

1

2,921,901

## LUBRICATING OIL COMPOSITION

Robert E. Karli, Hammond, Albert R. Sabol, Munster, and Eugene E. Richardson, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Application July 29, 1955  
Serial No. 525,386

6 Claims. (Cl. 252—32.7)

This invention relates to a novel lubricating oil composition and more particularly pertains to a lubricating oil composition having improved detergency characteristics.

In the lubrication of internal combustion engines of all types, particularly when severe operating conditions are encountered, plain lubricating oils often prove unsatisfactory because of the oxidative deterioration of the oil with the attendant deposition on the engine surfaces of varnish, gum and sludge and the formation of acidic compounds resulting in corrosion of the metal surfaces of the engine.

It has heretofore been discovered that certain reaction products of a phosphorus sulfide and a hydrocarbon, particularly an olefin or an olefin polymer, when added in small amounts to a hydrocarbon oil, are effective in inhibiting the formation of varnish, sludge, carbon and the like in lubricating oils during use. It has also been found that neutralizing these reaction products of a phosphorus sulfide and a hydrocarbon with a basic reagent having a metal constituent and particularly with a basic barium compound provides a composition which is effective as a detergent. However, it has since been found that under certain conditions, particularly when high sulfur fuels are employed, lubricants containing the neutralized, metal containing product of a phosphorus sulfide and a hydrocarbon does not effectively inhibit the formation of sludge, varnish and other resinous materials in the engine or provide adequate detergency.

It is an 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 additive which serves the functions of (1) inhibiting the oxidative deterioration of the lubricant, (2) preventing corrosion of the lubricated surfaces, and (3) acting as a detergent to prevent ring sticking, varnishing or coating of the metallic surfaces of internal combustion engines, as well as a suspending or dispersing agent for dispersing very small particles of deterioration products or contaminating materials in the oil. A more particular object is to provide a lubricant additive to serve the above enumerated functions when employed in an internal combustion engine using a fuel containing a relatively high percentage of sulfur. These and additional objects will become apparent as the description of the invention proceeds.

We have discovered that a product having the desired carbon and/or varnish formation inhibiting properties as well as improved corrosion inhibiting properties and detergent properties can be obtained by incorporating in a lubricant composition, provided with a metal containing neutralized reaction product of a phosphorus sulfide and a hydrocarbon, and particularly a barium containing neutralized reaction product of a phosphorus sulfide and an olefin, a small amount of a compound prepared by reacting a basic metal compound,

2

preferably a basic alkali metal or alkaline earth metal compound, and an alkyl alcohol having from 5 to 30 carbon atoms, and preferably from 8 to 20 carbon atoms, or an alkyl phenol having from 8 to 36 carbon atoms, and preferably from 12 to 26 carbon atoms; and contacting said reaction product with carbon dioxide. Reaction of the basic metal compound and the hydroxy compound may be carried out at a temperature from about 0° F. to about 400° F. and preferably in the range of from about 100° F. to about 350° F. The reaction of carbon dioxide and the intermediate reaction product may be carried out at a temperature in the range of from about 0° F. to about 300° F. and preferably in the range of from about 140° F. to about 250° F.

It has been found that from 0.01% to about 10% and preferably from about 0.10% to about 2% of this addition agent in a lubricating oil containing from about 0.001% to 10% of a metal containing neutralized reaction product of a phosphorus sulfide and a hydrocarbon provides a lubricating oil having excellent detergent characteristics which is effectively inhibited against the formation of varnish, sludge, carbon or the like.

While the hereinbefore described reaction product of a basic metal compound, a hydroxy compound and carbon dioxide can be used in combination with the hereinbefore described phosphorus sulfide-hydrocarbon reaction product, it is often desirable to employ the former product in combination with the phosphorus sulfide-hydrocarbon reaction product and an organic sulfur compound as described and claimed in U.S. Re. 22,464, issued to Kelso et al. April 4, 1944, or a sulfurized terpene as described and claimed in U.S. 2,422,585 issued to T. H. Rogers et al. June 17, 1947.

While the reaction product of a basic metal compound, a hydroxy compound and carbon dioxide in the hereinbefore described class are effective in increasing the detergency of a lubricating oil in the presence of the metal containing neutralized reaction product of a phosphorus sulfide and a hydrocarbon, it is not to be implied that all are equally effective since the effectiveness can vary with the type of lubricating oil and the conditions of use.

As aforesaid, one of the components of the improved lubricant is the neutralized reaction product of a hydrocarbon and a phosphorus sulfide such as P<sub>2</sub>S<sub>3</sub>, P<sub>4</sub>S<sub>3</sub>, P<sub>4</sub>S<sub>7</sub>, or other phosphorus sulfides, and preferably phosphorus pentasulfide, P<sub>2</sub>S<sub>5</sub>. The hydrocarbon constituent of this reaction is preferably a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefinic hydrocarbons or isomono-olefin hydrocarbons such as propylenes, butylenes, and amylenes or the copolymers obtained by the polymerization of hydrocarbon mixtures containing isomono-olefins and mono-olefins of less than 6 carbon atoms. The polymers may be obtained by the polymerization of these olefins or mixtures of olefins in the presence of a catalyst such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and isomono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably from about 500 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid phase of a hydrocarbon mixture containing mono-olefins and isomono-olefins such as butylene and isobutylene at a temperature of from about -80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts type such as, for example, boron fluoride, aluminum chloride and the like. In the prep-

3

aration of these polymers we may employ, for example, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline.

A suitable polymer for the reaction with phosphorus sulfide is the product obtained by polymerizing in the liquid phase a hydrocarbon mixture containing butylenes and isobutylenes together with butanes and some C<sub>3</sub> and C<sub>5</sub> hydrocarbons at a temperature between about 0° F. and 30° F. in the presence of aluminum chloride. A suitable method for carrying out the polymerization is to introduce the aluminum chloride into the reactor and introduce the hydrocarbon mixture cooled to a temperature of about 0° F. into the bottom of the reactor and pass it upwardly through the catalyst layer while regulating the temperature within the reactor so that the polymer product leaving the top of the reactor is at a temperature of about 30° F. After separating the polymer from the catalyst sludge and unreacted hydrocarbon, the polymer is fractionated to obtain a fraction of the desired viscosity such as, for example, from about 80 seconds to about 2000 seconds Saybolt Universal at 210° F.

Another suitable polymer is that obtained by polymerizing in the liquid phase a hydrocarbon mixture comprising substantially C<sub>3</sub> hydrocarbons in the presence of an aluminum chloride-complex catalyst. The catalyst is preferably prepared by heating aluminum chloride with iso-octane. The hydrocarbon mixture is introduced into the bottom of the reactor and passed upwardly through the catalyst layer, while a temperature of from about 50° F. to about 110° F. is maintained in the reactor. The propane and other saturated gases pass through the catalyst, while the propylene is polymerized under these conditions. The propylene polymer can be fractionated to any desired molecular weight, preferably from about 500 to about 1000 or higher.

Other suitable polymers can be obtained by polymerizing a hydrocarbon mixture containing about 10% to about 25% isobutylene at a temperature of from about 0° F. to about 100° F. and preferably 0° F. to about 32° F. in the presence of boron fluoride. After the polymerization of the isobutylene together with a relatively minor amount of the normal olefins present, the reaction mass is neutralized, washed free of acidic substances and the unreacted hydrocarbons subsequently separated from the polymers by distillation. The polymer mixture so obtained, depending upon the temperature of reaction, varies in consistency from a light liquid to viscous, oily material and contains polymers having molecular weights ranging from about 100 to about 2000 or higher. The polymers so obtained may be used as such, or the polymer may be fractionated under reduced pressure into fractions of increasing molecular weights, and suitable fractions reacted with the phosphorus sulfide to obtain the desired reaction products. The bottoms resulting from the fractionation of the polymer may have Saybolt Universal viscosities at 210° F. ranging from 50 seconds to about 10,000 seconds and are well suited for the purpose of the present invention.

Essentially paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, petrolatums, or paraffin waxes may be used. There can also be employed the condensation products of any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbons and then reacting with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride and the like.

Examples of high molecular weight olefinic hydrocarbons which can be employed as reactants are cetene (C<sub>16</sub>) and cerotene (C<sub>26</sub>) melene (C<sub>30</sub>) and mixed high molecular alkenes obtained by cracking petroleum oils.

Other preferred olefins suitable for the preparation of the herein-described phosphorus sulfide reaction products

4

are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained by the dehydrogenation of paraffins, such as by the cracking of paraffin waxes, or by the dehydrohalogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

The olefins obtained by dehydrohalogenation of long chain alkyl halides are preferably those obtained by dehydrohalogenation of monohalogenated waxes, such as for example, those obtained by dehydrochlorination of monochlor paraffin wax. The alkyl halides are decomposed to yield olefins according to the reaction



in which *n* is a whole number, preferably 20 or more, and X is a halogen. It is preferred to employ paraffin waxes having at least about 20 carbon atoms per molecule, and melting points upwards from about 90° F. to about 140° F.

To obtain the halogenated paraffin wax, for example, chlorinated paraffin wax, chlorine is introduced into the wax, maintained in a molten state, until the wax has a chlorine content of from about 8% to about 15%. The chlorinated wax product is a mixture of unchlorinated wax, monochlor wax and polychlor wax. This chlorinated product may be used as such, but it is advantageous to use the substantially monochlor wax fraction. The monochlor wax fraction can be segregated from the unchlorinated wax and the polychlor wax fractions by taking advantage of the differences in the melting points of the various fractions, since the melting point of the wax varies with the extent of chlorination, i.e., the melting point of the unchlorinated wax is greater than that of the monochlor wax, and the melting point of the latter is greater than that of the polychlor wax. Thus, the monochlor paraffin wax can be separated from the unchlorinated and the polychlor wax fractions by means such as sweating, fractional distillation, solvent extraction, solvent precipitation, and fractional crystallization.

The high molecular weight olefins are obtained by removing the halogen as hydrogen halide from the halogenated paraffin wax. For example, the corresponding olefin is obtained from the monochlor paraffin wax by removing the chlorine from the latter as hydrogen chloride. The monochlor wax can be dehydrochlorinated by heating to a temperature of from about 200° F. to about 600° F. in the presence of a dehydrochlorinating agent such as an alkali metal hydroxide or an alkaline earth metal hydroxide or oxide. Other alkaline inorganic or organic materials can also be used. The chlorine can also be removed from the chlorowax by heating the same for a prolonged period in the absence of any dehydrochlorinating agent. After the dehydrohalogenation has been completed, the olefin so obtained can be further purified by removing the dehydrohalogenating agent by means of filtration or by other suitable means.

As other starting materials there can be used the polymer or synthetic lubricating oil obtained by polymerizing unsaturated hydrocarbons, resulting from the vapor phase cracking of paraffin waxes, in the presence of aluminum chloride, which is fully described in United States Patents Nos. 1,955,260, 1,970,402 and 2,091,398. Still another type of olefin polymer which may be employed is the polymer resulting from the treatment of vapor phase cracked gasoline and/or gasoline fractions with sulfuric acid or solid absorbents such as fuller's earth whereby unsaturated polymerized hydrocarbons are removed. Also contemplated within the scope of this invention is the treatment with phosphorus sulfide of the polymers resulting from the volatilization of hydrocarbons as described, for example, in United States Patents Nos. 2,197,768 and 2,191,787.

Also contemplated within the scope of the present in-

vention are the reaction products of a phosphorus sulfide with an aromatic hydrocarbon such as for example benzene, naphthalene, toluene, xylene, diphenyl and the like, or with an alkylated aromatic hydrocarbon such as, for example, benzene having an alkyl substituent having at least four carbon atoms and preferably at least eight carbon atoms such as, for example, long chain paraffin waxes, olefin polymers and the like.

The phosphorus sulfide-hydrocarbon reaction product can be readily obtained by reacting a phosphorus sulfide, for example,  $P_2S_5$  with the hydrocarbon at a temperature of from about 200° F. to about 500° F. and preferably from about 200° F. to about 400° F., using from about 1% to about 50% and preferably from about 5% to about 25% of the phosphorus sulfide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere such as, for example, an atmosphere of nitrogen above the reaction mixture. Usually it is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a solvent such as hexane, filtering and subsequently removing the solvent by suitable means such as by distillation. If desired, the reaction product can be further treated with an agent having an active hydrogen atom such as steam at an elevated temperature of from about 100° F. to about 600° F.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The phosphorus sulfide-hydrocarbon reaction product when neutralized with a basic reagent containing a metal constituent is characterized by the presence or retention of the metal constituent of the basic reagent. Other metal constituents such as a heavy metal constituent can be introduced into the neutralized product by reacting the same with a salt of the desired heavy metal.

The term "neutralized phosphorus sulfide-hydrocarbon reaction product" as used herein means a phosphorus sulfide-hydrocarbon reaction product having at least about 1% of its titratable acidity neutralized by reaction with a basic reagent and includes the neutralized phosphorus sulfide-hydrocarbon reaction products containing a metal constituent resulting from said neutralization or resulting from the reaction of a heavy metal salt with the phosphorus sulfide-hydrocarbon reaction product treated with a basic reagent.

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the reaction product with a suitable basic compound such as a hydroxide, carbonate, oxide or sulfide of an alkaline earth metal or an alkali metal such as, for example, potassium hydroxide, sodium hydroxide, sodium sulfide, etc. Other basic reagents can be used such as, for example, ammonia or an alkyl or aryl substituted ammonia such as amines. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the reaction product either as such or dissolved in a suitable solvent such as naphtha with a solution of the basic reagent, for example, potassium hydroxide or sodium hydroxide dissolved in alcohol. As an alternative method, the reaction product can be treated with solid alkaline compounds such as KOH, NaOH,  $Na_2CO_3$ ,  $K_2CO_3$ , CaO,  $Na_2S$ , and the like at an elevated temperature of from about 100° F. to about 600° F. As was aforesaid, when the phosphorus sulfide-hydrocarbon reaction product is neutralized with a basic reagent containing a metal constituent, the neutralized reaction product is characterized by the presence of the metal constituent of the basic reagent. Neutralized reaction products containing a heavy metal constituent such as, for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron, and the like,

can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocarbon reaction product which has been treated with a basic reagent. 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 neutralized phosphorus sulfide-hydrocarbon reaction product can be prepared by the method described in U.S. 2,688,612 issued to Watson on September 7, 1954.

The reaction product of a basic metal compound, a hydroxy compound and carbon dioxide of the hereinbefore described class which is used in combination with the neutralized reaction product of a phosphorus sulfide and a hydrocarbon is a preferentially oil-soluble product.

One of the classes of hydroxy compounds, as pointed out hereinbefore, is the alkyl phenols having from 8 to 36 carbon atoms and preferably from about 12 to about 26 carbon atoms. Thus the substituted phenol may contain one or more side chains and the total number of carbon atoms in the side chains may be from about 2 to about 30. These alkylated phenols may be obtained by any of the conventional methods for preparing such compounds; for instance, they may be alkylated in the presence of aluminum chloride or the like. Inasmuch as the method of preparing the alkylated phenols is not germane to this invention, they may be obtained in any manner or by any method. The alkyl groups on such alkylated phenols are provided to increase the oil solubility and viscosity characteristics of the compound. Hence they may be substituted on more than one of the carbon atoms of the aromatic nucleus. For instance, the alkylated phenols may range from ethyl phenol to dinonyl phenol or trihexyl phenol or the like or any combination of substituents provided that the required solubility and viscosity characteristics are obtained.

Another class of hydroxy compounds referred to hereinbefore is the alkyl alcohols having 5 to 30 carbon atoms, and preferably from about 8 to about 20 carbon atoms. Neither the number of the carbon atoms in the alkyl group nor their configuration is critical provided that the requisite oil solubility and viscosity characteristics are provided.

The reaction of a basic reagent having a metal constituent with the hereinbefore described hydroxy containing hydrocarbons may be carried out within wide temperature limits; for example, temperatures as low as 0° F. and as high as 400° F. may be employed, although temperatures within the range of from about 100° F. to about 350° F. are generally preferred. Carbon dioxide is reacted with the metal containing compound at a temperature in the range of from about 0° F. to about 300° F., although temperatures within the range of about 140° F. to about 250° F. are preferred.

The following reactions are proposed to facilitate comprehension of the invention, but they are in no way to be considered limitative or definitive. A hydroxy compound of the class described hereinbefore is reacted with a basic metal compound, such as, for example, barium oxide, thereby forming a normal or basic barium salt of such hydroxy containing compound depending upon the relative amount of barium reacted with the hydroxy compound; this reaction product is then contacted with carbon dioxide to form a normal or basic barium carbonate, bicarbonate or the like. In view of the mild reaction conditions used, i.e., carbonation at essentially atmospheric pressure and at a temperature not exceeding about 300° F., a carboxylation reaction is not contemplated; such a carboxylation reaction would result in the formation of alkyl substituted, carboxylated phenols.

To more fully illustrate the preparation of the reaction product of a basic metal compound, a hydroxy compound and carbon dioxide, the following examples are presented. Although barium is employed in the examples, it is to be understood that other metals may be employed. For instance, any of the alkaline earth metals,

alkali metals or heavy metals such as, for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron and the like may be used in place of barium. Introduction of the aforesaid heavy metal constituents can be obtained by reacting a salt of the desired heavy metal with the hydroxy constituent of the desired hydrocarbon which has been treated with a basic reagent. It is also to be understood that various other modifications of the reaction can be made without departing from the spirit of the invention.

#### EXAMPLE I

One mol (130 g.) of 2-ethyl hexyl alcohol was treated with 0.5 mol (78 g.) of barium oxide at 230° F. in the presence of 0.5 to 1.0 cc. of water. A very rapid temperature rise to 300° F. resulted within a short time after the barium oxide was added. The temperature was maintained at 300–320° F. for a period of 4 hours. The barium alcoholate was cooled to 160° F. and treated with CO<sub>2</sub> for 1 hour at a temperature of 140–160° F. The resulting product was diluted with 50 ml. of benzene and filtered to remove unreacted barium salts. After removal of the benzene by distillation, the product contained 27.19% barium.

#### EXAMPLE II

One mol (144 g.) of nonyl alcohol was reacted with a slight excess of barium hydroxide (91 g.) at a temperature of 355–375° F. After the theoretical amount of water was distilled off, the reaction mixture was cooled to 160° F. and treated with CO<sub>2</sub> for one hour at temperature of 140 to 160° F. The resulting product was diluted with 50 ml. of benzene and filtered to remove unreacted barium salts. The product contained 17.8% barium after removal of benzene by distillation.

#### EXAMPLE III

2.5 mols (515 g.) of octylphenol was reacted with 2.5 mols of barium oxide (420 g. of a mixture containing about 10% BaCO<sub>3</sub>) in the presence of 935 g. of solvent extracted SAE 5 base oil at a temperature of about 300° F. for a period of 4 hours. The reaction mixture was cooled to about 200° F. and treated with CO<sub>2</sub>. Unreacted barium salts were removed and the oil-diluted product was found to contain 11.91% barium. This represents 20% more than the calculated amount of barium to form the normal salt. Thus the product was a basic barium salt, 20% alkaline.

#### EXAMPLE IV

Forty grams of BaO were added to 117 g. of diamyl phenol at 230° F. Water (1 g.) was added and the temperature slowly increased to 300° F. After stirring for 2 hours at 300° F., the barium diamyl phenate was cooled to 140–175° F., diluted with 150 cc. of benzene and treated with a stream of CO<sub>2</sub> for 6 hours. The product was filtered and the solvent removed by distillation. The

product, a viscous brown liquid, contained 25.3% Ba. It is contemplated that various other of the well known corrosion inhibitors, anti-oxidants, anti-foaming agents, pour point depressors, extreme pressure agents, anti-wear agents, V.I. improvers, etc. may be incorporated in lubricating oils containing the additives of our invention.

As pointed out hereinbefore, compositions containing our additives have excellent detergency characteristics. Engine tests were made to demonstrate this effect using the following compositions:

*Example A.*—SAE 30 solvent extracted base oil containing 1.65% of a barium containing neutralized P<sub>2</sub>S<sub>5</sub> butene polymer (3000 SUS at 210° F. and a molecular weight of about 940) reaction product and 0.5% sulfurized dipentene.

*Example B.*—Same as Example A but containing 3.30% of the barium-containing neutralized P<sub>2</sub>S<sub>5</sub>-butene polymer.

*Example C.*—Example A plus 0.85% of (oil free basis) the product of Example III.

*Example D.*—Example A plus 0.67% of the product of Example I.

*Example E.*—Example A plus 1.17% of the product of Example I.

These tests were made on a single cylinder Caterpillar engine according to a modified L-1 test procedure, operating for 120 hours at 1,000 r.p.m. with a load of 19.8 B.H.P., with an oil sump temperature of 145–150° F. and a water outlet temperature of 175–180° F. In all of the tests a fuel having 1% sulfur was employed. The results of these tests are shown on Table I. The engine ratings employed give the actual percentage of carbon deposits in the ring grooves. The lacquer ratings, however, take into consideration the type of lacquer, i.e., light, amber or dark.

The data shown in Table I demonstrate the improvement in lacquer rating when employing the reaction product of a basic metal compound, a hydroxy compound and carbon dioxide with the neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

Concentrates of a suitable lubricating oil base containing from about 10% to about 50% or more of the here-indescribed additive, alone or in combination with various amounts of other additives, can be used for blending with other hydrocarbon lubricating oils or other lubricating oil bases in the proportion desired for the particular conditions of use to give a finished product containing from about 0.01% to about 20% of the mixture of the neutralized reaction product of a phosphorus sulfide and a hydrocarbon, and the reaction product of a basic metal compound, a hydroxy compound and carbon dioxide.

While the present invention has been described by the use of our composition in petroleum lubricating oils, other lubricating oil bases may be employed such as hydrocarbon oils, natural or synthetic, such as those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide types, and the

Table I

[Caterpillar engine tests, L-1. 120 hours, 1% sulfur fuel. SAE 30 solvent extracted base oil+0.5% sulfurized terpene.]

Additive Composition	Additive Concentration, percent	Engine Rating				
		Top Groove		2nd Groove		3rd Groove, Lacquer
		Carbon, Percent	Lacquer	Carbon, Percent	Lacquer	
Example A.....	(Ba-P <sub>2</sub> S <sub>5</sub> -Olefin.....) 1.65 (Other.....) None	7	45	0	93	25
Example B.....	(Ba-P <sub>2</sub> S <sub>5</sub> -Olefin.....) 3.30 (Other.....) None	0	36	0	1	0
Example C.....	(Ba-P <sub>2</sub> S <sub>5</sub> -Olefin.....) 1.65 (Octylphenol-Ba-CO <sub>2</sub> .....) 0.85	11	14	0	3	0
Example D.....	(Ba-P <sub>2</sub> S <sub>5</sub> -Olefin.....) 1.65 (Octanol-Ba-CO <sub>2</sub> .....) 0.67	1	21	0	5	0
Example E.....	(Ba-P <sub>2</sub> S <sub>5</sub> -Olefin.....) 1.65 (Octanol-Ba-CO <sub>2</sub> .....) 1.17	10	16	0	3	0

polycarboxylic acid ester type oils such as the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, etc.

Unless otherwise stated, the percentages stated herein and in the claims are weight percentages.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto, but includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. A lubricant composition having improved detergency properties and suitable for use in an internal combustion engine operating on a high sulfur fuel, said lubricating composition comprising a major proportion of a lubricating oil and in combination therewith an amount within the range of from about 0.001 to about 10% sufficient to impart detergency of a neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a butene polymer obtained by reacting a phosphorus sulfide with a butene polymer and subsequently neutralizing the reaction product with a basic reagent containing a metal constituent, and from about 0.01% to about 2% of a compound prepared by reacting a basic metal compound and a monohydroxy compound selected from the group consisting of alkyl alcohols having from about 8 to about 20 carbon atoms and alkyl phenols having from about 12 to about 26 carbon atoms and contacting said reaction product with carbon dioxide at a temperature of from about 0° F. to about 300° F.

2. A lubricant composition having improved detergency properties and suitable for use in an internal combustion engine operating on a high sulfur fuel, said lubricating

composition comprising a major proportion of a lubricating oil and in combination therewith an amount within the range of from about 0.001 to about 10% sufficient to impart detergency of a neutralized phosphorus and sulfur-containing reaction product of a phosphorus sulfide and a mono-olefin polymer obtained by reacting a phosphorus sulfide with a mono-olefin polymer and subsequently neutralizing the reaction product with a basic reagent containing a metal constituent, and from about 0.01% to about 2% of a compound prepared by reacting a basic metal compound and a monohydroxy compound selected from the group consisting of alkyl alcohols having from about 8 to about 20 carbon atoms and alkyl phenols having from about 12 to about 26 carbon atoms and contacting the resulting product with carbon dioxide at a temperature of from about 0° F. to about 300° F.

3. The lubricant composition of claim 1 wherein the monohydroxy compound is 2-ethylhexanol.

4. The lubricant composition of claim 1 wherein the monohydroxy compound is nonyl alcohol.

5. The lubricant composition of claim 1 wherein the monohydroxy compound is octyl phenol.

6. The lubricant composition of claim 1 wherein the monohydroxy compound is diamyl phenol.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

2,252,664	Reiff -----	Aug. 12, 1941
2,365,011	Rosen -----	Dec. 12, 1944
2,422,585	Rogers -----	June 17, 1947
2,647,889	Watson -----	Aug. 4, 1953
2,762,774	Popkin -----	Sept. 11, 1956