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ANTIOXIDANTS FOR MINERAL OIL LUBRICANTS AND COMPOSITIONS CONTAINING THE SAME

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This invention relates to antioxidants for mineral oil lubricants and compositions containing the same, and more particularly, it relates to addition agents for mineral oil lubricants which inhibit the oxidative deterioration of said lubricants.

In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, ordinary mineral lubricating oils often prove unsatisfactory in service because of the oxidative deterioration of the oil, with the attendant deposition on the engine surfaces of varnish, gum or sludge. Furthermore, many lubricating oil compositions which may be highly satisfactory for the lubrication of other mechanisms have been found wholly unsuitable for use as turbine oils.

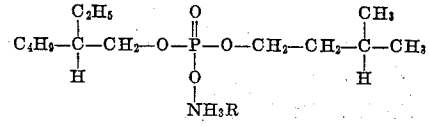
The formation of varnishes, gums and sludges on engine surfaces is due at least in part to oxidation effects on mineral lubricating oils. In turbine oils the problem of oxidation is further aggravated, because in normal use turbine oils rapidly become contaminated with water. This also tends to intensify the corrosion and rusting problems encountered in turbine systems.

Accordingly, it is an object of this invention to provide addition agents for mineral oil lubricants which will inhibit the oxidative deterioration of such lubricants.

It is a further object of this invention to provide improved mineral oil lubricant compositions which are remarkably stable against oxidation under service conditions.

A still further object of this invention is to provide addition agents for mineral oil lubricants which inhibit rusting and corrosion of metal parts in addition to inhibiting the oxidative deterioration of lubricants with which they are incorporated.

These and other objects are accomplished by the present invention wherein, as an addition agent for mineral oil lubricants, there is provided a substantially neutral unsaturated primary aliphatic amine addition salt of 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid, said salt having the formula:



wherein R is an alkenyl, alkadienyl or alkinyl radical. The above salts, when added to mineral oil lubricants, confer a remarkable stability

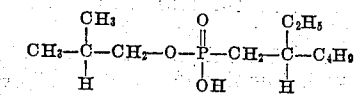
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against deterioration by oxidation, and further, inhibit corrosion and rusting. These salts and mineral oil lubricant compositions containing them are believed to be novel and are considered parts of our invention.

This application is a continuation-in-part of our prior copending application Ser. No. 775,566 filed September 22, 1947, now abandoned. In that application, we have described and claimed diesel fuel oil compositions containing substantially neutral salts of 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid and both saturated and unsaturated primary aliphatic amines having at least 10 carbon atoms. The purpose for which such additives were compounded in diesel fuel oils was to increase the power output and performance characteristics of diesel engines using such fuels. The present application is directed to salts of the acid phosphate ester and unsaturated primary aliphatic amines only, and embraces such products per se and as antioxidants for mineral oil lubricant compositions containing the same.

As indicated above, the unsaturated primary aliphatic amines used in preparing the compounds of the present invention include primary alkene, alkadiene or alkine amines. Illustrative of the alkene amines are allyl, methallyl, ethyl-isopropenyl, citronellyl (2,6-dimethyl octenyl) hexadecenyl, oleyl (9,10-octadecenyl) and eicosenyl amines. Of the alkadiene amines, butadienyl, heptadienyl, 2,6-dimethyl octadienyl (citral), 3,7-dimethyl octadienyl (linaloyl) amines are illustrative. The alkine amines include propinyl (propargyl), butinyl, and eicosinyl amines. While the short chain primary unsaturated aliphatic amines are useful and advantageous, the long chain amines having at least 7 carbon atoms and as many as 20 carbon atoms in the chain are preferred. However, primary unsaturated aliphatic amines having more than 20 carbon atoms in the chain may also be employed. Oleyl amine gives excellent results.

The acid phosphate ester referred to hereinabove is a diester of ortho phosphoric acid having the following formula:



The compound is known as 3-methyl-butyl, 2-ethyl-hexyl phosphoric acid, or 3-methyl-butyl, 2-ethyl-hexyl ortho phosphate, and may be conveniently prepared by the procedure disclosed in Smith and Cantrell Patent 2,441,295.

In preparing our new compounds, the amine and acid are employed in equimolecular proportions. The reaction between the amine and the acid phosphate ester proceeds exothermically and the temperature may advantageously be controlled by cooling as desired, although the temperature may be somewhat elevated in the later stages to complete the reaction. Thus, it is generally desirable to keep the temperature below 180° F. in order to avoid splitting out water from the addition salt obtained, but after the reaction has subsided it is permissible to raise the temperature to about 220° F. for a short period of time, say one-half hour, to complete the reaction.

When the additive is to be employed for its antioxidant effects alone, the pH of the additive is not critical. However, if rust and corrosion inhibiting effects are also desired, it is necessary that the additive have a pH between 6.5 and 7.5. Any substantial departure from this range on either the alkaline or acid side gives less desirable results. Thus in preparing the additives of our invention, where the final product has a pH falling without the range 6.5–7.5, the pH may be adjusted by adding the required small additional proportions of the amines (if on the acid side) or the 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid (if on the alkaline side).

The following examples illustrate the preparation of our antioxidants.

Example I

One mol of commercial oleylamine was introduced into a reaction kettle equipped with means for heating, cooling and agitation. Then one mol of 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid was gradually added to the kettle, at such a rate and under such cooling conditions that the reaction temperature was not permitted to exceed about 180° F., the reaction being quite vigorous and exothermic. After all of the phosphoric acid ester had been added the mixture was warmed to about 220° F. for a period of 30 minutes to complete the reaction. The product so formed was a viscous liquid having a pH of 7.2. It was soluble in hydrocarbons and decomposed on boiling.

Advantageously, our antioxidants may be prepared in situ in a mineral oil, since the amines and the phosphate ester from which they are prepared are also soluble in mineral oils. In such an embodiment, the amine is first dissolved in the mineral oil, following which the acid phosphate ester is added, in accordance with the procedure outlined in Example I. The products so formed are concentrated oil solutions of the neutral reaction product which advantageously may be blended with various types of lubricants. The preparation of such a concentrate is illustrated by the following example:

Example II

About 644 pounds of light mineral oil having a viscosity of 50 seconds SUV at 100° F. were blended with 268 pounds of oleylamine in a reaction vessel similar to that used in Example I. Then 194 pounds of 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid were added to the mixture over a period of 2 hours, during which time the temperature was not permitted to exceed 180° F. The temperature was then elevated to 220° F. for a period of 30 minutes to complete the reaction. The concentrate so prepared had the following properties:

Gravity: °API	10.2
Viscosity, SUV 210° F	71
pH	7.3

As a class the unsaturated amine salts of our invention are relatively non-volatile even at elevated temperatures and are therefore particularly suited for use as mineral oil lubricant additives. The salts of our invention are readily soluble in all types of mineral oils, and are quite miscible with other hydrocarbons. As stated above, when incorporated in mineral oils of the type and viscosity used for lubricating purposes, our salts impart marked antioxidant qualities, thereto. For such purpose, relatively small amounts, from 0.05 to 5.0 per cent by weight, are sufficient, although larger amounts as high as 15.0 per cent by weight may also be employed. In addition our new salts are potent rust inhibitors.

The following example, which compares an uninhibited lubricating base oil with the same oil containing 0.2 per cent and 0.5 per cent by weight of the additive prepared in accordance with Example I, illustrates the remarkable antioxidant effects produced by our additive.

Example III

	Uninhibited Lubricating Oil	Lubricating Oil Containing 0.2% Inhibitor	Lubricating Oil Containing 0.5% Inhibitor
Gravity: ° API	28.4	28.3	28.3
Viscosity, SUV:			
100° F	1,068	1,071	1,073
210	39.0	39.0	39.1
Flash, OC: ° F	345	345	345
Fire, OC: ° F	390	390	390
Color, NPA	1.75	1.75	1.75
Corrosion Test—ASTM D 665-44 T, Synthetic Sea Water, 140° F., Steel Rod: Appearance	rust	bright	bright
Oxidation Test—ASTM D 943-47 T: 203° F., 3 L., Oxygen/Hr.:			
Time Oxidized: Hr	180	2,550	3,175
Neutralization No	2.0	2.0	2.0

The oxidation test referred to in Example III is a standard test which measures the stability of oils to oxidation.

Briefly, the test comprises subjecting the oil sample to oxygen at a temperature of 95° C. (203° F.) in the presence of water and an iron-copper catalyst, and determining the time required to build up a neutralization number of 2. The flow of oxygen through the oil is maintained at the rate of 3 liters per hour.

The high antioxidant potency of the unsaturated aliphatic primary amine salts of 3-methyl-butyl, 2-ethyl-hexyl orthophosphoric acid could not have been predicted from the antioxidant

effects obtained from the use of saturated aliphatic primary aliphatic amine salts of 3-methyl-butyl, 2-ethyl-hexyl orthophosphoric acid. In order to compare the antioxidant effects of the saturated and unsaturated aliphatic primary amine salts, the stearyl amine salt of 3-methyl-butyl, 2-ethyl-hexyl orthophosphoric acid was prepared exactly as in Example I, substituting stearyl amine for the oleylamine. The stearyl amine salt was a solid having an indefinite melting point of around 100° F. The stearyl amine salt in an amount of 0.7 per cent by weight was then added to the same uninhibited lubricating oil base described in Example III. The oil containing the additive had the following properties:

Gravity: °API	28.3
Viscosity, SUV:	
100° F	1064
210	39.5
Flash, OC: °F	345
Fire, OC: °F	390
Corrosion test, ASTM D665-47T synthetic sea water, 140° F. steel rod: appearance	bright
Area rusted: per cent	0
Oxidation test, ASTM D943-47T 203° F., 3 L. oxygen/hr.:	
Time oxidized: hr	1820
Neutralization No	2.0

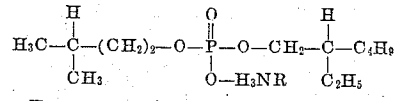
Comparing the effects of the stearyl amine salt with those of the oleylamine salt in Example III, it may be seen that although both salts are excellent corrosion inhibitors, the oleylamine salt is an unexpectedly much more powerful antioxidant. Thus, only 0.2 per cent by weight of the oleyl amine salt (less than ⅓ the dosage of the stearyl amine salt) increased the antioxidant stability from 1820 to 2550 hours, an increase of 730 hours, or 40 per cent. And 0.5 per cent by weight of the oleyl amine salt (about ⅓ less than the dosage of the stearyl amine salt) increased the antioxidant stability from 1820 to 3175 hours, an increase of 1355 hours, or 74 per cent. The marked increase in antioxidant potency of the unsaturated aliphatic primary amine salts is obviously an unexpected beneficial property not possessed by the saturated aliphatic primary amine salts.

While we have shown in the above examples, the preparation of compounded lubricating oils, our invention is not limited thereto, but comprises all mineral oil lubricant compositions containing our new addition agents, such as greases and the like. Furthermore, in such compositions, other ingredients such as pour point depressants, viscosity index improvers, extreme pressure agents and the like may also be added.

Resort may be had to such modifications and variations as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. The compound:

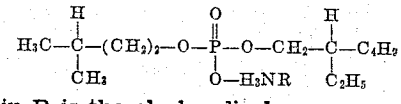


wherein R represents an unsaturated aliphatic radical selected from the group consisting of alkenyl, alkadienyl and alkinyl radicals.

2. The compound of claim 1, wherein R is oleyl.

3. A lubricant composition comprising a major amount of mineral lubricating oil and a minor amount, from 0.5 to 15 per cent by weight on the mineral lubricating oil, of the substantially neutral addition salt of oleyl amine and 3-methyl-butyl, 2-ethyl-hexyl ortho phosphoric acid.

4. A lubricant composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to stabilize the composition against oxidative deterioration, of a compound having the formula:



wherein R is the oleyl radical.

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