FLUORINATED ORGANIC COMPOUNDS AS OIL AND DISTILLATE FUEL ADDITIVES

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14 Claims

ABSTRACT OF THE DISCLOSURE

An oil soluble nitrogen-containing reaction product of an aromatic amine having about 6 to 40 carbon atoms and a fluorinated organic compound selected from the group consisting of a fluorinated monobasic saturated carboxylic acid having 2 to 21 carbon atoms and having no secondary or tertiary hydrogens or a fluorinated monobasic saturated carboxylic acid chloride having 2 to 21 carbon atoms and having no secondary or tertiary hydrogens inhibits the corrosivity of lubricating oils and distillate oils and in addition displays load carrying ability and cleanliness characteristics in such oils not shown by similar additive compounds.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to lubricating compositions which contain as additives certain fluorinated organic compounds. More particularly, it relates to fluorinated compounds as lubricating oil additives which are prepared from aromatic amines and fluorinated carboxylic acids or acid chlorides.

Description of the prior art

Problems associated with lubricating compositions, especially those compositions prepared for use in high performance jet aircraft such as the SST engine, include its corrosivity to metals, lack of cleanliness during engine operation, and inadequate load carrying ability. Lubricating oils under the stress of high temperatures and pressures decompose into products which may corrode vital engine parts or leave harmful deposits which interfere with efficient engine operation. Also, in jet engines, the load the lubricant is forced to bear is high. The lubricating art is filled with myriads of corrosion inhibitors and load carrying improvers, among these being certain fluorinated compounds as found in U.S. Pat. 3,269,948, and Canadian Pat. No. 764,482. These fluorinated compounds, however, have been found to be unsatisfactory, as they produce sludge and other deposits on lubricating surfaces.

SUMMARY OF THE INVENTION

A new lubricating composition has been developed which demonstrates the properties of being minimally corrosive to engine parts while also exhibiting cleanliness properties and load carrying abilities not demonstrated by similar art-known compositions. This lubricating composition comprises (a) a major amount of lubricating oil and (b) a minor amount of an oil soluble nitrogen-containing reaction product of an aromatic amine having about 6 to 40 carbon atoms and a fluorinated organic compound selected from the group consisting of a fluorinated monobasic saturated carboxylic acid having 2 to 21 carbon atoms and having no secondary or tertiary hydrogens and a fluorinated monobasic saturated carboxylic acid chloride having 2 to 21 carbon atoms and having no secondary or tertiary hydrogens.

The oil soluble nitrogen-containing reaction product will be an amide or amine salt depending on whether the acid or acid chloride of the fluorinated compound is employed as a reactant material. If the fluorinated acid is the reactant, the product will be an amine salt, whereas the acid chloride will produce an amide. The fluorinated additive of this invention is prepared in the usual manner of producing amine salts or amides. The reactants are mixed together with an inert organic solvent and refluxed for a time sufficient to produce the product. The product may then be purified by art-known filtering, washing and recrystallization procedures.

The aromatic amine reactant is generally characterized as having 6 to 40 carbon atoms, preferably 6 to 28 carbon atoms. The aromatic amine may also be characterized as being polynuclear, i.e. having two or three fused rings, but preferably is mononuclear, i.e. having no fused aromatic rings. This reactant may be a poly- or mono-amino, preferably a mono-amino. The aromatic amine may be primary, secondary or tertiary, preferably primary. The aromatic ring of the amine may be substituted or unsubstituted. There may be attached to the aromatic ring functional groups other than an amino group, such as alkyl hydroxy, alkoxy, halo, or ester groups. Heterocyclic amines may also be employed as reactants. Specific examples of aromatic amines include aniline, toluidine, o-toluidine, bis-(octylphenyl)-amine, 2,4,6-trifluoro-m-toluidine, N-ethyl bis-(octylphenyl)-amine, phenyl naphthalamine, p-aminophenol, and p-nitrophenol. Specific examples of heterocyclic amines may include 2-amino pyridine.

The preferred aromatic amine has a general structural formula:

where R is H, C₂ to C₅ normal or branched alkyl, or —COOR₁, where R₁ is a C₁ to C₅, preferably C₁ to C₃ normal or branched alkyl group. Specific examples of these aromatic amines include methyl antranilate, propyl antranilate, ethyl antranilate, ethyl p-amino benzoate, toluidine, octylaniline and aniline.

The fluorinated acid or acid chloride reactants will preferably have 1 to 12 carbon atoms and may have a branched or normal structure, preferably normal. It is essential that no secondary or tertiary hydrocarbons occupy any position in the fluorinated compound, as the fluorinated compound is under the high stress of engine operation. This elimination is not likely if the hydrocarbon occupies a primary position at the end of the acid or acid chloride.

The preferred fluorinated reactant has the general structural formula:

where R₂ is selected from the group consisting of hydroxyl and fluoro, preferably fluoro. Z is selected from the group consisting of hydroxyl and chlorine and n is a number which varies from 1 to 20, preferably 1 to 12. This fluorinated reactant is preferably of a normal structure.

Examples of operable acid and acid chlorides include, but are not limited to, the following: trifluoroacetic acid, hexafluorobutyric acid, pentadecafluorocitramide acid, and their corresponding acid chlorides.

The liquid lubricating oil composition of this invention will comprise a major portion of the lubricating oil, that is greater than 50 wt. percent, and 0.01 to 5 wt. percent, usually 0.1 to 3 wt. percent, based on the total weight of the composition, of the additive compounds described above. The lubricating oil composition may also be pre-
pared in concentrate form, in which case the nitrogen-containing reaction product additive would form 10 to 80 wt.

The liquid compositions useful in this invention are mineral lubricating oils, synthetic lubricating oils and dis-
tillate fuels boiling in the range from about 50° F. to 750° F. Some synthetic lubricating oils include diethyl-
hexyl sebacate, carbonate esters, glycol esters such as C_{12} o xo acid diesters of tetraethylene glycol, ether diesters,
silicone polymers, complex esters as, for example, the complex ester formed by the reaction of 1 mole of sebacic
acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid, etc. The fluorinated additive is pref-
erably used in synthetic ester base stocks such as esters of trimethylolpropane and normal or branched C_{5} to
C_{7} monocarboxylic acids, esters of pentaerythritol and such carboxylic acids, and esters of neopentyl glycol and such carboxylic acids. The lubricating oil will have a viscosity at 210° F. in the range of 30 to 200 SUS, preferably 35 to 100 SUS at 210° F. and a viscosity index in the range of 0 to 150.

The oil-soluble nitrogen-containing additive is incorpo-
rated into the lubricating composition by dissolving it in the desired quantity into warm lubricating oil. No special procedures are required.

In addition to reducing wear and deposits in lubricating compositions, the nitrogen-containing reaction product of the aromatic amine and fluorinated acid or acid chloride may also be employed in distillate fuels for the same purpose. The liquid fuel composition will comprise a ma-
jor portion of liquid fuel (above about 50 wt. percent) and about 0.01 to 5 wt. percent, based on the total weight of the composition of the nitrogen-containing reaction product.

The distillate fuels which may be employed include avi-
ation turbo-jet fuels, rocket fuel (MIL-R-25576B), gas-
olines, kerosenes, diesel fuels and heating oils. Aviation turbo-jet fuels in which the amine salts of the present invention may be used normally boil between about 50° F. and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL-F-5624F, MIL-F-
25565A, MIL-F-25554A, MIL-F-25558B, and amend-
ments thereto, and in ASTM D-1655–62T. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully de-
scribed in ASTM Specification D-396–48T and supple-
ments thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the amine salts may be employed are described in detail in ASTM Specification
D-975–35T and later versions of the same specification.

Gasolines which may be beneficial include both mot-
or gasolines and aviation gasolines such as those defined by

Other additives which may be used in the liquid fuel
and lubricant compositions of this invention include vis-
cosity index improvers, pour point depressors, corrosion
inhibitors, thickeners, sludge dispersants, rust inhibitors,
anti-embrittling agents, anti-oxidants, dyes, dye stabilizers
and the like.

**DESCRIPTION OF THE PREFERRED EMBODIMENT**

The following examples are submitted as illustrating the practice of this invention. Such examples are not to be
considered as limiting the scope of this invention, how-
over.

**EXAMPLE I**

A solution of 60.5 g. (0.4 mole) methyl anthranilate in 300 ml. of anhydrous ether was charged to a 1 liter
flask fitted with an air stirrer, condenser, thermometer and dropping funnel. A solution of 165.7 g. (0.4 mole)
pentadecafluoroocanocanoic acid in 300 ml. of anhy-
drous ether was added dropwise with rapid stirring over 1 period of 30 minutes. The mixture was stirred at reflux
for about 2 hours and cooled to 0° C. The product, a white precipitate, was filtered, washed with additional cold ether and dried. The crude product was recrystallized from chloroform to yield 158 g. (70.5% yield) of white needles having a melting point of 124.5–125° C. The em-

**EXAMPLE II**

Methyl anthranilate and heptafluorobutyric acid were reacted according to the procedures of Example I. The puri-

**TABLE I**

| Lubricant composition | Cu | Mg | Per- | T.A.N. |
|-----------------------|----|----|cent|-------|
| Base oil base oil | -0.11 | -0.95 | 35.65 | 5.38 |
| Base oil (100 parts by wt.) plus 0.25 parts by wt. of Re I amine salt | -0.34 | -0.61 | 36.28 | 8.63 |
| Base oil (100 parts by wt.) plus 0.25 parts by wt. of Re II amine salt | -0.59 | -0.92 | 35.55 | 6.62 |

The 425° F. Oxidation-Corrosion-Stability Test was carried out by blowing air at the ratio of 5 liters per hour through 100 grams of the lubricating composition main-
tained at a temperature of 425° F. for 72 hours. At the end of the test, the percentage increase in viscosity and change in total acid number (T.A.N.) were determined.

The corrosive characteristics of the lubricant were deter-
mained by immersing various weighed metal coupons in
the oil and measuring weight change at the end of the test.

The change in weight signifies either corrosion due to
dissolution of the metal or weight gain due to deposits.

The test is used to determine if lubricants offer sufficient
protection for critical metal components of engines and
accessories when operated at high temperatures.
From the data in Table I it an be readily seen that the additive reaction products of Examples I and II dramatically reduce magnesium corrosion.

**EXEMPLARY III**

To a 5 liter 4-neck flask fitted with a stirrer, condenser, thermometer and funnel was charged 432.6 g. (1.0 mole)pentadecafluoroctanoic chloride, 1600 ml. of dry toluene and 158 g. pyridine. This mixture was heated to 90°C and a hot (about 80°C) solution of 165.2 g. (1.0 mole) ethyl p-amino-benzamide dissolved in 1400 ml. of toluene added over a 30-minute period. This mixture was then refluxed for four hours and filtered hot through a steam-jacketed Buchner funnel. The filtrate was then cooled to —20°C, which resulted in the crystallization from solution of a pink solid. The crude product was filtered from solution and recrystallized from 2 liters of toluene to yield 440 g. (78.5% yield) of white needles having a melting point of 127.5—129°C.

As some pyridine hydrochloride was still present in this product, further purification was necessary. Two hundred fifty grams of the product was dissolved in acetone and filtered. The filtrate was added dropwise with stirring to 450 ml. of distilled water to precipitate the product. A solution of 75 parts acetone and 45 parts water was added to facilitate the stirring, which was continued for one hour. The resulting white solid was filtered, washed with an acetone-water solution and dried to constant weight. A white solid weighing 230 grams was obtained.

The empirical formula of the expected product was C_{32}H_{35}O_{2}N_{2}F_{14}. A elemental analysis of the carbon fluorine and chloride carried out with the following results:

Theory (percent): C, 36.38; F, 50.78; Cl, nil. Found (two trials), percent: C, 36.65, 36.90; F, 52.1, 49.5; Cl, 0.01, 0.00.

The reaction product was then determined to be ethyl (p-pentadecafluoroctanamido) benzene, an amide.

To determine the cleanliness of lubricating compositions containing the aromatic reaction product of the invention, such compositions were subjected to the Type II Bearing Rig Test. For purposes of comparison, lubrication compositions containing the aliphatic amine salt of U.S. 3,269,948 were also tested. The results of these tests are listed in Table II.

<table>
<thead>
<tr>
<th>Lubricant composition</th>
<th>Demerit rating</th>
<th>ΔV, 90°</th>
<th>ΔT.A.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil A</td>
<td>82.5</td>
<td>266</td>
<td>6.34</td>
</tr>
<tr>
<td>Oil B (100 parts by wt. plus 1 part by wt. auxiliary additive),</td>
<td>86.2</td>
<td>224</td>
<td>4.69</td>
</tr>
<tr>
<td>plus 0.5 parts by wt. PFAS-808</td>
<td>86.3</td>
<td>221</td>
<td>4.67</td>
</tr>
<tr>
<td>Oil C (100 parts by wt. plus 0.25 part by wt. PFAS-808),</td>
<td>103.9</td>
<td>101</td>
<td>4.74</td>
</tr>
<tr>
<td>plus 0.25 part by wt. FAB</td>
<td>95.9</td>
<td>230</td>
<td>0.25</td>
</tr>
<tr>
<td>Oil D (100 parts by wt. plus 1 part by wt. auxiliary additive),</td>
<td>78.4</td>
<td>220</td>
<td>0.50</td>
</tr>
<tr>
<td>plus 0.5 parts by wt. FAB</td>
<td>65.3</td>
<td>195</td>
<td>0.50</td>
</tr>
</tbody>
</table>

1 Oil A is a conventional lubricant composition having a synthetic ester base plus various conventional anti-rustants, dispersants, and corrosion inhibitors.
2 Auxiliary additive, a dimer acid derivative.
3 PFAS-80 is a amine, a reaction product of pentadecafluoroctanoic acid and Primene JM-T, the aliphatic amine H—CH—NH₂ where it is a mixture of isomers having 18-22 carbon atoms with a tetra-silyl structure.
4 Oil B is a conventional lubricant composition having a synthetic ester base plus various conventional anti-rustants, dispersants and corrosion inhibitors.
5 PFAS-808 is the amine salt of Example I.
6 FAB is the amine of Example III.

In a Type II Bearing Rig Test a 100 mm. diameter aircraft type steel roller bearing rotated at 10,000 r.p.m. is maintained at a temperature of 500°F, while being sprayed with a jet of the oil composition heated to a temperature of about 440°F, in a sump so as to have a jet temperature of 400°F. The oil falls off the bearing into a reservoir or sump which is picked up by a pump and recirculated. The total amount of oil in the circulating system is about 2 gallons. The viscosity of the oil is checked at 10 hour periods until a period of 100 hours has passed. Oils showing good oxidation stability will show very little change in viscosity and total acid number during the bearing test, while oils poor in oxidation stability will tend to break down and rapidly increase in viscosity and total acid number. Also at the end of the 100 hour test, the bearing is examined for cleanliness.

Cleanliness is determined by the amount of deposits on bearing parts. The parts are visually inspected and each part given a rating from 0 to 20, with 0 being clean. Each bearing part is weighed in importance and a total rating called a demerit rating compiled for the entire bearing assembly. The lower the demerit rating, the cleaner the bearing assembly. This procedure can be found in Method No. 3410 of Federal Test Method Standard Number 791. The oil temperature in a Type II test is 450±5°F.

No substantial difference in change in viscosity or total acid number is observed between the aliphatic and aromatic additives. The advantage of the aromatic reaction product over the aliphatic reaction product can be seen by comparing the demerit rating results obtained. The demerit rating for oils containing the additive of Example I and Example III was 82.9 and 78.4 respectively, while the demerit rating for the oil containing the aliphatic salt was 106.9. This represents about a 15% improvement over containing aliphatic salts, which is a significant improvement. The effect of the auxiliary additive on demerit rating is essentially negligible, as can be seen from comparing its effect in Oil A in Table II.

**EXEMPLARY IV**

According to the procedure of Example I, an amine salt of morpholine and pentadecafluoroctanoic acid was prepared. The salt had a melting point of 110.5-111.5°C. According to the procedures of Example I an amine salt of 2-amino pyridine and pentadecafluoroctanoic acid was prepared. The salt had a melting point of 135-137°C.

According to the procedures of Example I an amine salt of 1-aminoanthraquinone and heptafluorobutyric acid was prepared having a melting point of 201-205°C.

According to the procedures of Example I an amine salt of benzotriazole and pentadecafluoroctanoic acid was prepared having a melting point of 68-70°C.

According to the procedures of Example III, an amine was prepared from butyl p-amino-benzene and pentadecafluoroctanoic acid having a melting point of 113.5-115.5°C.

The amine salt and amine products described in this example are added to mineral or synthetic base lubricating oils in amounts ranging from 0.01 to 5 wt. percent, based on the total lubricating composition, to form lubricants having improved corrosivity and cleanliness properties.

The effect of the fluorinated organic compound described herein on the load carrying ability of the lubricating compositions of this invention was determined through Ryder Gear Load Tests. The results of these tests are recorded in Table III below.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Ryder Gear Load, p.s.i. (avg. of two sides)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Base oil</td>
<td>2,400</td>
</tr>
<tr>
<td>Base oil (100 parts by wt.) plus 0.5 part by weight of the amine of Example I</td>
<td>2,110</td>
</tr>
<tr>
<td>Base oil (100 parts by wt.) plus 0.25 part by weight of the amine of Example I</td>
<td>2,130</td>
</tr>
<tr>
<td>Base oil (100 parts by wt.) plus 0.5 parts by weight of amine salt of butylatherfluorobutyric acid</td>
<td>2,106</td>
</tr>
</tbody>
</table>

1 The base oil is Oil A of Table II.

The Ryder Gear Load's test number is Federal Test Method Standard No. 791, Test No. 6508. From the data of Table III it can be seen that the fluorinated material
of the lubricating composition of this invention imparts excellent load carrying ability to that composition.

What is claimed is:

1. A liquid composition comprising:
   (a) a major amount of a liquid selected from the group consisting of lubricating oils and distillate fuels boiling in the range of 50° F. to 750° F.; and
   (b) about 0.01 to 5 wt. percent, based on the total weight of the composition, of (1) an amide of a fluorinated monobasic saturated carboxylic acid chloride having 2 to 21 carbon atoms and having no secondary or tertiary hydrogen atoms and an aromatic amine having 6 to 40 carbon atoms or (2) an amine salt of a fluorinated monobasic saturated carboxylic acid having 2 to 21 carbon atoms and having no secondary or tertiary hydrogen atoms and an aromatic amine having 6 to 40 carbon atoms.

2. A liquid composition as in claim 1 wherein the aromatic amine has the general structural formula:

\[
\begin{array}{c}
\text{R} \\
\text{NH}_2
\end{array}
\]

where \( R \) is selected from the group consisting of \( \text{H}, \text{a C}_1-\text{C}_{20} \text{ alkyl group and COOR}_2, \text{where C}_1 \text{ is a C}_4 \text{ to C}_{14} \text{ alkyl group.} \)

3. A liquid composition as in claim 2 wherein the fluorinated organic compound has the general structural formula:

\[
\text{R}_2(\text{CF}_2)_n\text{COZ}
\]

where \( R \) is selected from the group consisting of hydroxyl and fluoride, \( Z \) is selected from the group consisting of hydroxyl and chloride and \( n \) is a number which varies from 1 to 20.

4. A liquid composition as in claim 3 wherein the liquid is a lubricating oil.

5. A lubricating oil composition as in claim 4 wherein \( R_2 \) is a fluorine atom.

6. A lubricating oil composition as in claim 5 wherein \( R \) is a C, to C, normal alkyl group.

7. A lubricating oil composition as in claim 6 wherein the lubricating oil is a synthetic oil.

8. A lubricating oil composition as in claim 7 wherein the fluorinated organic compound reactant has a normal structure.

9. A lubricating oil composition as in claim 8 wherein \( n \) varies from 1 to 12.

10. A lubricating oil composition as in claim 9 wherein \( R_2 \) is a C, to C, normal alkyl group.

11. A lubricating oil composition as in claim 10 wherein \( R_2 \) is ethyl.

12. A lubricating oil composition as in claim 11 wherein the fluorinated organic reactant is pentadecafluoroocanic acid.

13. A lubricating oil composition as in claim 12 wherein \( Z \) is chlorite.

14. An additive concentrate comprising a lubricating oil and from 10 to 80 wt. percent of the nitrogen-containing reaction product of claim 13.

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W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

252—34, 51.5A, 392, 403; 44—58, 66, 71