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3,642,632

ANTHRANILIC ACID ESTERS AS LUBRICANT ADDITIVES

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No Drawing. Filed May 24, 1968, Ser. No. 731,735

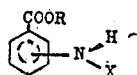
Int. Cl. C10m 1/26, 1/32

U.S. Cl. 252—51.5 A

4 Claims

ABSTRACT OF THE DISCLOSURE

An ester of anthranilic acid or an ester of a derivative such acid having the general structural formula:



where R is a C₁ to C₁₀ alkyl group and X is hydrogen, alkyl or a phenyl group, has been found to be an effective oxidation and corrosion inhibitor in lubricating oils, especially synthetic ester oils.

BACKGROUND OF THE INVENTION

Field of the invention

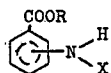
The invention relates to lubricant compositions and in a more particular sense to synthetic oil compositions having improved resistance to deterioration under high performance service conditions. The improved resistance to deterioration may be attributed to the incorporation of esters of anthranilic acid as additives to the lubricant.

Description of the prior art

The problem of deterioration of lubricating oils and formation of harmful deposits under high performance service conditions has been the cause of much concern in providing satisfactory lubrication of internal combustion engines. This problem is especially acute in lubricating engines of the gas turbine type, e.g. turbojet, turboprop and turbofan engines, where lubricants encounter extremely high temperatures. These severe service conditions, which favor oxidation reactions, may break a lubricant down into harmful acidic products which attack the metal parts of the engine or which may act as further oxidation catalysts. The problem is especially serious with regard to magnesium corrosion. Magnesium, which is finding ever increasing use as a constituent of light weight metal engines, is especially susceptible to attack by the acidic products of a deteriorated lubricant. In recent years it has been the practice to incorporate into lubricating oils additive compositions to inhibit oxidation and corrosion. Anthranilic acid has been mentioned in U.S. Pats. 3,151,075 and 3,146,201 as additives for lubricating oils. This compound, however, is totally unacceptable for use in jet type engines. Investigation has shown that anthranilic acid at high temperatures becomes extremely corrosive to engine parts.

SUMMARY OF THE INVENTION

It has now been found that an anthranilic acid derivative having the general structural formula:



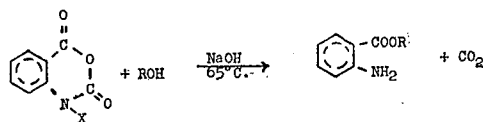
where R is a C₁ to C₁₀, preferably a C₁ to C₈ normal or branched alkyl group and X is selected from the group consisting of hydrogen, a C₁ to C₆ normal or branched alkyl group and an unsubstituted or alkyl substituted phenyl group, is an effective oxidation and corrosion in-

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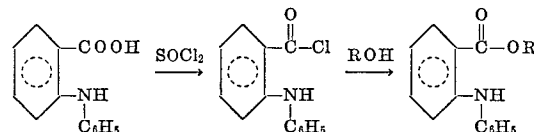
hibitor in lubricating oils. This compound is especially effective in inhibiting magnesium corrosion. This additive, which will be recognized as a specific class of amines, is an ester of anthranilic acid or an ester of a derivative of that acid. The amount of the ester incorporated into the lubricating oil is a minor corrosion and oxidation inhibiting amount, usually 0.5 to 4.0 wt. percent based on the total amount of the final lubricating composition.

Examples of anthranilic acid derivatives which may be employed in the lubricating composition of this invention include esters of anthranilic acid such as methyl anthranilate, ethyl anthranilate, propyl anthranilate, 2-ethylhexyl anthranilate, etc. and esters of derivatives of anthranilic acid (i.e. X is other than hydrogen) such as methyl-N-methyl-anthranilate, 2-ethylhexyl-N-methyl anthranilate, methyl-N-phenyl anthranilate, 2-ethylhexyl-N-phenyl anthranilate, isodecyl-N-phenyl anthranilate, methyl-N-ethylphenyl anthranilate, etc.

The esters described above may generally be prepared by reacting an anthranilic anhydride with an appropriate alcohol according to the following reaction:



where X is hydrogen or an alkyl group. The ester may also be prepared via the acid chloride route which is particularly appropriate, where X is a phenyl group.



Isatoic anhydride (the anhydride of anthranilic acid) is available from Maumee Chemical Company. N-methyl isatoic anhydride is available from Aldrich Chemical Company. N-phenylanthranilic acid is available from Eastman Kodak Company. Methods of producing the esters generally described above have been discussed in French Pat. 1,363,127 and in the Journal of Organic Chemistry, volume 24, p. 1214 (1959).

The ester additive will generally be used in lubricants which encounter high performance service conditions such as encountered in the operation of modern jet type aircraft. Generally, the basestocks of such lubricants are synthetic ester oils. It is in this type of lubricant which the ester dramatically demonstrates its effectiveness. It is contemplated, however, that the ester additive can be used in mineral oils.

The mineral or synthetic oils in which these esters are employed generally should have a viscosity within the range of about 35 to 200 SUS at 210° F. and flash points of about 350° to 600° F. Lubricating oils having a viscosity index of 100 or higher may be employed.

The synthetic oils include synthetic lubricating oils having a viscosity of at least 30 SUS at 100° F., such as esters of monobasic acids (e.g. ester of C₈ Oxo alcohol with C₈ Oxo acid, ester of C₁₃ Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e.g. di-2-ethyl hexyl sebacate, dinonyl adipate, etc.), esters of glycols (e.g. C₁₃ Oxo acid diester of tetraethylene glycol, etc.), complex esters (e.g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, complex ester formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl hex-

anol, complex ester formed by reacting together one mole of azelaic acid, one mole of tetraethylene glycol, one mole

the tests, an average of several runs, are recorded in the table below.

TABLE

Lubricant additive	425° F., 48 hour O.C.S. test					$\Delta kv/$ 100° F. cs.	Δtan
	Δ metal weight, mg./cm. ²						
	Cu	Mg	Steel	Al	Ag		
Methyl anthranilate	+0.01	-0.03	-0.01	-0.01	-0.04	15.30	3.26
2-Ethylhexyl anthranilate	-0.05	+0.01	+0.01	-0.05	-0.04	14.00	1.41
Methyl-N-phenyl anthranilate	-0.02	-0.07	+0.01	+0.04	+0.04	16.59	7.21
2-ethylhexyl-N-phenyl anthranilate	+0.21	-0.91	+0.09	+0.04	+0.07	15.56	9.84
Isodecyl-N-phenyl Anthranilate	+0.23	-10.43	+0.15	+0.09	+0.14	16.43	11.25
Methyl-N-methyl anthranilate	0.00	+0.02	+0.04	+0.03	-0.01	15.31	3.11
2-ethylhexyl-N-methyl anthranilate	-0.04	+0.01	+0.03	+0.01	-0.03	15.33	3.67
Di-(octylphenyl)amine	-0.25	-13.23	+0.01	+0.01	-0.02	22.07	4.90

of C₈ Oxo alcohol, and one mole of C₈ Oxo acid), or mixtures of any of the above in any proportions.

The preparation of the lubricating compositions involves no special techniques. Generally, the lubricants are formed by adding an appropriate amount of the ester to the basestock and heating and stirring the composition until the additive is dissolved.

Other lubricating additives can also be added to the compositions of the invention in amounts of about 0.001 to 10.0 weight percent each, based on the total weight of the composition. Examples of such additives include: rust preventives, such as calcium petroleum sulfonate or sorbitan monooleate; V.I. improvers, such as the polymethacrylates; load carrying agents, such as tricresyl phosphate and free sebacic acid; pour point depressants; dyes; grease thickeners; and the like.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following example is demonstrative of the preparation of the lubricating composition of this invention.

EXAMPLE

To 100 grams of a synthetic lubricating base oil was added 1.3 grams of methyl anthranilate and 3.14 grams of a combination of conventional antioxidants, corrosion inhibitors and load carrying agents. This combination was heated and stirred at a temperature of 210° F. until a solution was effected. The conventional additives were employed so the finished lubricant would have the qualities more nearly exhibited by a working lubricant. The synthetic lubricating base oil was composed of a mixture of a bout 25 wt. percent of an ester of neopentylglycol and fatty acids having an average chain length of C₈ and about 75 wt. percent of an ester of trimethylolpropane and the same fatty acid. The methyl anthranilate was prepared by reacting isatoic anhydride (a commercial product of Maumee Chemical Company) with methyl alcohol at a temperature of about 65° C. in the presence of sodium hydroxide.

An Oxidation-Corrosion-Stability Test was carried out on several lubricating compositions containing the anthranilic esters described above. Such test determines the oxidation and corrosion inhibiting effect of the ester additive. The same test was conducted on a lubricant containing di-(octylphenyl) amine, a standard oxidation and corrosion inhibiting additive. The base oil in which the additives were incorporated was the synthetic lubricant as described in the example. Also included in the lubricant compositions which were tested was the combination of conventional additives described in the above example. The lubricant composition contained 100 parts by weight of synthetic oil. The ester additive and the di-(octylphenyl) amine were present in amounts of 13 parts by weight. The conventional auxiliary additives were present in a total amount of 3.14 parts by weight. The results of

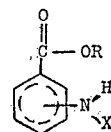
The 425° F. Oxidation-Corrosion-Stability Test was carried out by blowing air at the rate of 100 volumes per hour through 1 volume of the lubricating composition maintained at a temperature of 425° F. for 48 hours. At the end of the test, the increase in viscosity and the increase in total acid number (T.A.N.) were determined. The corrosive characteristic of the lubricant was determined by immersing various weighed metal strips in the oil and measuring weight change at the end of the test. The change in weight signifies either corrosion due to oxidation of the metal or weight gain due to deposits. The test is a close simulation of the conditions under which high performance jet type engines operate and is an appropriate test of the serviceability of a lubricant.

As seen from the test above, the oxidative stability of a lubricant containing the anthranilate esters was generally greatly superior to the lubricant containing the standard antioxidant. This is indicated by a smaller change in total acid number, which was observed in most cases when the ester was used, and in a smaller change in viscosity, which was observed in all cases where the anthranilate ester was used. The corrosivity of a lubricant containing the anthranilate ester to the various metals described in the above table was minimal in all cases and the ester was distinctly superior to di-(octylphenyl) amine in inhibiting the corrosion of magnesium. This was most dramatically illustrated in the cases of 2-ethylhexyl anthranilate and 2-ethylhexyl-N-methyl anthranilate, which were 1300 times more effective in inhibiting corrosion than the di-(octylphenyl) amine.

What is claimed is:

1. A lubricating composition suitable for high performance service at high temperature in internal combustion engines consisting essentially of:

- a major amount of a synthetic ester lubricating oil; and
- a minor corrosion and oxidation inhibiting amount of 0.5-4.0% by weight of a compound having the formula:



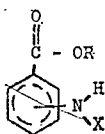
wherein R is C₁ to C₈ alkyl group, and X is selected from the group consisting of hydrogen, C₁ to C₆ alkyl groups and phenyl groups.

2. A lubricating composition as in claim 1 wherein X is hydrogen.

3. A lubricating composition as claimed in claim 1 wherein the compound is selected from the group consisting of methyl anthranilate, 2-ethylhexyl anthranilate, methyl-N-phenyl anthranilate, methyl-N-methyl anthranilate, 2-ethylhexyl-N-methyl anthranilate.

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4. A method of lubricating which comprises coating rubbing magnesium surfaces with a lubricating composition comprising a major amount of a synthetic ester lubricating oil containing a minor corrosion and oxidation inhibiting amount of 0.5-5.0% by weight of a compound having the formula:



where R is a C₁ to C₈ alkyl group, and X is selected from the group consisting of hydrogen, C₁ to C₆ alkyl groups and phenyl groups.

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15 DANIEL E. WYMAN, Primary Examiner
W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

252—392, 403

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,642,632 Dated February 15, 1972

Inventor(s) John F. Coburn et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 1, line 6, after "07076" insert
--, assignors to Esso Research and Engineering Company,
a corporation of Delaware.--.

In column 1, line 13, after "derivative" insert
--of--.

In column 4, line 66, before "C₁" insert --a--.

Signed and sealed this 28th day of November 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents