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3,133,022
LUBRICANT ADDITIVE AND COMPOSITION CONTAINING SAME

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19 Claims. (Cl. 252—46.7)

The present invention relates to an improved lubricant additive and lubricant compositions containing the same for meeting requirements of current internal combustion engine lubrication.

Neutralized reaction products of a phosphorus sulfide and a hydrocarbon, particularly olefin polymer, are widely used as detergent-type additives in lubricants, especially in crankcase lubricating oils of internal combustion engines. The use of such additives in lubricant compositions is described in U.S. Patents No. 2,316,080, and No. 2,316,082, issued April 6, 1943, to C. M. Loane et al. Such detergent-type additives are most effective under heavy duty, high temperature conditions of engine operation. However, in engines operating under moderate or light duty service and under intermittent operating conditions, wherein low engine jacket and crankcase temperatures prevail, such detergent additives often are of limited effectiveness in combating sludge conditions of the low-temperature type which may result from extreme oil contamination with combustion chamber blow-by products. For such low-temperature operating conditions lubricant detergent-type additives of higher ratios of alkaline earth metal to detergent phosphorus are desired. Also, it is desirable to provide a low-temperature detergent-type additive which is effective in preventing the corrosion of copper and silver which are components of bearings, etc. in present day internal combustion engines.

It is an object of the present invention to provide a method of preparing an improved lubricating oil low-temperature detergent-type additive having a high alkaline earth metal to detergent phosphorus ratio. Another object is to provide a lubricating oil additive having a high alkaline earth metal to detergent phosphorus ratio and which possesses improved detergency and bearing corrosion inhibiting properties. Another object of the invention is to provide an additive as an alkaline earth-containing neutralized reaction product of a phosphorus sulfide and a hydrocarbon having a high alkaline earth content, which additive has improved detergency and corrosion inhibiting properties. Still another object of the invention is to provide a lubricant composition containing the improved additive. Other objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the present invention, the foregoing objects are attained by the use of an oil-soluble additive complex obtained by reacting a phosphorus sulfide, e.g. phosphorus pentasulfide, with a high boiling hydrocarbon, as hereinafter described, hydrolyzing the resultant reaction product, and subsequently forming a complex by reacting the hydrolyzed reaction product with a dialkyl dithiophosphorus compound and a basic alkaline earth compound in the presence of water and an alkanol of 1 to 3 carbon atoms or a mixture of such alkanols and a phenol or any alkylated phenol having from about 5 to about 12 carbon atoms in the alkyl group or groups under the hereinafter described conditions. The resulting products are used in lubricating oils as detergent-type corrosion-inhibiting additives in concentrations of from .002 to 15 weight percent and may be used in additive concentrates in amounts greater than 15 weight percent and preferably less than 50 weight percent.

In the preparation of the phosphorus sulfide-hydrocarbon reaction products, the hydrocarbon is reacted with a phosphorus sulfide, such as P_2S_3, P_4S_3, P_4S_7 or other phosphorus sulfides, and preferably phosphorus pentasulfide, P_2S_5.

The hydrocarbon constituent of this reaction is suitably a high boiling hydrocarbon such as is described in detail in U.S. 2,316,080, 2,316,082, and 2,316,088, each issued to Loane et al. on April 6, 1943. While the hydrocarbon constituent of this reaction can be any of the type hereinafter described, it is preferably a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefinic hydrocarbons or isomono-olefinic hydrocarbons, such as butylenes or the copolymers obtained by the polymerization of hydrocarbon mixtures containing isomono-olefins and mono-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 300 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 types such as, for example, boron fluoride, aluminum chloride, and the like. In the preparation 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.

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, with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride, and the like.

Other preferred olefins suitable for the preparation of the herein described phosphorus sulfide reaction products 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 dehalogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

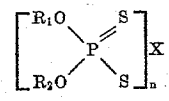
The phosphorus sulfide-hydrocarbon reaction product is prepared by reacting the phosphorus sulfide, e.g. P_2S_5, with the hydrocarbon at a temperature of from about 150° F. to about 600° F., preferably from about 300° F. to about 500° F., using from 1% to about 50%, preferably from about 5% to about 25% of phosphorus sulfide; the reaction is carried out in from about one to about ten hours. It is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification is necessary; however, an excess of the phosphorus sulfide can be used, and the unreacted material separated by filtration. The reaction, if desired, can be carried out in the presence of a sulfurizing agent such as sulfur or a halide of sulfur as described in U.S. 2,316,087, issued to J. W. Gaynor et al., April 6, 1943. It is advantageous to maintain a non-oxidizing atmosphere, for example an atmosphere of nitrogen, in the reaction vessel. The reaction product ob-

tained is then hydrolyzed at a temperature of from about 200° F. to about 500° F., preferably at a temperature of about 300° F.–400° F. by suitable means, such as for example, by introducing steam through the reaction mass. The hydrolyzed product, containing inorganic phosphorus acids formed during the hydrolysis, can be used as such in the subsequent neutralization stage; or it can be substantially freed of the inorganic phosphorus acids by contacting with an adsorbent material such as Attapulgus clay, fuller's earth and the like at a temperature of 100° F.–500° F. as fully described and claimed in U.S. 2,688,612, issued to R. Watson, September 7, 1954, or by extraction with phenol or an alkanol of 1 to 5 carbon atoms in admixture with water as described and claimed in Lemmon et al. U.S. application Serial No. 588,262, filed May 31, 1956, now U.S. Patent No. 2,843,579, issued July 15, 1958.

The additive compositions of our present invention are prepared by neutralizing a hydrolyzed phosphorus sulfide-hydrocarbon reaction product, which may be formed, for example, by the above recited process and complexing in the presence of a dialkyl dithiophosphorus compound. The hydrolyzed reaction product is neutralized with a basic alkaline earth compound in the presence of water, an alkanol, and a dialkyl dithiophosphorus compound. The neutralization is effected at the reflux temperature of the alkanol, normally corresponding to from about 155° F. to about 185° F. at atmospheric pressure, and the water is added to the reactants to inhibit gelling of the reaction mixture. During neutralization, the dialkyl dithiophosphorus compound and additional alkaline earth are complexed with the hydrolyzed phosphorus sulfide-hydrocarbon reaction product in some unknown manner to form a composition having high alkaline earth content in comparison with detergent phosphorus content. The detergent phosphorus is the phosphorus of the hydrolyzed phosphorus sulfide-hydrocarbon reaction product used as a starting material for neutralization and does not include the non-detergent phosphorus of the dialkyl dithiophosphorus compound added for complex formation during neutralization.

The formation of the complex may be effected by adding the reactants directly to the hydrolyzed phosphorus sulfide-hydrocarbon reaction product, but it is preferred to form a slurry of the hydrolyzed phosphorus sulfide-hydrocarbon reaction product in a lubricating oil, such as for example, a 5W oil, although any suitable normally liquid hydrocarbon or oil diluent may be used. The reaction product is thereby diluted to facilitate handling. We prefer to slurry the hydrolyzed phosphorus sulfide-hydrocarbon reaction product and add thereto from about 0.1 mole to about 4.0 moles of the dialkyl dithiophosphorus compound and neutralize the mixture with from about 1 mole to about 5 moles of basic alkaline earth compound in the presence of from about 0.2 mole to about 2 moles water and from about 3 moles to about 10 moles of an alkanol or alkanol and phenol mixture as described below per mole of the basic alkaline earth compound. The reaction mixture is heated at the reflux temperature of the alkanol for a period of from about 1 to about 10 hours. The reaction vessel is equipped with a reflux condenser to avoid loss of alkanol, phenol and water vapors. The reaction mixture is refluxed for the required period of time and then the temperature is raised to a temperature corresponding to about 200° F.–350° F. at atmospheric pressure, preferably 210° F.–240° F., to distill off alkanol, phenol and water. Substantial raising of the temperature above 350° F. has been found in some cases to affect the product such that the product is not suitably stable under the conditions of use in an internal combustion engine. Such excessive temperatures should, therefore, be avoided. After driving off the volatiles, the resultant neutralized complex may be recovered from the reaction mixture by filtering through a suitable adsorbent material such as, for example, Celite, Attapulgus clay, fuller's earth and the like. Most of the alkaline earth used in the reactants is chemically bonded into the complex.

The dialkyl dithiophosphorus compounds which may be used in the formation of the complexes of the present invention are the dialkyl dithiophosphorus acids, the metallic salts of the dialkyl dithiophosphorus acids and the esters of dialkyl dithiophosphorus acids which esters decompose to give their corresponding acids. Although the preferred dialkyl dithiophosphorus compounds are the pentavalent dialkyl dithiophosphorus compounds such as the dialkyl dithiophosphoric acids, metal salts and decomposable esters, and particularly a zinc dialkyl dithiophosphate, any compound corresponding to the following general formula is preferred:



wherein R_1 and R_2 are alkyl groups having from 1 to 10 carbon atoms, X is hydrogen or a metal, and n is the valence required by X.

The metal salts of dialkyl dithiophosphoric acid, i.e., metal dialkyl dithiophosphates, corresponding to the above formula, have long been well known in the art; for example, see Salzberg et al., U.S. 2,063,629, patented December 8, 1936; Rutherford et al., U.S. 2,252,984, patented August 19, 1941; L. H. Mulit U.S. 2,274,302, patented February 24, 1942, and H. C. Freuler U.S. 2,364,283, patented December 5, 1944. The polyvalent metal salts are more common in the art than the monovalent salts.

The basic alkaline earth compound which may be used is, for example, the oxide, hydroxide, carbonate or sulfide of calcium, barium, strontium or magnesium, although barium oxide is preferred.

The alkanol and alkanol and phenol mixture present during neutralization may be the alkanols having from 1 to 3 carbon atoms or a mixture of such an alkanol with a phenol or alkylated phenol. Examples of these organic mono-hydroxy compounds are methanol, ethanol, propanol or isopropanol, phenol, amyl phenol, octyl phenol, nonyl phenol, dodecyl phenol, etc. of which methanol or a mixture of methanol and nonyl phenol are preferred. When using an alkanol and phenol mixture, the mixture should contain the alkanol and phenol compounds in a ratio of from about 2:1 to about 10:1. Conveniently, from about 0.1 mole to about 3 moles of phenol or alkylated phenol per mole of basic alkaline earth compound may be added along with the above defined amounts of alkanol in the neutralization.

The following examples are illustrative of specific preparation of the additive complexes of our present invention and it is to be understood that the examples are not to be regarded as limitations of the invention.

HYDROLYZED INTERMEDIATE

A butylene polymer having a molecular weight of about 780 was reacted with 15.5 wt. percent phosphorus pentasulfide at about 450° F. for about 5.5 hours. The resulting reaction product was hydrolyzed by steaming at 300° F. for about 5½ hours. The hydrolyzed product was diluted to 2.51% phosphorus and 1.70% sulfur with SAE 5W motor oil base.

Example I

The hydrolyzed intermediate was diluted with an SAE 5W motor oil base and an amount of the diluted hydrolyzed product containing a total of 8.43 grams (0.27 mole) of detergent phosphorus was reacted with 190 grams (1.23 moles) of barium oxide (sufficient to give about 20 to 1 barium detergent phosphorus ratio) and 675 grams (0.58 moles) of zinc dialkyldithiophosphate [1]

[1] Prepared from a mixture of 65 mole percent of isopropyl alcohol and 35 mole percent of octyl alcohol.

in the presence of 3 ccs. water (0.5 mole per mole BaO) and 250 ccs. methanol (5 moles per mole BaO) at the reflux temperature of the methanol (about 160° F.) for 3 hours. The product was then heated to 250° F., the methanol and water distilled off and the remaining product filtered through Celite. The filtrate contained 2.11% P, 3.57% S, 7.86% Ba and 1.58% Zn. Twenty percent of the total phosphorus content was detergent phosphorus (0.42% of the total product). The ratio of barium to detergent phosphorus was 18.6:1 and the product had an alkalinity of 45 mg. KOH/g.

Example II

A mixture of 7100 grams (3.75 moles of detergent phosphorus) of the hydrolyzed intermediate, 2230 grams (2.20 moles) of zinc dialkyldithiophosphate [2] (6.11% P and 6.40% Zn), and 3000 grams of SAE 30 motor oil was treated with 2100 grams (13.7 moles) of barium oxide (sufficient to give about a 16 to 1 barium to detergent phosphorus ratio) in the presence of 50 ml. (0.2 mole per mole of BaO) of water and 2850 ml. (5 moles per mole of BaO) of methanol at the reflux temperature (about 160° F.) for 3 hours. The methanol and water were removed by heating the mixture to 300° F. The product was filtered through Celite. The filtered product contained 1.74% P, 11.02% Ba, and 1.03% Zn. Forty-six percent of the total phosphorus was detergent phosphorus (0.80% of the total product). The ratio of barium to detergent phosphorus was 13.8:1.

Example III

A mixture of 625 grams (0.5 mole of detergent phosphorus) of the hydrolyzed intermediate, 325 grams (0.72 mole) of dialkyldithiophosphoric [2] acid (6.88% P and 12.7% S) and 625 grams of SAE 5W motor oil was treated with 300 g. (1.97 moles) of barium oxide (sufficient to give about a ratio of 11 to 1 of barium to detergent phosphorus and a basic barium dialkyldithiophosphate) in the presence of 7 ml. (0.2 mole per mole of BaO) of water and 400 ml. (5 moles per mole of BaO) of methanol. The mixture was refluxed for 3 hours at about 160° F. The mixture was then heated to 300° F. to drive off methanol and water and filtered through Celite. The filtrate contained 2.10% P, 2.65% S and 12.11% Ba. Of the total phosphorus, 41% was detergent phosphorus (0.93% of the total product). The ratio of barium to detergent phosphorus was 8.61:1 after allowing for the barium in the basic barium dialkyldithiophosphate.

Example IV

A mixture of 1250 grams (1.0 mole of detergent phosphorus) of the hydrolyzed intermediate, 565 grams (1.25 moles) of dialkyldithiophosphoric [2] acid (6.88% P and 12.70% S), and 625 grams of SAE 5W motor oil was treated with 190 grams (3.35 moles) of calcium oxide in the presence of 60 ml. (1 mole per mole of CaO) of water and 650 ml. (5 moles per mole of CaO) of methanol at the reflux temperature of the methanol (about 160° F.) for 3 hours. The methanol and water were then removed by heating the mixture to 300° F. The product was recovered by filtering through Celite. The filtrate contained 2.66% P, 4.16% S and 2.47% Ca. Forty percent of the total phosphorus was detergent phosphorus. The product contained calcium corresponding to a ratio of 1.0 to 1 mole calcium to detergent phosphorus and a neutral calcium dialkyldithiophosphate.

The low-temperature detergency property of the complex of the present invention is demonstrated by the data in Table I, below, which data were obtained in the engine test designed to determine the low temperature detergency of motor oils. The test, known as the L–1 Test, having C.R.C. designation L–1–545 is fully described in C.R.C. Handbook 1946 edition, of the Coordinating Research Council, New York. Briefly, the test is conducted in a 1A–S1 single cylinder Caterpillar engine operating at 1000 r.p.m. at a load of 19.8 B.H.P. with an oil temperature to bearings of 145°–150° F. and a water jacket outlet temperature of 175°–180° F. and an inlet temperature of 10°–15° F. below the outlet temperature. The test is run for 480 hours, with inspections at the end of each 120, 240, and 480 hour period for carbon in the ring grooves, expressed in terms of percent groove filled; 25% carbon or less at 480 hours is regarded as passing.

The following samples were subjected to the above test at the Supplement 1 level, 1% sulfur fuel, and the results are indicated in Table I.

Sample A [3]—SAE 30 base motor oil containing 45. wt. percent of a barium salt of the hydrolyzed intermediate product having a barium to detergent phosphorus ratio of 5.5:1 and 0.75 wt. percent of commercial zinc dialkyldithiophosphate corrosion inhibitor.

Sample B—SAE 30 base motor oil containing 10.7 wt. percent of the product of Example I.

Sample C—SAE 30 base motor oil containing 5.25 wt. percent of the product of Example II.

TABLE I

Sample	Percent Detergent Phosphorus in Oil	L–1 Results		
		120 hrs.	240 hrs.	480 hrs.
A	*0.062	1	----------	5
B	0.045	3	9	10
C	0.02	----------	10	15

*Minimum passing concentration.

The superior effectiveness of the high barium compositions prepared in Examples I and II above over the lower barium salt without reacted dialkyl dithiophosphorus compound at low concentrations is demonstrated by the data of Table I.

The L–4 engine test, designed for evaluating the oxidation and bearing corrosion characteristics of motor oils is conducted according to the procedure specified by the CRC designation L–4–545, CRC Handbook, 1946 edition, Coordinating Lubricants Research Council, New York. Briefly, the test procedure involves the operation of a special six-cylinder automotive engine at constant speed and load for a period of 36 hours. The engine is operated at 3150 r.p.m.±25 at an engine load of 30 B.H.P.±1 with a jacket coolant outlet temperature of 200° F.±2° and an inlet temperature of 190° F. min. Oil sump temperature of 265–280° F. (depending on the base oil viscosity) is used. At the end of the test period, the engine is disassembled and inspected for deposits and rated on a cleanliness scale of 0 to 10; a rating 10 denoting a clean engine free of deposits. The bearings (A and B) are weighed to determine the weight loss due to corrosion. An oil blend of SAE 30 base motor oil containing 6.6 wt. percent of the product of Example II was subjected to the above test. The oil blend contained 0.053% detergent phosphorus and 0.068% zinc. The bearing weight loss per whole bearing was 0.07 gram for bearing A and 0.07 gram for bearing B. The piston varnish rating was 9.8.

The herein described additive compositions of the present invention can be used as indicated above in varying amounts of from .002 up to 15 percent in lubricating oils. Although the present invention has been illustrated by the use of the additive compositions in mineral lubricating oils, it is not restricted thereto. Other lubricating oil bases can be used, such as hydrocarbon oils, both natural and synthetic, for example, those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide type and the polycarboxylic acid type, such as the oil soluble esters of adipic acid,

[2] Prepared from a mixture of 70 mole percent of isopropyl alcohol and 30 mole percent of decyl alcohol.

[3] For comparison of a non-reacted zinc dialkyl dithiophosphate-containing composition with a composition in which the zinc dialkyl dithiophosphate is chemically bonded.

sebacic acid, azelaic acid, etc. It is also contemplated that various other well known additives, such as antioxidants, anti-foaming agents, pourpoint depressors, extreme pressure agents, antiwear agents, may be incorporated in lubricating oils containing the additives of our invention.

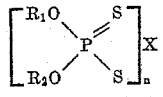
Concentrates of a suitable oil base containing more than 15 percent, for example up to 50 percent or more, of the additives of this invention alone or in combination with other additives can be used for blending with hydrocarbon oils or other oils in the proportions desired for the particular conditions of use to give a finished lubricating product containing the additives of this invention.

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

Although we have described our invention by reference to specific embodiments and examples thereof, such specific embodiments and examples as have been given are merely for the purpose of illustration of the invention and are not intended as limiting its scope. It is intended that modifications and variations of the present invention which are apparent from our foregoing description to those skilled in the art are to be considered within the scope of our present invention except as stated in the following appended claims.

We claim:

1. As a new composition of matter, an oil-soluble neutralized complex prepared by the process comprising reacting a high boiling hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature of from about 150° F. to about 600° F., hydrolyzing the resultant phosphorus sulfide-hydrocarbon reaction product at a temperature in the range of 200° F. to 500° F., and neutralizing the hydrolyzed product with a basic alkaline earth compound at a temperature in the range of 155° F. to 350° F. in mixture with water, from about 3 to 10 moles (per mole of alkaline earth compound) of a water-soluble monohydroxy compound selected from the groups consisting of an alkanol of from 1 to about 3 carbon atoms and mixtures of an alkanol of from 1 to about 3 carbon atoms and a phenol selected from phenol and an alkylated phenol having from about 5 to about 12 alkyl carbon atoms, and from about 0.1 to about 4.0 moles of a dialkyldithiophosphorus compound having the general formula:



wherein R_1 and R_2 are each alkyl groups having from one to ten carbon atoms, X is selected from the class consisting of hydrogen and zinc, and n corresponds to the valence required by X.

2. The composition of claim 1 where the phosphorus sulfide is phosphorus pentasulfide and the hydrocarbon is a butylene polymer.

3. The composition of claim 1 wherein the basic alkaline earth compound is a basic barium compound.

4. The composition of claim 1 wherein the basic alkaline earth compound is a basic calcium compound.

5. The composition of claim 1 wherein the dialkyl dithiophosphorus compound is zinc dialkyl dithiophosphate.

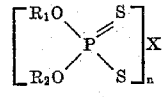
6. The composition of claim 1 wherein the dialkyl dithiophosphorus compound is dialkyl dithiophosphoric acid.

7. The composition of claim 1 wherein the water-soluble monohydroxy compound is methanol.

8. The composition of claim 1 containing added diluent before neutralization with the basic alkaline earth compound.

9. A lubricant composition comprising a major proportion of a normally liquid lubricating oil and from .002 to 15% of the composition of claim 1.

10. As a new composition of matter, an oil-soluble neutralized complex prepared by the process comprising reacting a high boiling hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature of from about 150° F. to about 600° F., hydrolyzing the resultant phosphorus sulfide-hydrocarbon reaction product, treating the hydrolyzed product with from about 0.1 to about 4.0 moles, per mole of phosphorus present in said hydrolyzed product, of a pentavalent dialkyldithiophosphorus compound having the general formula:



wherein R_1 and R_2 are each alkyl groups having from one to ten carbon atoms, X is selected from the class consisting of hydrogen and zinc and n corresponds to the valence required by X, and neutralizing the resultant treated hydrolyzed product with from about 1 to about 5 moles of a basic alkaline earth oxide per mole of phosphorus present in said hydrolyzed product, at a temperature of from about 155° F. to about 185° F., water and a water-soluble monohydroxy compound selected from the group consisting of an alkanol of from 1 to about 3 carbon atoms and mixtures of an alkanol having from 1 to about 3 carbon atoms with a phenol selected from phenol and an alkylated phenol having from about 5 to about 12 alkyl carbon atoms, under reflux conditions for a period of time within the range of from about 1 to about 10 hours.

11. The composition of claim 10 wherein the phosphorus sulfide is phosphorus pentasulfide and the hydrocarbon is a butylene polymer.

12. The composition of claim 10 wherein the basic alkaline earth oxide is barium oxide.

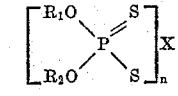
13. The composition of claim 10 wherein the basic alkaline earth compound is calcium oxide.

14. The composition of claim 10 wherein X is defined as zinc and n is 2.

15. The composition of claim 10 wherein X is defined as hydrogen and n is 1.

16. A lubricant composition comprising a major proportion of a normally liquid mineral lubricating oil and from about .002% to about 15% of the composition of claim 10.

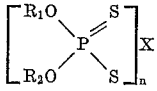
17. As a new composition of matter, an oil-soluble neutralized complex prepared by the process comprising reacting a high boiling hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature of from about 150° F. to about 600° F., hydrolyzing the resultant phosphorus sulfide-hydrocarbon reaction product treating the hydrolyzed product with from about 0.1 to about 4.0 moles, per mole of detergent phosphorus of the hydrolyzed product, of a pentavalent dialkyldithiophosphorus compound having the general formula:



wherein R_1 and R_2 are each alkyl groups having from one to ten carbon atoms, X is selected from the class consisting of hydrogen and zinc, and n corresponds to the valence required by X, and neutralizing the resultant treated hydrolyzed product at a temperature from about 155° F. to 350° F. with from about 1 to about 5 moles of a basic barium compound per mole of phosphorus present in said hydrolyzed product in the presence of said pentavalent dialkylidithiophosphorus compound, 0.2 to 2.0 moles of water per mole of basic barium compound and from about 3 moles to about 10 moles of a water-soluble monohydroxy compound selected from the group consisting of an alkanol of from 1 to about 3 carbon atoms and mixtuers of an alkanol having from 1 to about 3 carbon atoms with a phenol selected from phenol and an alkylated phenol having from about 5 to about 12 alkyl carbon atoms said mixture having an alkanol to

phenol ratio of from 2 to 1 to 10 to 1, under reflux conditions of the monohydroxy compound.

18. An addition agent concentrate for lubricating oils comprising essentially a major proportion of a lubricating oil containing more than about 15% of an oil-soluble neutralized complex capable of dilution with a lubricating oil to a concentration in the range of from about .002 to about 15% said oil soluble neutralized complex being prepared by the process comprising reacting a hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature of from about 150° F. to about 600° F., hydrolyzing the resultant phosphorus sulfide-hydrocarbon reaction product, and neutralizing the hydrolyzed product with a basic alkaline earth compound in the presence of water, a water-soluble monohydroxy compound selected from the group consisting of an alkanol of from 1 to 3 carbon atoms and mixtures of an alkanol of from 1 to about 3 carbon atoms and a phenol selected from phenol and an alkylated phenol having from about 5 to about 12 alkyl carbon atoms, and a dialkyldithiophosphorus compound having the general formula:



wherein R_1 and R_2 are each alkyl groups having from one to ten carbon atoms, X is selected from the class consisting of hydrogen and zinc, and n corresponds to the valence required by X.

19. As a new composition of matter, an oil-soluble neutralized complex prepared by the process comprising reacting a butene polymer with from about 1% to about 50% of a phosphorus sulfide at a temperature of from about 150 to about 600° F., hydrolyzing the resulting reaction product at a temperature of from about 150° to about 600° F., treating the hydrolyzed reaction product with from about 0.1 to about 4.0 moles, per one mole of phosphorus contained in the hydrolyzed reaction product, of a zinc dialkyl dithiophosphate in which the alkyl groups each contain from 1 to 10 carbon atoms to form a reaction mixture, neutralizing the reaction mixture at a temperature in the range of from about 155° F. to about 185° F. with from about 1 to about 4 moles of barium oxide per mole of phosphorus in said hydrolyzed reaction product in the presence of from about 0.2 to about 2.0 moles of water per mole of barium oxide and from about 1 to about 10 moles of methanol per mole of barium oxide for a period of time of from about 1 to about 10 hours under methanol reflux conditions.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,133,022

May 12, 1964

Albert R. Sabol et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 14, for "45. wt." read -- 4.5 wt. --.

Signed and sealed this 5th day of January 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents