyl alcohol, 2-ethylhexanol, n-hexyl alcohol, C_8 Oxo alcohol and C_{10} Oxo alcohol, etc.; the corresponding fatty or monocarboxylic acids; C_6 to C_{10} dicarboxylic acids such as sebacic, adipic and azelaic; and glycols such as polyethylene glycol. In general the complex esters will have a total of 20 to 80, preferably 40 to 65, carbon atoms. These complex esters and methods for their preparation are known in the art and have been described in various patents.

The composition can also include other additives (e.g. 0.01 to 10.0 wt. percent). Included are oxidation inhibitors such as phenothiazine, dioctyl phenothiazine, dioctyl diphenylamine, phenyl α-naphthylamine, p-amino diphenyl amine; viscosity index improvers such as polymethacrylates, polystyrene; anti-foamants such as dimeth-

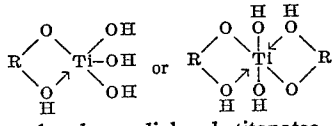
ylsilicone polymers; anti-wear agents such as tricresyl phosphate; load-carrying agents; etc.

Particularly, desirable load-carrying agents are various alkylene glycol titanates. These materials may be represented by the general formula:



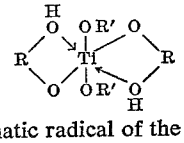
where R is an aliphatic radical having from about 3 to 15, and preferably from 6 to 12, carbon atoms. It is, of course, possible for both hydroxyl groups of one glycol to react with two of the acidic groups of titanic acid molecules to form polymeric materials.

The more probable formulae for the glycol titanates are



for the monoglycol or diglycol titanates, respectively, where R is the aliphatic radical of the glycol as heretofore stated.

Alkoxy glycol titanates are also contemplated, represented by the formula:



where R is the aliphatic radical of the glycol as heretofore stated and R′ is an aliphatic radical of from 3 to 12 carbon atoms, e.g. dibutoxy di(hexylene glycol) titanate.

Specific examples of the titanates include hexylene glycol titanate, dodecylene glycol titanate, octylene glycol titanate, and dibutoxy di(hexylene glycol) titanate. Titanates of the preceding types are known in the art and have been described in various patents, e.g. U. S. Patent No. 2,643,262.

The titanates are preferably used in amounts of 0.01 to 5.0 wt. percent as load-carrying agents. While extremely effective for carrying load, titanates are very corrosive to copper and lead. Although conventional lead and copper corrosion inhibitors were not effective with titanates, the anhydrides of the present invention are effective.

The present invention will be further understood by reference to the following examples which include preferred embodiments of the present invention:

EXAMPLE I

A base oil material was prepared consisting of 100 parts by weight of 50 volume percent of a di-C_{10} Oxo adipate and 50 volume wt. percent of di-C_8 Oxo adipate, and 1 part by weight of phenothiazine as an antioxidant.

To the above base oil was added pyromellitic dianhydride, and/or an alkylene glycol titanate in various amounts. The titanate was a solution of about 30 wt. percent n-butyl alcohol and about 70 wt. percent of tetra-(octylene glycol) titanate prepared by transesterification of one molar amount of tetra n-butyl titanate with four molar amounts of 2-ethyl-hexane diol. This was a commercial product sold by DuPont under the tradename OGT-41. The resulting blends were then tested for lead corrosion inhibition in accordance with the MIL-L-7808 specification procedure. This test procedure is carried out by rapidly rotating a weighed bi-metallic strip, consisting of a lead strip and a copper strip bound together, in the oil sample maintained at 325° F. while air is bubbled through the sample. The weight loss of the strip is determined in terms of milligram weight loss per sq. inch of lead surface at the end of 1, 4, 8 and 12 hours of operation. The compositions prepared and the results obtained are summarized in Table I, which follows:

Table I

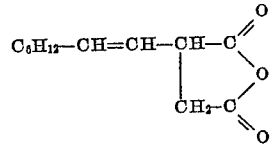
EFFECT OF PYROMELLITIC DIANHYDRIDE (PMDA) ON LEAD CORROSION

	Lead corrosion test loss in mg./in.²			
	1 hour	4 hours	8 hours	12 hours
A. Base [1]	0.4	0.6	0.6	1.8
B. A plus 0.05 weight percent PMDA	0	0	0	0
C. A plus 1 weight percent tetra-(octylene glycol) titanate	65	195	454	750
D. C plus 0.1 weight percent PMDA	0	0	30	220
E. C plus 0.2 weight percent PMDA	0	0	0	0
F. C plus 0.3 weight percent PMDA	0	0	1	1
G. C plus 0.4 weight percent PMDA [2]	0.2	0.4	16	51
H. A plus 3 weight percent tetra-(octylene glycol) titanate	37	172	477	798
I. H plus 0.1 weight percent PMDA	25	124	447	788
J. H plus 0.2 weight percent PMDA	0	4	36	441
K. H plus 0.3 weight percent PMDA	1	42	323	682
L. H plus 0.4 weight percent PMDA [2]	0	0	8	400

[1] 50 vol. percent di-C_{10} Oxo adipate, 50 vol. percent di-C_8 Oxo adipate plus 1 weight percent phenothiazine.
[2] Some PMDA precipitated.

EXAMPLE II

An ester oil mixture was prepared consisting of 50 volume percent di-C_8 Oxo adipate and 50 volume percent of di-C_{10} Oxo adipate. To this oil mixture was added 0.5 wt. percent phenothiazine as antioxidant, and 0.001 wt. percent of a diamethyl silicone having a viscosity of 60,000 cs. at 25° C. as an antifoamant. To this base oil composition was added 0.6 wt. percent of a C_8 alkenyl succinic anhydride having the formula:



The base oil composition per se and the base oil composition containing the succinic anhydride were tested in the lead corrosion test previously described above, and in an oxidation-corrosion test which determined the oxidative stability and the corrosivity of the compositions to copper, magnesium, iron, aluminum and silver. These tests were carried out in accordance with MIL-L-7808C specification procedures. In the oxidation-corrosion test, weighed strips of the metals to be tested were immersed in 100 cc. of the oil sample maintained at 347° F. for 72 hours while 0.5 liter per hour of air was bubbled through the sample. The metal strips were then reweighed to determine the corrosivity of the oil as indicated by the weight change in mg./cm.². The oxidative stability of the oil was shown by the change in viscosity and neutralization number of the oil after testing.

The results of the above tests are summarized in Table II which follows:

Table II

EFFECT OF C_8 ALKENYL SUCCINIC ANHYDRIDE

	Adipate base [1]	Adipate base plus 0.6% anhydride
Lead corrosion test, mg./in.²:		
1 hr.	4.4	0
4 hrs.	21	0
8 hrs.	89	0
12 hrs.	340	1.2
347° F. oxidation corrosion test:		
Cu	0.01	0.01
Mg	0.01	0.03
Fe	0.01	0.01
Al	0.01	0.02
Ag	0.01	−0.02
Δ neut. number	0.87	0.47
Δ vis./100%	3.6	2.0

[1] Adipate Base: 50 vol. percent C_8 Oxo adipate plus 50 vol. percent C_{10} Oxo adipate plus 0.5 weight percent phenothiazine plus 0.001 weight percent DC-200 (60,000 cs.) silicone.

EXAMPLE III

A base oil composition consisting predominantly of di-C_8/C_{10} Oxo adipate and di-octyl sebacate plus various lubricating oil additives was prepared and stored for six months, during which time it had developed a high corrosivity toward lead. To samples of this highly corrosive base oil were then added phthalic anhydride and pyromellitic anhydride to determine their effect on reducing the lead corrosion of the base oil. From the results shown in the following table it will be noted that each anhydride inhibits the lead corrosivity of the base oil but that the pyromellitic dianhydride is more effective than the phthalic anhydride. This is also true when the corrosive oil is stored under high temperature conditions for 14 days.

Table III

EFFECT OF PHTHALIC ANHYDRIDE AND PYROMELLITIC DIANHYDRIDE ON LEAD CORROSION

	Lead corrosion test loss in mg./in.^{2}			
	1 hour	4 hours	8 hours	12 hours
Base oil	0	625	975	1,430
Base oil plus 0.2 weight percent phthalic anhydride	0	95	103	107
Base oil plus 0.2 weight percent pyromellitic dianhydride	0	0	0	0

EXAMPLE IV

It has been found that when the acid anhydride is to be used with an alkylene glycol titanate, excellent results are also obtained upon heating the titanate and anhydride to temperatures of about 275° to 325° F. for about 0.1 to 1.0 hour. It is believed that this heating results in the formation of a complex between the glycol titanate and the anhydride. Alternatively the two materials may be mixed cold, i.e. at room temperature in the ester oil relying upon the heating of the lubricating oil during use to help promote the reaction.

100 grams of the previously described tetra (octylene glycol) titanate prepared from 2-ethylhexane diol was dissolved in 100 grams of di(C_{10} Oxo) adipate and the solution heated to 300° F. to remove much of the diluent n-butyl alcohol introduced with the titanate. At this point 10 grams of pyromellitic dianhydride was added and stirred into the mixture. The mixture was then further heated for about 0.3 hour. Upon cooling, the resulting complex titanate solution was then used in formultaing two lubricating oil blends as follows:

Blend A.—The blend was prepared, wherein all parts are by weight, by simple mixing of 100 parts of di(2-ethylhexyl) sebacate, 1 part phenothiazine, 0.001 part of silicone anti-foamant and 0.7 part of the solution of complex of octylene glycol titanate and pyromellitic dianhydride. The composition carried 3,765 pound/inch load in the Ryder gear test and showed no corrosion in the lead corrosion test after 12 hours. On the other hand, the sebacate ester without the complex will carry only about 1,900 lb./in. in the Ryder gear test, while the addition to the titanate per se to the ester oil would result in severe lead corrosion.

Blend B.—To 100 parts by weight of a 50/50 volume mixture of di(C_8 Oxo) adipate and di(C_{10} Oxo) adipate was added 0.7 part by weight of phenothiazine and 0.7 part by weight of the solution of complex titanate. This composition carried 3,440 lb./in. load in the Ryder gear test. It also showed only 5.0 mg./in.^{2} weight loss in the lead corrosion test at the end of 12 hours, which is within acceptable limits.

In sum, the present invention includes the addition to lubricating oils of mono- and di-anhydrides of the formula: $R(X)_n$ where R is a hydrocarbon radical, X is the anhydride group and n is one or two. R can also include a carboxylic acid group substituted on the hydrocarbon chain. The total number of carbon atoms in the molecule will be 8 to 50, e.g. 8 to 30. As a further aspect of the invention, heating the anhydride with alkylene glycol titanates, either mono-, di-, tri-, or tetra-titanates or mixtures thereof results in some sort of a complex which is particularly useful as a load-carrying agent with low corrosivity to lead.

What is claimed is:

1. A synthetic ester lubricating oil composition comprising a major proportion of carboxylic acid ester lubricating oil and about 0.001 to 5.0 wt. percent of pyromellitic dianhydride.

2. A synthetic ester lubricating oil composition according to claim 1, which also contains about 0.01 to 5.0 wt. percent of an alkylene glycol titanate prepared from C_3 to C_{15} aliphatic glycol.

3. A lubricating oil composition comprising a major proportion of diester of the formula:

ROOCR'COOR

wherein R represents a C_6 to C_{13} alkyl radical and R' is a C_2 to C_8 aliphatic hydrocarbon radical, and about 0.001 to 5.0 wt. percent based upon the total composition, of pyromellitic dianhydride.

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