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LUBRICANT

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This invention relates to an improved multifunctional lubricant additive and to lubricants containing the same. More particularly the invention relates to lubricating oil compositions adapted for use in internal combustion engines of the spark-ignition and compression-ignition types wherein, under operation conditions, corrosion, piston ring sticking, cylinder wear, carbon and/or 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 an object of this invention to provide a multifunctional additive for petroleum products which will inhibit corrosion, sludge, acidity and varnish formation, and also impart a desirable bloom to the lubricants to which it is added.

It is another 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 inducive 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.

I have discovered that an improved lubricant having a highly desirable bloom and/or cast satisfying the foregoing objects can be attained by adding to a suitable lubricating oil base small amounts of a wholly neutralized, or partially neutralized, reaction product of a phosphorus sulfide and a particular high molecular weight hydrocarbon oil. This hydrocarbon oil because of its high molecular weight, appearance and physical characteristics is sometimes referred to as a "resin" or "resinous oil," although its chemical characteristics are far different from those materials more commonly and more properly called resins. For the purpose of identification this high molecular weight hydrocarbon oil will be referred to hereinafter and in the appended claims as "resin-like oil."

The resin-like oil, which has a molecular weight of from about 1000 to about 2000 or higher, can be obtained preferably from a paraffinic oil, such as a Pennsylvania cylinder stock which has been dewaxed, preferably at a temperature in the order of about —40° F. The dewaxed oil is then treated with from about 5 to about 10 volumes of a liquefied normally gaseous hydrocarbon, for example propane, at a temperature from about 150° F. to about 180° F. to produce two fractions, a lighter propane-soluble fraction and a heavy propane-insoluble fraction which contains the resin-like oils. The heavy fraction is then treated with additional liquefied propane at from about 130° F. to about 170° F., usually at about 145° F., the ratio of propane to heavy oil being from about 5 to 1 to about 10 to 1, and usually about 7 to 1. By this treatment about 3% to about 3½% of resin-like oil, based on the original amount of dewaxed oil, precipitates out from the propane-soluble constituents of the heavy fractions. This resin-like oil is a substantially wax-free and asphalt-free product having a Saybolt Universal viscosity at 210° F. of from about 1000 seconds to about 4000 seconds or more, a viscosity index of about 90 or more, and a relatively high pour point.

Although liquefied propane is preferred, it will be understood that the propane may contain or be replaced by other liquefied normally gaseous hydrocarbons, particularly ethane, isobutane, butane, propylene, butylene, etc.

Resin-like oils having suitable characteristics, similar to the above can be obtained from a mixed base oil such as a Mid-Continent crude oil. When a mixed base oil is used it is necessary to deasphalt as well as dewax the oil before precipitation of the resin-like oil. Such oils can be deasphalted by treatment wth a liquefied normally gaseous hydrocarbon, such as liquefied propane, at temperatures of from about 105° F. to about 115° F. with an oil-to-propane ratio of about 1 to 2.

A more detailed description of the process for obtaining these resin-like oils will be found in U. S. Patents 2,143,872 and 2,143,882.

The phosphorus sulfide-resin-like oil reaction product may be obtained by reacting a phosphorus sulfide such as P_2S_3, P_2S_5, P_4S_7, P_4S_3, etc., preferably P_2S_5, with a resin-like oil polymer of the type herein described at a temperature of from about 200° F. to about 500° F., and preferably from about 300° F. to about 400° F. It is advantageous to maintain a non-oxidizing atmosphere such as, for example, an atmosphere of

nitrogen, above the reaction mixture. From about 1% to about 50%, and preferably from about 5% to about 25% of the phosphorus sulfide, may be used. Usually it is preferable to use an amount of phosphorus sulfide that will completely react with the resin-like oil, for example, 10%, so that no purification is necessary. However, excess phosphorus sulfide may be used and separated from the product after the reaction is completed, by filtering or by diluting with a solvent such as hexane, filtering, and distilling off the solvent. The reaction mixture may be further treated by blowing with steam or nitrogen at an elevated temperature to improve the odor thereof.

The reaction product of a phosphorus sulfide and the resin-like oil normally shows a titratable acidity ranging from about 10 to about 50 milligrams KOH per gram of product. Although the unneutralized reaction product can be used as such in lubricants, it is preferable to treat the acidic product with an alkaline material to effect the neutralization of at least about 1% of the titratable acidity. It will be understood that when the neutralization is accomplished with a polyvalent basic material such as lime, a product having excess basicity may be obtained.

The neutralization of the phosphorus sulfide resin-like oil reaction product may be effected by adding to the reaction product a suitable alkaline compound such as a hydroxide, a carbonate, or an oxide of an alkali or alkaline earth metal, and preferably potassium hydroxide, or an alkali metal sulfide, for example, sodium sulfide. Ammonia or alkyl or aryl substituted ammonia such as amines may be used. A neutralized product containing a heavy metal constituent such as, for example, tin, titanium, aluminum, chromium, cobalt and the like, may be obtained by treating the neutralized product with a salt of the desired heavy metal.

The term "neutralized phosphorus sulfide resin-like oil" as used herein means a phosphorus sulfide resin-like oil reaction product having at least about 1% of its titratable acidity, reduced by the reaction with a basic reagent, and includes the neutralized phosphorus sulfide resin-like oil reaction products containing a metal constituent resulting from said neutralization or resulting from the reaction of a heavy metal salt with the phosphorus sulfide resin-like oil reaction product treated with a basic reagent. The final product resulting from the neutralization of the phosphorus sulfide resin-like oil reaction product is characterized by the presence or retention of the metal constituent of the neutralizing reagent.

The neutralization can be carried out by contacting the phosphorus sulfide-resin-like oil reaction product, either as such or dissolved in a suitable solvent such as a naphtha with a solution, preferably an alcoholic solution, of the neutralizing agent, for example an oxide, hydroxide or a carbonate of an alkali metal or an alkaline earth metal, such as NaOH, KOH, Na_2CO_3, K_2CO_3 and CaO, or with ammonia. The neutralization can also be accomplished by contacting the reaction product with the dry neutralizing agent, such as KOH, NaOH, Na_2CO_3, K_2CO_3, CaO, or dry ammonia, preferably at an elevated temperature of from about 100° F. to about 500° F., and preferably in a non-oxidizing atmosphere.

The neutralized product as aforesaid can be further treated with a salt of a heavy metal to obtain the heavy metal derivative.

The neutralized product or the heavy metal derivative thereof can be employed in lubricants in amounts ranging from about 0.001% to about 20% or higher and preferably from about 0.01% to about 5%. While it is preferred to employ the neutralized reaction product, the unneutralized reaction product can be advantageously employed in the same amounts in lubricants, either alone or in combination with the neutralized product.

The following example is illustrative of the preparation of a neutralized phosphorus sulfide-resin-like oil reaction product.

A resin-like oil obtained by the propane precipitation of a Pennsylvania bright stock and having a Saybolt Universal viscosity at 210° F. of about 2900 seconds was reacted with 10% P_2S_5 at a temperature of about 370–390° F. for about seven hours. The reaction product was then mixed with an equal weight of a S. A. E. 20 motor oil and this mixture was reacted with KOH pellets by agitation at about 380° F. for about four hours. 4% by weight of KOH was used based on the P_2S_5-resin-like oil reaction product in its mixture with the motor oil. The partially neutralized reaction product was allowed to cool and settle. Inspection of the decanted product was as follows:

Acidity	7.2 mg. KOH/gram product
Phosphorus	2.8%
Sulfur	1.8%
Potassium	3.0%

All of these values are on the reaction product if it was straight, i. e. not a 50% concentrate in motor oil.

A S. A. E. 20 motor oil containing 2.0% of this 50% concentrate of the reaction product in oil, i. e. 1.0% of the straight reaction product, and the motor oil without the additive were submitted to the following test: Two hundred and fifty cc. of each of the oils was heated at 330°–332° F. in 500 cc. glass beakers in the presence of five square inches of copper and ten square inches of iron. Four glass rods of about six millimeter diameter were suspended in each of the oil samples. During the test the oils were stirred at about 1300 R. P. M. with a glass stirrer having a 40° blade pitch. At stated intervals oil samples were taken and sludge, acidity and viscosity determinations made. The glass rods were also inspected for evidence of varnish formations. Varnish values reported are based on a usual rating in which a glass rod free of any varnish is given a rating of 10, while a badly coated rod is given a rating of 1. Rods having appearances between these extremes are given intermediate values.

The results obtained by the above-described test are tabulated below:

Oil	Viscosity[1] increase	Sludge mg./10 gr. oil		Acidity, mg. KOH/gr. oil		Varnish[2]	
	48 hrs.	24 hrs.	48 hrs.	24 hrs.	48 hrs.	24 hrs.	48 hrs.
Oil A	1540	233	1017	4.5	10.0	5	2
Oil B	119	26	38	2.0	4.0	10	10

Oil A=control S. A. E. 20 motor oil.
Oil B=oil A+1.0% neutralized P_2S_5-resin-like oil reaction product.
[1] Saybolt Universal viscosity at 100° F.
[2] Rating scale: 10=no deposit.
1=very heavy deposit.

The above data illustrate the marked effectiveness of the additive of the present invention in improving the stability of the oil to which it is added. The additive is also effective in inhibiting corrosion to bearings and the like.

In addition to exhibiting the above properties of inhibiting viscosity increase, sludge, acidity and/or varnish, the additive also possesses the property of imparting a highly desirable green bloom to oils. These multifunctional properties of the reaction product make it a valuable additive.

While I have described the use of my additives in lubricating oils, my invention is not limited to such use, since these reaction products may be employed in other petroleum products such as insulating oils, turbine oils, white oils, greases, waxes and the like to increase the resistance thereof to oxidation, sludging, and to inhibit the tendency thereof to corrode metals. The additive of the present invention can be employed in oils other than mineral oils, for example vegetable oils, animal oils, marine oils and the like.

While I have described preferred embodiments of my invention, other modifications thereof may be made without departing from the scope and spirit of the invention and I do not wish to limit my invention to the examples set forth herein except in so far as the same is defined by the following claims.

I claim:

1. A lubricant containing a small amount of a phosphorus sulfide-resin-like oil reaction product having at least a portion of the titratable acidity thereof reduced by reaction with a basic reagent, said resin-like oil being obtained from a substantially wax-free and asphalt-free lubricating oil stock by precipitation with a liquefied normally gaseous hydrocarbon.

2. A lubricant containing a small amount of a phosphorus sulfide-resin-like oil reaction product having at least a portion of the titratable acidity thereof reduced by reaction with a basic reagent having a metal constituent, said resin-like oil being obtained from a substantially wax-free and asphalt-free lubricating oil stock by precipitation with a liquefied normally gaseous hydrocarbon.

3. A lubricant as described in claim 2 in which the basic reagent contains a metal of the alkali metal group of the Periodic Table.

4. A lubricant as described in claim 2 in which the basic reagent contains a metal of the alkaline earth group of the Periodic Table.

5. A lubricant as described in claim 2 in which the basic reagent contains potassium.

6. A lubricant as described in claim 2 in which the basic reagent contains sodium.

7. A lubricant as described in claim 2 in which the basic reagent contains calcium.

8. A lubricant containing a lubricating oil and a small amount of a neutralized reaction product of a phosphorus sulfide and a resin-like oil, said resin-like oil having a Saybolt Universal viscosity at 210° F. of from about 1000 seconds to about 4000 seconds, and being obtained from a substantially wax-free and asphalt-free lubricating oil stock by precipitation with a liquefied normally gaseous hydrocarbon.

9. A lubricant as described in claim 8 in which the phosphorus sulfide is phosphorus pentasulfide.

10. A lubricant as described in claim 8 in which the neutralized reaction product contains a metal constituent.

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