United States Patent [19]

Miller

[11] **3,920,567**

[45] **Nov. 18, 1975**

[54] **NOVEL OXAZOLINE-ALKYL ACID PHOSPHATE ADDUCTS USEFUL AS ASHLESS ANTIWEAR ADDITIVES**

[75] Inventor: **Alfred H. Miller,** Somerset, N.J.

[73] Assignee: **Exxon Research & Engineering Co.,** Linden, N.J.

[22] Filed: **Dec. 27, 1974**

[21] Appl. No.: **536,822**

[52] **U.S. Cl.** **252/32.5**

[51] **Int. Cl.**[2]. **C10M 1/44;** C10M 3/38; C10M 5/24; C10M 7/24

[58] **Field of Search** 252/32.5

[56] **References Cited**

UNITED STATES PATENTS

3,819,647	6/1974	Foley	252/32.5
3,844,957	10/1974	Robinson et al.	252/32.5

Primary Examiner—Delbert E. Gantz
Assistant Examiner—I. Vaughn
Attorney, Agent, or Firm—Wayne Hoover

[57] **ABSTRACT**

Ashless antiwear additives for lubricating oils are prepared by reacting a monoester or diester alkyl acid phosphate having 2 to 6 carbon atoms in its alkyl group with a hydroxyalkyl substituted oxazoline having an alkyl or alkene radical of 8 to 22 carbon atoms attached to the ring carbon atom between the nitrogen and oxygen atoms of the oxazoline ring and at least one hydroxyalkyl group having 1 to 4 carbon atoms attached to one of the other two ring carbon atoms. The additives show improved antiwear properties as compared to conventional ash producing antiwear additives.

11 Claims, No Drawings

NOVEL OXAZOLINE-ALKYL ACID PHOSPHATE ADDUCTS USEFUL AS ASHLESS ANTIWEAR ADDITIVES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to new chemical compositions and to lubricating oil compositions containing these compositions. More particularly, it relates to a novel class of chemical compositions which act as antiwear or extreme pressure agents in lubricating oils.

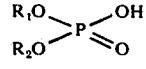
2. Description of the Prior Art

The prior art has taught the need for antiwear or extreme pressure agents in lubricating oils. This type agent affords protection against excessive wear and scuffing of lubricated metal parts which are subjected to relatively high pressures such as piston rings and cylinder liners.

Zinc dialkyl dithiophosphates have been employed in the prior art as antiwear and extreme pressure agents, but they have a high metal content and a correspondingly high ash content and they therefore cannot be used in the formulation of ashless oils. High ash additives can cause undesirable emissions to the atmosphere, can adversely affect catalysts used in catalytic exhaust treaters, and can cause excessive engine deposits composed of ash-forming metal salts. Accordingly, it would be desirable to provide ashless antiwear and extreme pressure agents.

SUMMARY OF THE INVENTION

It has now been discovered that a quaternary salt formed as the reaction product of (a) an alkyl acid phosphate of the formula



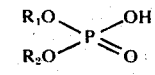
where R_1 and R_2 independently can be hydrogen or the same or different C_2 to C_6 alkyl groups, provided that R_1 and R_2 simultaneously are not hydrogen, with (b) a hydroxyalkyl substituted oxazoline having an alkyl or alkene radical of 8 to 22 carbon atoms attached to the ring carbon atom between the nitrogen and oxygen atoms of the oxazoline ring and at least one hydroxyalkyl group having 1 to 4 carbon atoms attached to one of the other two ring carbon atoms.

In a preferred embodiment of the invention, the oxazoline is a bis hydroxyalkyl substituted oxazoline having two hydroxyalkyl radicals of from 1 to 4 carbon atoms. It is also preferred that these two hydroxyalkyl groups be attached to the same ring carbon atom. The preferred alkyl acid phosphate for use in the invention is di-n-butyl acid phosphate.

The reaction products of the present invention are incorporated into lubricating oils in an amount of between about 0.001 to 10 weight percent, based on the weight of the oil. The additives of the present invention, in addition to being ashless, impart good antiwear and extreme pressure properties to the lubricating oil.

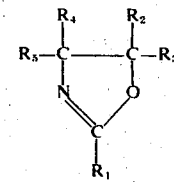
DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, the alkyl acid phosphate used in the present invention has the general formula



where R_1 and R_2 may be hydrogen or the same or different C_2 to C_6 alkyl groups, provided that R_1 and R_2 simultaneously are not hydrogen. Dialkyl phosphate esters are preferred and di-n-butyl acid phosphate presently is most preferred. Other suitable esters that can be in the present invention include monoesters such as propyl phosphate, butyl phosphate, pentyl phosphate, hexyl phosphate, sec-butyl phosphate, isopentyl phosphate, diesters such as dibutyl phosphate, dihexyl phosphate, dipropyl phosphate and dipentyl phosphate, and mixtures of such acid mono- and/or di-alkyl esters. These esters can be obtained commercially or prepared by conventional procedure.

In accordance with the invention, a hydroxyalkyl substituted oxazoline is reacted with the alkyl acid phosphate. The hydroxyalkyl substituted oxazoline useful in the present invention has an alkyl or alkene radical of 8 to 22 carbon atoms attached to the ring carbon atom between the nitrogen and oxygen atoms of the oxazoline ring and at least one hydroxyalkyl group having 1 to 4 carbon atoms attached to one of the other two ring carbon atoms. Such hydroxyalkyl substituted oxazolines are represented by the formula:



where R_1 is an alkyl or alkene radical having 8 to 22 carbon atoms, at least one of R_2, R_3, R_4 and R_5 is a hydroxyalkyl radical having from 1 to 4 carbon atoms and the remaining R_2, R_3, R_4 and R_5 radicals are independently selected from the group consisting of hydrogen, C_1–C_6 alkyl, C_6 aryl, substituted alkyl and substituted aryl groups. Preferably, the R_1 group is a $C_{17}H_{33}$ alkene group and two or more of the radicals R_2, R_3, R_4 and R_5 are hydroxyalkyl groups having 1 to 4 carbon atoms. A bis hydroxyalkyl substituted oxazoline having two hydroxyalkyl groups (preferably two hydroxymethyl groups) attached to the same ring carbon atoms is most preferred.

The oxazoline compounds useful in the present invention generally can be obtained commercially or can be readily prepared by any one of a number of well-known methods. Thus, for example, the oxazolines can be prepared from amino hydroxy compounds through their fatty amides, or the oxazolines can be prepared by reacting an amino hydroxy compound with a nitrile.

In preparing the oxazolines through their fatty acid amides, a suitable amino hydroxy compound is reacted with a desirable aliphatic carboxylic acid at an elevated temperature to yield an amide. The temperature is then increased to split out water and form the oxazoline. The temperature for the initial amide formation and final oxazoline formation depends on the reacting materials employed and generally is within the range of 150° to 170°C. for the initial reaction and around about 250°C. for the final reaction.

Examples of suitable hydroxy amine compounds are the primary aliphatic amines having the hydroxy group on the carbon atom adjacent to the carbon atom bearing the amine radical and include such amines as 2-amino-2-ethyl-1, 3-propanediol, 2-amino-2-methyl-1-propanol, and 2-amino-2-hydroxymethyl-1,3-propanediol and the like.

The acids which can be used to prepare oxazolines from the above amino compounds are saturated and unsaturated aliphatic acids such as oleic acid, palmitic acid, stearic acid, lauric acid, decanoic acid, dodecanoic acid, eicosanic acid, nonadecanoic acid and the like. These acids generally have from 9 to 22 carbon atoms.

The reaction products of the present invention are adducts and generally prepared by forming a mixture of the alkyl acid phosphate and the oxazoline as reactants. In general, an excess of either reactant can be used in the preparation of the adduct. Preferably, 0.5 to 1.5 mols of alkyl acid phosphate are used per mole of oxazoline, and most preferably a 1:1 equimolar ratio of reactants is used. The mixture is stirred during the reaction and a homogeneous product is obtained. The reaction takes place very rapidly over a wide range of temperature, including normal room temperature of about 70° to 80°F. When the reactants are both liquids, the reaction mixture can be prepared simply by adding the reactant together to form a solution which is allowed to react, preferably while stirring to form the novel adducts of the present invention. When at least one of the reactants is a solid however, it is preferred first to heat the solid reactant to effect its solution. When it is found preferable to heat the reactants to expedite their dissolution, the temperature should not be allowed to reach the temperature at which any of the reactants or the products of reaction will be deleteriously affected, as for example, by chemical decomposition of the reactants or products of reaction. The reaction proceeds rapidly and generally a reaction time of from about 30 minutes to about 2 hours is sufficient to complete the reaction.

The adducts of the present invention are used in lubricating oils including mineral lubricating oils and synthetic oils. The mineral lubricating oils can be of any type, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Suitable synthetic oils include synthetic hydrocarbon lubricating oils, as well as dibasic acid esters such as di-2-ethylhexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, glycol esters, such as C_{13} oxo acid diesters of tetraethylene glycol, and 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 hexaconic acid. Polyol esters, such as those made by the reaction of polyols (e.g., pentaerythritol) having 3 to 6 hydroxyl groups with C_4 to C_{12} fatty acids can also be used.

While the lubricant compositions herein described are primarily designated as internal combustion engine crankcase lubricants, the adducts of the present invention can also be employed in other oil compositions, including turbine oils, various industrial oils, gear oils, hydraulic fluids, transmission fluids and the like.

The adducts of the present invention are used in the above-described lubricating oils in the amounts of about 0.001 to about 10, preferably 0.05 to 0.5, weight per cent, based on the weight of the oil. The lubricating compositions containing the adducts of the present invention can be prepared simply by adding the adduct in the proper amount to the lubricating oil and stirring.

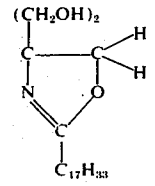
In any of the above-described lubricant compositions, other conventional additives can also be present, including dyes, pour point depressants, antioxidants, viscosity index improvers, color stabilizers, antifoam agents, and the like, as well as other dispersants. Suitable additives for these purposes are known to those skilled in the art. For example, crankcase lubricating oils can contain polymers such as polyisobutylene, polymethacrylates, copolymers of alkyl fumarates with vinyl acetate and various other long chain polymers as viscosity index improvers and pour point depressants. Oxidation inhibitors frequently used in such compositions include, for example, phenyl α-naphthylamine.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples will serve to illustrate methods of preparing the compositions of this invention and include preferred embodiments of the invention.

EXAMPLE 1

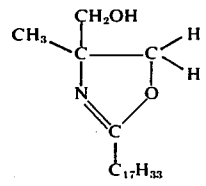
412 grams of a commercially available dihydroxyalkyl substituted oxazoline having the formula



and known as 2-heptadecyl-4,4-di-hydroxymethyloxazoline were heated to 75°C. and then combined with 51 grams of di-n-butyl acid phosphate so as to form a mixture which was then stirred and heated to 100°C. and held at this temperature for 2 hours. A clear reaction product was obtained. The reaction product was a solid at room temperature and was soluble in a variety of lubricating basestocks such as a 1,060 SUS viscosity at 100°F. hydrocarbon oil derived from a solvent extracted naphthenic crudes and a 300 SUS (100°F.) viscosity oil derived from a solvent extracted paraffinic base crude.

EXAMPLE 2

80 grams of a commercially available monohydroxyalkyl substituted oxazoline having the formula



and known as 2-heptadecyl-4-methyl-4-hydroxymethyloxazoline were heated to 75°C. and then combined with 20 grams of the di-n-butyl acid phosphate to form a mixture which was maintained at 75°C. and is stirred for 1 hour. The reaction product which was obtained was solid at room temperature and was soluble upon

heating in a variety of lubricating basestocks such as a 1,060 SUS viscosity at 100°F. hydrocarbon oil derived from a solvent extracted naphthenic crudes and a 300 SUS (100°F.) viscosity oil derived from a solvent extracted paraffinic base crude.

EXAMPLE 3

In this Example, comparative data were obtained using the GE Scuff Test on the product of Example 1 and on a commercial zinc dialkyl dithiophosphate product known for its antiwear properties and prepared from primary alcohols. As is, of course, well known, the GE Scuff Test uses a mechanical device in which a segment of a piston ring is mounted in contact with a segment of a cylinder wall liner. Pressure is applied to the rubbing piston ring against the cylinder liner hydraulically. Pressure against the ring is applied in 6 preset increments to a maximum ring interface pressure of 4,160 p.s.i. A base oil containing the additive or additives to be tested is used to lubricate the ring-cylinder liner interface and is supplied by two electrically driven positive displacement type pumps. Oil flow is increased with each increase in pressure. At least two minutes of oil flow is allowed before beginning the oscillation at each pressure increment. The test is carried out for 270 minutes. A Scuff Demerit rating from 0 to 10 is given for each test run with 0 indicating no scuffing and 10 indicating severe scuffing.

The base oil used in both of these Scuff Tests was a hydrocarbon oil of 1,060 (SUS) viscosity at 100°F. and the same was derived from a solvent extracted naphthenic crude. The results of the comparative Scuff Tests are shown in the Table below which also reflects the amount of each additive used and the Scuff Test rating for the base oil without additive.

TABLE 1

Additive	Wt.%	Scuff Rating (Demerit)
None	—	8
Zinc dialkyl dithiophosphate	1	4
Reaction Product of Ex. 1.	0.5	4

As can be seen from Table 1, the product of Example 1, even though used at one-half the concentration of the other additive had a better Scuff Test rating comparable to that of the zinc dialkyl dithiophosphate.

EXAMPLE 4

In this example, comparative wear data were obtained, using a four-ball wear test, on base oil samples containing the additives of Examples 1 and 2, the oxazoline used to prepare these additives and a commercial zinc dialkyl dithiophosphate antiwear additive prepared from primary alcohols. The base oil used in each of these tests was a hydraulic oil antiwear formulation prepared from a basestock of 300 SUS (100°F.) solvent extracted base oil containing a hindered phenolic antioxidant and a sulfonated rust inhibitor. The four-ball wear test is one of the most common methods of evaluating lubricant performance. It is carried out on a GE-Brown modification of the Shell four-ball wear tester. The wear system consists essentially of an upper ball, fixed in a rotating chuck, sliding on three lower balls. The three lower balls are each held stationary by a chuck attached to the lubricant reservoir. The three lower balls and hence the contact areas between the lower balls and the upper ball remain fully submerged in lubricant throughout a test. The test load is applied by a pneumatic piston which serves to press the three lower balls up against the rotating upper ball. The test balls are usually 0.5 inch in diameter and those most commonly used are AISI 52,100 steel test balls with a Rockwell hardness of 60–62. Wear performance may be assessed by measurement of the average wear scar developed on the three lower balls during the test. The lower the wear scar diameter (WSD) the more severe the wear. The lower the wear scar diameter the better the antiwear properties.

In one series of runs, the four ball wear test was conducted at 1,200 r.p.m. for fifteen minutes in dry air at room temperature of 77°F. with loads of from 25 kg to 60 kg. The stationary members (the lower balls) and the rotating member (the upper ball) were 6.35 mm radium 52,100 steel balls having a hardness of 60–62 Rockwell. The results of these tests are summarized in the Table below which also shows the amount of additive in the base oil and the four-ball wear test result for the base oil.

TABLE 2

		Four Ball Test (Room Temperature)	
Additive		WSD at 25Kg Load	WSD at 60Kg Load
	t.%		
None	—	.42 mm	.44 mm
Reaction Product Ex. 1	0.5	.27	.35
Reaction Product Ex. 2	0.5	.28	.41
Zinc dialkyl dithiophosphate	1%	.29	.43
Oxazoline used in Ex. 1	1%	.39	—
Oxazoline used in Ex. 2	1%	.38	—

In a second series of runs, the same conditions were used, except that the temperature was increased to 200°F. The results of these tests are summarized below:

FOUR BALL WEAR TEST (200°F.)

Additive		WSD at 25Kg	WSD at 60Kg Load
	t.%	Load	
None	1	Scuffing	—
Zinc dialkyl-dithiophosphate	1%	0.27 mm	0.47 mm
Reaction Products from Ex. 1	0.5%	0.29	0.38

As can be seen from the above data, the products of the present invention and particularly those comprising two hydroxy-substituted alkyl groups, such as prepared in Example 1 are superior to the zinc dialkyldithiophosphate antiwear additive in reducing sliding wear at both ambient and elevated temperatures in an industrial oil formulation even though used at one-half the concentration of the zinc dialkyldithiophosphate. On the other hand, the oxazoline compounds by themselves are not as effective as the commercial zinc dialkyldithiophosphate. The other products of the present invention, on

the other hand, such as that produced in Example 2 are comparable to the zinc dialkyldithiophosphate in effectiveness.

EXAMPLE 5

In this Example, comparative wear data were obtained using the Silver Lubricity Test on base oil samples containing the additives of Examples 1 and 2, the oxazoline used to prepare this additive and a commercial zinc dialkyldithiophosphate antiwear agent derived from primary alcohols. The base oil used in these tests was a hydrocarbon oil of viscosity 900 SUS at 100°F. and was derived from a solvent extracted naphthenic crude.

The Silver Lubricity Test was conducted under the Pennsylvania Railroad Test Procedure using a 20 kilogram load, 600 rpm, 350°F. and a run time of 30 minutes. The upper steel ball was of 52,100 steel, Rockwell hardness 60–63. The lower three discs were silver. The results of these tests are interpreted in terms of the average wear scar diameter (WSD) on the silver discs. The results obtained and the compositions used are summarized below. The lower the WSD the more effective the lubricant in preventing wear.

Silver Lubricity Test

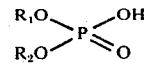
Additive	Wt.%	WSD (mm)	Average Torque (g.)
None	—	1.333	67.5
Oxazoline used in Example 1	1	0.908	20
Oxazoline used in Example 2	1	0.916	18.5
Dialkyldithio-phosphate	—	0.933	15
Reaction Product of Example 2	1	0.899	10
Reaction Product of Example 1	0.5	0.966	6

As can be seen from these data, the product of the present invention as produced in Example 1 was more effective in reducing wear than any of the compounds tested while the product of the present invention as produced in Example 2 was comparable, in effectiveness, to commercially available antiwear agents.

The invention in its broader aspects is not limited to the specific details shown and described and departures may be made from such details without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. A composition comprising a lubricating oil and a quaternary salt formed by reacting (a) an alkyl acid phosphate characterized by the general formula:



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen and alkyl radicals having 2 to 6 carbon atoms, provided that R_1 and R_2 simultaneously are not hydrogen, with (b) a hydroxyalkyl substituted oxazoline having an alkyl or alkene radical of 8 to 22 carbon atoms attached to the ring carbon atom between the nitrogen and oxygen atoms of the oxazoline ring and at least one hydroxyalkyl group having 1 to 4 carbon atoms attached to one of the other two ring carbon atoms.

2. The composition of claim **1** wherein the oxazoline contains at least two hydroxyalkyl groups.

3. The composition of claim **1** wherein the oxazoline is a bis hydroxyalkyl substituted oxazoline having two hydroxyalkyl groups.

4. The composition of claim **3** wherein said two hydroxyalkyl groups are attached to the same ring carbon atom.

5. The composition of claim **4** wherein said two hydroxyalkyl groups are hydroxymethyl groups.

6. The composition of claim **5** wherein the oxazoline is 2-heptadecyl-4,4-di-hydroxymethyloxazoline.

7. The composition of claim **3** wherein the alkyl acid phosphate is di-n-butyl-acid phosphate.

8. The composition of claim **1** wherein the alkyl acid phosphate is di-n-butyl-acid phosphate.

9. The composition of claim **8** wherein the oxazoline is 2-heptadecyl-4-methyl-4-hydroxymethyloxazoline.

10. The composition of claim **1** containing 0.001 to 10 weight percent of said quaternary salt, based on the weight of lubricating oil.

11. A composition comprising a lubricating oil and 0.001 to 10 weight percent of a quaternary salt, based on the weight of lubricating oil, said quaternary salt being formed by reacting di-n-butyl-acid phosphate with 2-heptadecyl-4,4-di-hydroyxmethyloxazoline.

* * * * *