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LUBRICANT

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The present invention relates to improvements in lubricants and more particularly to lubricants containing an adjunct which imparts to the lubricants varnish inhibiting properties.

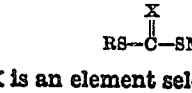
More particularly the invention relates to lubricating oil compositions adapted for use in internal combustion engines of the spark ignition and compression ignition types wherein under operation conditions corrosion, piston ring sticking, cylinder wear and varnish formation are substantially reduced.

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

It is an object of this invention to provide a lubricant which is resistant to the formation of varnish. It is another object of this invention to provide a hydrocarbon oil composition adapted for use in internal combustion engines and which is resistant to the formation of sludge, acidity and varnish and which is non-corrosive to bearing metals, particularly bearing metals of the hard metal alloy type. Other objects and advantages of this invention will become apparent as the description thereof proceeds.

I have discovered that the foregoing objects can be attained by adding to a lubricant composition containing a lubricating oil such as, for example, an animal, vegetable, marine, or a hydrocarbon oil such as a mineral or petroleum oil, a metallic salt of an organic polythiocarbonate in small but sufficient quantities to inhibit varnish and/or sludge formation in such lubricant. Generally from about 0.05% to about 10% of the metallic salt of the organic thiocarbonate can suitably be used, although, depending on the conditions encountered, smaller or greater amounts can be employed.

The metal salt of the organic polythiocarbonate used in the present invention has the general formula



in which X is an element selected from the group consisting of oxygen and sulfur, R is an organic

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group such as an alkyl, aryl, alkaryl, aralkyl, alicyclic or heterocyclic radical, and M represents a metal such as, for example, lithium, sodium, potassium, magnesium, calcium, strontium, barium, copper, aluminum, chromium, tin, lead, iron, cobalt, nickel, titanium, tungsten, vanadium, and zinc. The organic group may contain inorganic substituents such as oxygen, sulfur and phosphorus. Particularly effective for the herein-described purpose are the metal salts of terpene polythiocarbonate and the metal salts of keryl polythiocarbonates. The term "keryl polythiocarbonate" denotes a substituted polythiocarbonate in which the hydrocarbon constituent is a petroleum fraction having distillation characteristics corresponding to that of a kerosene fraction.

The metal salts of the organic polythiocarbonates can be prepared by reacting an alcoholic solution of a hydrocarbon mercaptan and caustic such as KOH with carbon disulfide. The alkali metal organic polythiocarbonate can then be treated with a polyvalent salt to obtain any desired metal salt of the organic polythiocarbonate. The preparation of these compounds is exemplified by the following examples which are given by way of illustration only and are not intended as limiting the scope of the invention. The zinc salt of terpene trithiocarbonate was prepared in the following manner: 108.5 grams of terpene mercaptan and 42 grams of KOH was dissolved in 500 cc. of ethyl alcohol. To this alcohol solution was added 48 grams of carbon disulfide and the mixture was stirred for about 15 minutes at a temperature of about 80° F. Upon completion of this reaction 45 grams of zinc chloride dissolved in 100 cc. of water was added to the mixture with stirring. The zinc salt of the terpene trithiocarbonate was separated from the reaction mass as a reddish yellow oil by hexane extraction.

The zinc salt of keryl trithiocarbonate was prepared in the following manner: 108 grams of keryl mercaptan was dissolved in 300 cc. of ethyl alcohol. To this alcohol solution was added 50 grams of carbon disulfide and the mixture was stirred for about 15 minutes at about 80° F. At the end of this reaction a slight excess of zinc chloride dissolved in water was added to the mixture with stirring. The zinc salt of the keryl trithiocarbonate was separated from the reaction mass as a reddish yellow oil by hexane extraction.

The metal salts of the organic polythiocarbonates of the type herein-described are particu-

larly efficient varnish inhibitors and can be used as such in lubricants or in conjunction with other additives. Thus they can be used in combination with additives which impart detergency and corrosion inhibiting properties to such lubricants, for example, the neutralized phosphorus sulfide-hydrocarbon reaction products such as are described in U. S. 2,316,082 and U. S. 2,316,087. Other types of additives can also be used in conjunction with the metal salts of organic polythiocarbonates such as, for example, sulfurized hydrocarbons such as sulfurized mineral oils, sulfurized terpenes, substituted amines such as, for example, polyamino polyaryl methanes such as aminomethyl-aminodiphenyl methane, tetramethyl-diamino-diphenyl methane, di(methyl amino) dinaphthyl methane and derivatives of the same.

The effectiveness of the metallic salts of organic polythiocarbonates in inhibiting varnish formation in internal combustion engines is illustrated by the following data. These data were obtained by subjecting oils containing the additives to accelerated engine tests made in the standard six cylinder spark ignition internal combustion engines operating for 60 hours at 35 B. H. P. and 3000 R. P. M. with an oil sump temperature of 285° F. At the end of the test period the engines are dismantled, inspected and given visual ratings. In this visual rating system a rating of 10 means that the engine had substantially the appearance of the engine at the start of the test while a rating of 1 indicates that the engine after the test showed very extensive deposits of varnish and sludge. Engines having appearances between these extremes are given intermediate rating values. An engine lubricated with good conventional motor oil for a 60 hour period usually merits a visual rating of about 5. The data presented herein were obtained by subjecting the following oils to the foregoing tests:

Oil A.—98.75% acid treated SAE–30 M. C. motor oil, 0.75% KOH neutralized reaction product of P_2S_5 and isobutylene polymer, 0.25% sulfurized mineral oil, 0.25% sulfurized terpene.

Oil B.—Oil A+0.5% zinc terpenyl trithiocarbonate.

Oil C.—Oil A+0.5% zinc keryl trithiocarbonate.

Oil Sample	Overall Rating	Varnish Rating
A	8.0	6.0
B	8.5	6.9
C	8.8	8.7

The above data demonstrate the improvement in the overall and varnish rating due to the presence of the metallic soap of the organic polythiocarbonate.

The present invention also contemplates the addition of other additives to lubricant compositions such as, for example, antioxidants, pour point depressors, V. I. improvers, oiliness agents, anti-rust agents, extreme pressure agents and the like.

While I have described my invention with reference to specific embodiments thereof, it is to be understood that the same are given merely by way of illustration and are not intended to limit the scope of the herein-described invention except insofar as the same are defined by the appended claims.

I claim:

1. A normally liquid lubricant composition comprising a major proportion of a hydrocarbon oil and from about 0.05% to about 10% of a zinc organo trithiocarbonate of the group consisting of a zinc alkyl trithiocarbonate and a zinc alicyclic trithiocarbonate.

2. A normally liquid lubricant composition resistant to the formation of products of oxidative deterioration of the type of varnish and sludge, comprising a major proportion of a hydrocarbon oil normally susceptible to oxidative deterioration and in combination therewith from about 0.05 per cent to about 10 per cent of a zinc salt of an organic trithiocarbonate selected from the class consisting of an alkyl trithiocarbonate and an alicyclic trithiocarbonate and an additive exhibiting detergency properties, the latter being used in small but sufficient quantities to inhibit the deposition of varnish and sludge on engine parts.

3. A normally liquid lubricant composition as described in claim 2 in which the additive exhibiting detergency properties is the neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

4. A normally liquid lubricant composition comprising a major proportion of a hydrocarbon oil and from about 0.05% to about 10% of a zinc salt of an alkyl trithiocarbonate.

5. A normally liquid lubricant composition comprising a major proportion of a hydrocarbon oil and from about 0.05% to about 10% of a zinc salt of an alicyclic trithiocarbonate.

6. A normally liquid lubricant composition containing a major proportion of a hydrocarbon oil and from about 0.05% to about 10% of zinc terpenyl trithiocarbonate.

7. A normally liquid lubricant composition containing a major proportion of a hydrocarbon oil and from about 0.05% to about 10% of zinc keryl trithiocarbonate.

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