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LUBRICANT

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17 Claims. (Cl. 252—48)

This invention relates to lubricants and particularly to improvements in lubricating oil compositions intended for use in internal combustion engines under severe conditions wherein corrosion, piston ring and cylinder wear, carbon, and varnish formation may be encountered.

Straight petroleum lubricants are effective within certain defined limits of engine operating conditions and when these limits are exceeded, such lubricants frequently fail to give the desired performance demanded of them. Since, in modern engines designed to give increased performance these limits are frequently exceeded, the use of straight mineral oils as lubricants produces undesirable conditions within the engine; thus varnish and carbon formation is excessive, and corrosion of improved hard metal alloy bearings is encountered.

It is the object of the present invention to provide a lubricant for internal combustion engines which will be effective in providing adequate lubrication for such engines.

It is a further object of the invention to provide a lubricant which will not be conducive to the formation of varnish and/or carbon. Another object of the invention is to provide a lubricant which will reduce engine wear and be non-corrosive to bearings. Other objects and advantages of the invention will become apparent as the description thereof proceeds.

We have discovered that an improved lubricant can be obtained by blending a mineral lubricating oil with from about .05% to about 10%, preferably from about 0.5% to about 5%, of a sulfurized olefin polymer and from about .05% to about 5%, preferably from about 0.5% to about 2%, of a complex glyceride phosphoric acid ester and/or salt. The quantity of the sulfurized olefin polymer employed is preferably that sufficient to result in a blended lubricant having from about .01% to about 1% added sulfur.

The glyceride phosphoric acid esters and/or salts which may be used for this purpose are, for example, natural and synthetic phosphatides, such as, lecithin and cephalin, as well as the mixed phosphatides derived from soybean oil or other commercial sources. Also suitable for this purpose are other acid esters of phosphoric acid, preferably those containing an amine or quaternary ammonium group.

The olefin polymer to be sulfurized may be the polymers resulting from the high temperature polymerization of low molecular weight iso-olefins such as isobutylene and isoamylene and/or the copolymers obtained by the polymerization of hydrocarbon mixtures containing iso-olefins and normal olefins preferably those of less than 6 carbon atoms. The polymers may be obtained by the polymerization of the various olefins or mixed olefins in the presence of catalysts such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type. Also contemplated within the scope of this invention are the sulfurized olefin polymers resulting from the treatment of olefinic hydrocarbons with catalysts of the type of fuller's earth and/or other activated clays. The sulfurized cracked wax polymers are also suitable.

The sulfurization of the polymer may be accomplished by treating the same with elemental sulfur at a temperature range of about 300° F. to about 400° F. and preferably at a temperature of about 325° F. to about 375° F. until the sulfur has combined chemically with the polymer. The amount of sulfur which will combine with the polymer depends largely upon the amount of elemental sulfur used, the temperature employed and the time of reaction. At a temperature of about 325° F. to 375° F. from about 5% to about 20% sulfur can be combined with the polymer. Sulfurization may also be carried out by other means such as by treatment with a sulfur halide, for example, sulfur chloride or sulfur dichloride.

The polymers employed are preferably low molecular weight polymers, that is, polymers in which the molecular weight ranges from about 100 to 2000. These polymers may be obtained, for example, by the polymerization in the liquid phase of iso-olefins such as isobutylene or hydrocarbon mixtures containing the same at a temperature of from about 0° F. to about 100° F. in the presence of a catalyst such as boron fluoride. In the preparation of this low molecular weight polymer I may employ, for example, liquid isobutylene or a hydrocarbon mixture containing isobutylene, butane, and butylene, recovered from petroleum gases especially those gases produced in the cracking of petroleum oils of the manufacture of gasoline. This light fraction may contain from about 10% to about 25% isobutylene, the remainder being principally butanes and normal butylene.

The preparation of low molecular weight polymers from the butane-butylene-isobutylene fraction may be carried out as follows: The hydrocarbon mixture containing 10% to 25% isobuylene is maintained under pressure sufficient to keep it in the liquid phase and cooled to a tempera-

ture of, for example, about 32° F. and from about 0.1% to about 2% boron fluoride, based upon the isobutylene content of the material treated, added with vigorous agitation. Excessive rise in the temperature due to the heat of reaction may be avoided by efficient cooling. After the polymerization of the isobutylene together with a relatively minor amount of the n-olefins present, the reaction mass is neutralized and washed free of acidic substances arising from the catalyst, the oily layer is separated, and the polymer subsequently separated from the unreacted hydrocarbons by distillation. The polymer mixture so obtained, depending upon the temperature of reaction, varies in consistency from a light liquid to a viscous oily material and contains polymers having molecular weights ranging from about 100 to 2000. The polymers so obtained may be sulfurized as such or the polymer may be fractionated under reduced pressure into fractions of increasing molecular weights, for example, a trimer fraction having a boiling point of about 350° F., a tetramer fraction having a boiling point range between 400° F. and 420° F., or other desired fractions, and the fractions sulfurized.

Another source of an olefinic polymer suitable for sulfurization for the herein intended purpose is a fraction of the polymer obtained in the treatment of a gaseous hydrocarbon mixture containing isobutylene and normal butylene in the presence of phosphoric acid catalysts in the synthesis of iso-octane. The polymer may be obtained by subjecting a gas mixture comprising C_4 olefins and butanes to temperatures of about 270° F. to 430° F., preferably about 300° F. to about 330° F., and at a pressure of from about 500 pounds per square inch to about 750 pounds per square inch, and preferably about 600 pounds per square inch in the presence of a catalyst such as phosphoric acid on kieselguhr, diatomaceous earth or aluminum-free clay. The mixed polymer obtained consists essentially of dimer, but contains in addition about 5–10% and usually 6–7% of heavy polymer comprising trimer, tetramer and still higher polymers. This heavy polymer fraction may be separated and sulfurized as such or may be still further fractionated to give about 10–15% bottoms. Usually it is preferable to isolate and sulfurize these final bottoms, which consist essentially of a tetramer fraction and boils between about 400° F. and 520° F. The sulfurization of the tetramer may be accomplished by heating a mixture of the tetramer in the presense or absence of a diluent with sulfur at a temperature of about 300° F. to 400° F., and preferably at 300° F.–350° F. until the sulfurized product is non-corrosive to a copper strip, as determined by the A. S. T. M. method. The sulfurized product may then be acid treated and/or percolated through a decolorizing material such as fuller's earth to remove the objectionable dark bodies. If diluent is used in the sulfurization it may be removed by steam stripping.

The effectiveness of a mixture of sulfurized olefinic polymer and a glyceride phosphoric acid ester, such as lecithin, in improving the stability of a motor oil is demonstrated by the following data. About 250 c. c. of the oil to be tested was heated at about 330° F.–332° F. in a 500 c. c. glass beaker in the presence of five square inches of copper and ten square inches of iron. Four glass rods of about six millimeters diameter were suspended in the oil, which was stirred at about 1300 R. P. M. with a glass stirrer having 40° blade pitch. At stated intervals the oil samples were taken and sludge, acidity and viscosity values determined. The glass rods were also inspected for evidence of varnish formation thereon. The four samples tested were:

(A) A commercial 20 S. A. E. motor oil
(B) "A"+3% of a sulfurized tetramer
(C) "B"+¼% of a commercial lecithin
(D) "B"+1% of a commercial lecithin

The data obtained in the foregoing tests are set forth in the following table:

	Sample			
	A	B	C	D
Varnish:				
10 hrs.		7–8	9–10	9–10.
24 hrs.		1	9–10	9–10.
50 hrs.	Less than 1	Less than 1	5	8.
77 hrs.			3	6.
Sludge:				
10 hrs.		18.2 mg.	21.4 mg.	47.8 mg.
24 hrs.	250 mg.	101 mg.	36.4 mg.	61.4 mg.
50 hrs.	+1000 mg.	476 mg.	230 mg.	155 mg.
77 hrs.		845 mg.	483 mg.	164 mg.
Acidity:				
10 hrs.	3.5 mg. KOH/g. oil	1.1 mg. KOH/g. oil	1.0 mg. KOH/g. oil	1.7 mg. KOH/g. oil.
24 hrs.	10.2 mg. KOH/g. oil	2.7 mg. KOH/g. oil	1.6 mg. KOH/g. oil	2.7 mg. KOH/g. oil.
50 hrs.	23.2 mg. KOH/g. oil	4.2 mg. KOH/g. oil	3.6 mg. KOH/g. oil	3.6 mg. KOH/g. oil.
77 hrs.		11.7 mg. KOH/g. oil	11.1 mg. KOH/g. oil	5.2 mg. KOH/g. oil.
Saybolt visc. at 100° F.:				
0 hrs.	370 sec.	360 sec.	360 sec.	360 sec.
50 hrs.	2,300 sec.	851 sec.	637 sec.	616 sec.
77 hrs.		1,217 sec.	792 sec.	733 sec.

The varnish values in the above table are based on a visual rating in which a glass rod free of varnish is given a rating of 10.

The above data demonstrate the effectiveness of a mixture of a sulfurized polymer of olefinic hydrocarbons and a glyceride phosphoric acid ester in improving the properties of a mineral lubricating oil.

In engine tests made under severe operating conditions blends of mineral lubricating oils containing glyceride phosphoric acid esters and a sulfurized polymer of olefinic hydrocarbons have resulted in extremely clean engines, substantially free of carbon and/or varnish and no corrosion to bearings.

It is to be understood that modifications and variations falling within the terms and spirit of the appended claims are included within the scope of the invention which is not limited by the various details disclosed and described.

We claim:

1. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and

from about 0.05% to about 10.0% of a sulfurized polymer of olefinic hydrocarbons.

2. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and from about 0.05% to about 10.0% of a sulfurized polymer of normally gaseous olefinic hydrocarbons.

3. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and from about 0.05% to about 10.0% of a sulfurized polymer of a normally gaseous iso-olefinic hydrocarbon.

4. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and a sulfurized isobutylene polymer.

5. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and from about 0.05% to about 10.0% of a sulfurized co-polymer of an iso-olefin and a normal olefin.

6. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and from about 0.05% to about 10.0% of a sulfurized isobutylene tetramer.

7. A lubricant comprising a lubricating oil, having blended therewith from about 0.05% to about 5.0% of a glyceride phosphoric acid ester and from about 0.05% to about 10.0% of a sulfurized tetramer, said tetramer being obtained by co-polymerization of a normally gaseous hydrocarbon mixture containing isobutylene and normal butylene.

8. An improved lubricant comprising a mineral lubricating oil having blended therewith from about 0.5% to about 5% of lecithin and a sulfurized polymer of normally gaseous olefinic hydrocarbons having less than 6 carbon atoms.

9. An improved lubricant comprising a mineral lubricating oil having blended therewith from about 0.5% to about 5% of lecithin and sulfurized polymer of normally gaseous olefinic hydrocarbons.

10. A lubricant comprising a mineral lubricating oil, having blended therewith from about .05% to about 5% of lecithin and from about .05% to about 10% of a sulfurized isobutylene polymer.

11. A lubricant comprising a mineral lubricating oil, having blended therewith from about .05% to about 5% of lecithin and from about .05% to about 10% of a sulfurized tetramer, said tetramer being obtained by the polymerization of a hydrocarbon mixture containing four carbon atom hydrocarbons.

12. A lubricant comprising a mineral lubricating oil, having blended therewith from about 0.05% to about 5% of mixed phosphatides and from about 0.05% to about 10% of a sulfurized polymer, said sulfurized polymer being obtained by separating and sulfurizing the fraction boiling between about 400° F. and about 520° F. from the polymerization product of a hydrocarbon mixture containing four carbon atom hydrocarbons.

13. A lubricant comprising a mineral lubricating oil, having blended therewith from about 0.05% to about 5% of mixed phosphatides and from about 0.05% to about 10% of a sulfurized polymer, said sulfurized polymer being obtained by separating and sulfurizing the fraction boiling between about 400° F. and about 520° F. obtained as a fraction from the co-polymerization of a hydrocarbon mixture containing isobutylene, normal butenes, and butane to produce essentially iso-octane.

14. An improved lubricant comprising a mineral lubricating oil having blended therewith from about 0.05% to about 5% of mixed phosphatides and from about 0.05% to about 10% of a sulfurized polymer of normally gaseous olefinic hydrocarbons.

15. An improved lubricant comprising a mineral lubricating oil having blended therewith from about 0.05% to about 5% of mixed phosphatides and from about 0.05% to about 10% of a sulfurized tetramer, said tetramer separated from a mixture of polymerized hydrocarbons of less than six carbon atoms.

16. An improved lubricant comprising a mineral lubricating oil having blended therewith from about 0.05% to about 5% of a phosphatide and from about 0.05% to about 10% of a sulfurized polymer of normally gaseous olefinic hydrocarbons.

17. An improved lubricant comprising a mineral lubricating oil having blended therewith from about 0.05% to about 5% of a phosphatide and from about 0.05% to about 10% of a sulfurized tetramer, said tetramer separated from a mixture of polymerized hydrocarbons of less than six carbon atoms.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 17, claim 4, after the word "and" insert --from about 0.05% to about 10.0% of--; lines 39 and 44, claims 8 and 9 respectively, after "and" insert --from about "0.05% to about 10% of--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 5th day of September, A. D. 1944.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.