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3,086,940

LUBRICANT ADDITION AGENTS AND
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This invention relates to novel compositions of matter which are effective as multi-function addition agents in lubricant compositions. More particularly, this invention pertains to improved lubricant compositions containing novel oil-soluble barium-containing neutralized phosphorus sulfide-hydrocarbon reactions having the ability to improve detergency and rust inhibition properties of a lubricating oil.

Within recent years, it has become common practice to impart the improved properties to lubricants through the use of various types of addition agents. Lubricating oils employed in internal combustion engines, such as spark ignition and diesel engines generally require the use of more than one addition agent to improve the serviceability of the lubricating oil under conditions of operation of the engine. Because the conditions of operation of an engine are such as to require many different types of improvement in a lubricating oil, many different types of additives are employed. Among the more important additive employed, it is the type which functions to prevent the formation and accumulation of sludge and varnish deposits and coatings on cylinder and piston walls of engines. Such addition agents have the property of maintaining clean engines and are referred to as "detergent type" addition agents. Such detergent type addition agents generally must be effective under heavy duty, high temperature conditions of engine operation. It is desirable to provide detergency addition agents for such conditions.

In recent years, the use of neutralized phosphorus sulfide-hydrocarbon reaction products as detergency lubricant addition agents has become more and more prominent. Higher basic metal content in such neutralized products is desirable in that it results in a corresponding increase in detergency properties of the product. Increased detergency is particularly valuable in recent years as more advanced engine designs necessitate the use of higher detergency lubricants. Further, modern engines require other addition agents in larger amounts and each additional amount of addition agent added to the lubricant replaces lubricating oil in the lubricant and the lubricating ability of the lubricant is correspondingly decreased. Thus, it is desirable to increase the basic metal content and detergency properties of the detergency addition agent so that the same amount of more detergency may be obtained from a smaller amount of addition agent.

Further, when neutralizing such products with barium, in processes for preparing such addition agents, many problems in handling the reactants and reaction product have been incurred. Often in such neutralizations, the product is difficult to filter and has a hazy appearance, detracting from its commercial acceptability.

We have provided certain new and useful oil-soluble neutralized phosphorus sulfide-hydrocarbon reaction product complexes for use as multi-purpose addition agents in lubricants. The addition agents of this invention are easily filtered and clear in appearance and are useful as multi-purpose addition agents in lubricating oils in amounts from about .002 to about 25 weight percent for the purpose of imparting detergency to the lubricating oil. The addition agents of this invention are also

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effective in imparting rust inhibition properties to the lubricating oil. The process for preparation of the reaction product complexes eliminates hazy appearance in the final product. The additive complexes of this invention are formed by neutralizing a hydrolyzed phosphorus sulfide-hydrocarbon reaction product with an excess of an inorganic basic alkali metal or alkaline earth metal compound in the presence of boric acid and a petroleum sulfonic acid. The neutralization is carried out using an alcohol-containing reaction solvent for the neutralization reaction mixture.

The basic neutralization reagent, i.e. the inorganic basic alkali metal or alkaline earth metal compound, may be inorganic basic compound of a metal selected from the group consisting of the alkali metals and alkaline earth metals. The inorganic basic alkali metal or alkaline earth metal compound will hereinafter be referred to for convenience as "inorganic basic compound." Advantageously the inorganic basic compound is an oxide, hydroxide, carbonate, sulfide, or the like of lithium, sodium, potassium, calcium, barium, strontium, etc. Examples are barium oxide, barium sulfide, barium carbonate, calcium carbonate, calcium oxide, calcium sulfide, potassium hydroxide, sodium bicarbonate, sodium sulfide, sodium hydroxide, lithium hydroxide, lithium sulfide, strontium oxide, etc. Barium oxide is particularly preferred.

The alcohol reaction solvent may be any aliphatic alcohol boiling below about 350° F. or mixture of such alcohol with water. More advantageously the aliphatic alcohol is a saturated aliphatic alcohol having from 1 to about 7 carbon atoms. Methanol is particularly preferred. Where a mixture of alcohol and water is used as the alcohol reaction solvent, the water may be present in amounts up to about 2.0 mols, advantageously at least about .05 mol, and preferably from about 0.5 mol to about 1.5 mols per mol of basic alkali or alkaline earth compound. Examples of suitable aliphatic alcohols are methanol, ethanol, isopropanol, butanol, pentanol, pentanol, methyl-butyl alcohol, hexanol, hexenol, cyclohexanol, ethylhexyl alcohol, octyl alcohol, and the like. The alcohol reaction solvent is used during reaction with excess inorganic basic compound in amounts sufficient to provide from about 2 to about 15 mols of aliphatic alcohol per mol of inorganic basic compound and preferably from about 3 to about 7 mols per mol of inorganic basic compound.

The neutralization is carried out by reacting the inorganic basic compound, the hydrolyzed phosphorus sulfide-hydrocarbon reaction product, boric acid, and the petroleum sulfonic acid in admixture at a temperature in a range from about 120° F. to about 400° F. and preferably from about 140° F. to about 200° F. It is advantageous to carry the reaction out at or below the reflux temperature of the alcohol-containing reaction solvent since the reaction temperature can thereby be more easily controlled. The neutralization with the inorganic basic compound forms a neutralized product having a high ratio of alkali metal or alkaline earth metal to phosphorus. It is preferred to use from about 1.5 to about 4.0 mols of inorganic basic compound per mol of phosphorus in the hydrolyzed phosphorus sulfide-hydrocarbon reaction product in the reaction mixture although any amount of from about 0.8 to about 5.0 or more mols of inorganic basic compound per mol of phosphorus may be used. Preferably, the inorganic basic compound is added to the reaction mixture as a slurry in a diluent mineral oil or water or other diluent.

The neutralization reaction is carried out in the presence of the alcohol-containing reaction solvent, the boric acid, and the petroleum sulfonic acid until neutralization

is complete. After the neutralization with barium oxide, the resulting product is filtered to remove solid materials such as unreacted inorganic basic compound or inorganic salts thereof; filtration may be easily accomplished by diluting the product with a mineral lubricating oil and heating the diluted product to a temperature in the range of from about 200 to about 400° F. and preferably about 350° F. and then filtering the heated diluted product through an absorbent material such as silica gel, Celite, Attapulugus clay, fuller's earth, and the like.

As the preferred procedure, the alcohol-containing reaction solvent, the boric acid, and the petroleum sulfonic acid are heated to reaction temperature before addition of the inorganic basic compound for neutralization. Other procedures will be obvious to those skilled in the art. However, in any procedure, the hydrolyzed phosphorus sulfide-hydrocarbon reaction product should not be permitted to react substantially with the inorganic basic compound before addition of the boric acid and petroleum sulfonic acid. In the preferred embodiment, the boric and sulfonic acids are added before the inorganic basic compound or alternatively after or at the same time as the inorganic basic compound but before the reaction mixture is heated to reaction temperature.

The hydrolyzed phosphorus sulfide-hydrocarbon reaction product may be prepared by reacting a normally liquid hydrocarbon 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 , and hydrolyzing the resulting product.

The normally liquid 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, alumina 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 200° 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. on 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 obtained 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 Attapulugus clay, fuller's earth and the like at a temperature of 100° F.-500° F. as fully described and claimed in U.S. 2,688,412, issued to R. Watson on 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 U.S. 2,843,579, issued to N. E. Lemmon et al. on July 15, 1958.

The boric acid is used in the neutralization reaction mixture in amounts of from about 0.1 to about 5.0 mols and preferably from about 0.5 to about 2.5 mols per mol of phosphorus in the hydrolyzed phosphorus sulfide-hydrocarbon reaction product. The boric acid may be added as boric acid or may be prepared in situ in the reaction mixture by adding boric acid anhydride or a boric acid ester which is capable of decomposition to give boric acid in the reaction mixture, for example, by dissociation upon heating or by dissociation through hydrolysis or other means.

The petroleum sulfonic acid is present in the neutralization reaction mixture in amounts of from about 1 to about 30 parts by weight and preferably from about 4 to about 15 parts by weight per part by weight of phosphorus present in the hydrolyzed phosphorus sulfide-hydrocarbon reaction product.

The petroleum sulfonic acids are those sulfonic acids produced in the acid treatment of petroleum mineral oil fractions such as mineral lubricating oil fractions with such agents as sulfuric acids or chloro-sulfonic acids. The petroleum sulfonic acids are well known in the art. Such petroleum sulfonic acids normally contain sulfonated aromatic constituents. They can be obtained, for example, by treating any normally liquid petroleum fraction which contains aromatic hydrocarbons with concentrated sulfuric acid (or sulfur trioxide). A more particular petroleum sulfonic acid which is usable in this invention is the petroleum sulfonic acid obtained by sulfonating an aromatics containing solvent extract from an SAE 40 lubricating oil. Such sulfonation can be effected by treating the extract with sulfur trioxide or concentrated sulfuric acid. Petroleum sulfonic acids generally have a molecular weight within the range of from about 400 to about 700. The sulfonic acids con-

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templated herein are preferentially oil-soluble and are commonly called "mahogany acids" as distinguished from the water soluble "green acids." Although the green acids are not acceptable when used alone, in forming the reaction product of the invention, they may sometimes be used in admixture with the mahogany acids with acceptable results. Sulfonation of an aromatics-containing fraction produces a sulfonic acid-containing composition known in the art as "sour oil." Although the sulfonic acids are normally extracted from "sour oil" before its use in the industry, in the process of the present invention the "sour oil" is preferably used directly, without extraction, as the sulfonic acid component in the reaction for convenience and elimination of the necessity for extraction.

Although we do not wish to be held to any theories regarding the reaction, we believe that the addition of boric acid and petroleum sulfonic acid to the barium neutralization reaction mixture causes a complex of such components with the hydrolyzed phosphorous sulfide hydrocarbon reaction product to form. The complex, in turn, reacts with excess barium oxide to form the lubricant addition agents of this invention.

The following examples are included as illustrations of the preparation of reaction products of this invention and are not intended as limiting our invention.

PREPARATION: HYDROLYZED PHOSPHORUS SULFIDE-HYDROCARBON REACTION PRODUCT

As an illustration of the preparation of the hydrolyzed phosphorus sulfide-hydrocarbon reaction product used as an intermediate in the preparation of addition agents of this invention, a butene polymer having an average molecular weight in the range of about 750 to 800 was reacted with 15.5 wt. percent P_2S_5 at a temperature of about 450° F. for a period of about 5½ hours. The product was then hydrolyzed with steam at a temperature of about 340° F. until the acidity of the product remained substantially constant with continued steaming. The reaction product was diluted with a solvent extracted SAE 5 mineral lubrication oil to a phosphorus content of one mol per 900 grams.

Example I

900 grams of the hydrolyzed phosphorus sulfide-polybutene reaction product of the above preparation, 75 grams of boric acid and 550 grams of sour oil (containing 23% preferentially oil-soluble 600 average molecular weight petroleum sulfonic acid) were diluted with 300 grams of a Mid-Continent solvent extracted 5 weight mineral oil. 700 cc. of methanol and 20 cc. of water were added to the mixture and the mixture was heated at the reflux temperature of the methanol and water mixture (160° F.) for 2 hours. An oil slurry of 490 grams of barium oxide in 490 grams 5 weight oil was then added to the reaction mixture. After addition of the barium oxide, the mixture was heated at 160° F. for 2 hours. The temperature of the reaction mixture was then increased to 350° F. and the product was filtered. The filtered product contained 13.55% barium, 108% phosphorus, 0.75% sulfur, and 0.32% boron. The product had a barium to phosphorous weight ratio of 12.54:1.

Example II

The hydrolyzed phosphorus sulfide-polybutene reaction product of the above preparation was further diluted with a solvent extracted SAE 5 mineral lubricating oil to a phosphorus content of one mol per 1220 grams. 610 grams of the resulting diluted product, 2070 grams of sour oil (0.75 mol of preferentially oil-soluble sulfonic acid of average molecular weight of about 600) and 80 grams of boric acid were pretreated with 33 cc. H_2O and 650 cc. methanol for two hours at 160° F. (methanol reflux temperature). The resulting pretreated mixture was then neutralized with a slurry of 400 g. of barium oxide in 320 g. of solvent extracted SAE 5 mineral lubricating oil

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at about 160° F. for about two hours. The resulting product was heated to 350° F. and filtered. The filtered product contained 8.4% barium, 0.46% phosphorus, 0.3% boron and 1.6% sulfur.

The composition of this invention was tested as an addition agent in a lubrication oil in accordance with the procedure of the L-1 test, having CRC designation L-1-545 as fully described in CRC handbook, 1956 edition, Co-ordinating Research Counsel, 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. within an oil temperature of 145 to 150° F. and a water jacket outlet temperature of about 175 to 180° F. The test was run for 480 hours with inspections at the end of 240 and 480 hour periods for carbon in the ring grooves, expressed in terms of percent filling of the top ring groove with carbon. The sample (designated sample A) tested was formulated by adding 2.5% of the product prepared in Example I to SAE 30 mineral lubricating oil containing 1% of zinc dialkyl dithiophosphate and a polyisobutylene polymer viscosity index improver and having a viscosity index of about 62 sec. at 210° F. For comparison purposes a mixture (designated sample B) of components was also subjected to the L-1 test procedure. The mixture consisted of the above base lubricating oil containing 2.5% of a barium-containing alkaline detergent (barium:phosphorus weight ratio of 9:1) prepared by neutralizing a hydrolyzed phosphorus sulfide-butene polymer reaction product with barium oxide in the presence of methanol and water at about methanol reflux temperature and also containing 1% of a calcium-borate-sulfonate prepared by neutralizing a sulfonic acid with calcium in the presence of boric acid. The results of the L-1 test are reported below. More than 25% filling of the first ring groove is considered failing.

TABLE
[Caterpillar L-1, S-1 test results]

Sample	Wt. Ratio, Ba:P	Percent Filling of Top Ring Groove with Carbon	
		240 Hours	480 Hours
A	12.54:1	2	5
B	9:1	30 (fail) ¹	

¹ Discontinued after failing at 240 hours.

The data of the above L-1 test as reported in the table demonstrate improved detergency properties of the compositions of this invention. It is believed that the improved detergency is due to the increased barium content of the compositions, expressed as a barium to phosphorus ratio. Each of samples A and B had the same amount of phosphorus in the neutralized phosphorus sulfide-hydrocarbon reaction product. The data demonstrate that a mixture of ingredients does not give the improved detergency as the complexed reaction products of our invention.

The herein described additive compositions of the present invention can be used as indicated above in varying amounts of from .002 up to about 25% 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 ester type, such as the oil soluble esters of adipic acid, sebacic acid, azelaic acid, etc. It is also contemplated that various other well known additives, such as viscosity index improvers, anti-foaming agents, pourpoint depres-

¹ Alkyl groups derived from a mixture of 70 mol percent of isopropyl alcohol and 30 mol percent of the mixed decyl alcohols.

sors, extreme pressure agents, and the like, 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 normally liquid lubricating 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.

We claim:

1. As a new composition of matter, an oil-soluble detergent neutralized reaction product prepared by the process comprising reacting a normally liquid hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature in the range of from about 200° F. to about 600° F., hydrolyzing the resulting reaction product at a temperature in the range of from about 200° F. to about 500° F., reacting the resulting hydrolyzed reaction product with from about 0.1 to about 5.0 mols of boric acid per mol of phosphorus in said reaction product, from about 1 to about 30 parts by weight of petroleum sulfonic acid per part by weight of phosphorus in said reaction product and from about 0.8 to about 5.0 mols of an inorganic basic compound per mol of phosphorus in said reaction product at a temperature in the range of from about 120° F. to about 400° F. in the presence of an alcohol-containing solvent wherein the alcohol is an aliphatic alcohol boiling below about 350° F., said inorganic basic compound being selected from the inorganic basic compounds of alkali metals and the inorganic basic compounds of alkaline earth metals and said alcohol-containing solvent providing from about 2 to about 15 mols of aliphatic alcohol per mol of inorganic basic compound.

2. The composition of claim 1 in which said boric acid is obtained in situ by dissociation of a boric acid ester.

3. The composition of claim 1 in which said petroleum sulfonic acid is a sour oil obtained from the sulfuric acid treatment of a petroleum lubricating oil fraction.

4. As a new composition of matter, an oil soluble detergent-type neutralized reaction product prepared by the process comprising reacting a normally liquid hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature in the range of from about 200° F. to about 600° F., hydrolyzing the reaction product at a temperature in the range of from about 200° F. to about 500° F., reacting the resulting reaction product with from about 0.1 to about 5.0 mols of boric acid per mol of phosphorus in said reaction product, and from about 1 to about 30 parts by weight of petroleum sulfonic acid per part by weight of phosphorus in said reaction product at a temperature in the range of from about 120° F. to about 400° F. in the presence of an alcohol-containing reaction solvent wherein the alcohol is an aliphatic alcohol having from 1 to 7 carbon atoms, and reacting the resulting reaction mixture with from about 0.8 to about 5.0 mols of an inorganic basic compound of a metal selected from alkali metals and alkaline earth metals per mol of phosphorus in said reaction product at a temperature in the range of from about 120° F. to about 400° F. in the presence of said reaction solvent, said reaction solvent being present in the reaction mixture in an amount sufficient to provide from about 2 to about 15 mols of said

aliphatic alcohol per mol of inorganic basic compound.

5. The composition of claim 4 wherein said normally liquid hydrocarbon is a butene polymer having a molecular weight of from about 150 to about 50,000.

6. As a new composition of matter an oil soluble detergent neutralized reaction product prepared by the process comprising reacting a normally liquid hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature in the range from about 200° F. to about 600° F., hydrolyzing the reaction product at a temperature in the range of from about 200° F. to about 500° F., heating the resulting reaction product in the presence of from about 0.5 to about 2.5 moles of boric acid per mole of phosphorus in said reaction product, from about 4 to about 15 parts by weight of a petroleum sulfonic acid per part by weight of phosphorus in said reaction product and a solvent selected from methanol and a mixture of methanol and water at a temperature in the range from about 140° F. to about 200° F., neutralizing the resulting heated mixture with from about 1.5 to about 4.0 mols of barium oxide per mol of phosphorus in said reaction product at a temperature in the range of from about 140 to about 200° F., in the presence of said reaction solvent, said reaction solvent being present in the reaction mixture in an amount sufficient to provide from about 2 to about 15 mols of methanol per mol of barium oxide, and filtering the resulting neutralized product to remove inorganic contaminants therefrom.

7. A lubricant composition comprising a major portion of a normally liquid lubricating oil and from about .002 to about 25% of the composition of claim 1.

8. A lubricant composition comprising a major portion of a normally liquid lubricating oil of from about .002 to about 25% of the composition of claim 4.

9. An addition agent concentrate for lubricating oils consisting essentially of a lubricating oil containing more than about 15% of the oil soluble neutralized reaction product of claim 1, said concentrate being capable of dilution with a normally liquid lubricating oil to a concentration of said reaction product in the range of from about .002 to about 25%.

10. An addition agent concentrate for lubricating oils consisting essentially of a lubricating oil containing more than about 15% of the oil soluble neutralized reaction product of claim 4, said concentrate being capable of dilution with a normally liquid lubricating oil to a concentration of said reaction product in the range of from about .002 to about 25%.

11. A process for making new and useful oil-soluble detergent neutralized phosphorus sulfide-hydrocarbon reaction products, which process comprises reacting a hydrolyzed phosphorus sulfide-hydrocarbon reaction product, said hydrolyzed product having been prepared by reacting a normally liquid hydrocarbon with from about 1% to about 50% of a phosphorus sulfide at a temperature in the range of from about 200 to about 600° F. and hydrolyzing at a temperature in the range of from about 200 to about 500° F., with from about 0.1 to about 5.0 mols of boric acid per mol of phosphorus in said reaction product, from about 1 to about 30 parts by weight of petroleum sulfonic acid per part by weight of phosphorus in said reaction product and from about 0.8 to about 5.0 mols of an inorganic basic compound per mol of phosphorus in said reaction product at a temperature in the range of from about 120° F. to about 400° F. in the presence of an alcohol-containing solvent wherein the alcohol is an aliphatic alcohol boiling below about 350° F., said inorganic basic compound being selected from the inorganic basic compounds of alkali metals and the inorganic basic compounds of alkaline earth metals and said alcohol-containing solvent providing from about 2 to about 15 mols of aliphatic alcohol per mol of inorganic basic compound.

12. A process for producing new and useful oil-soluble detergent neutralized phosphorus sulfide-hydrocarbon re-

action products, which process comprises reacting a hydrolyzed phosphorus sulfide-hydrocarbon reaction product, said hydrolyzed product having been prepared by reacting a normally liquid hydrocarbon with from about 1% to about 50% phosphorus sulfide at a temperature in the range of from about 200 to about 600° F. and hydrolyzing at a temperature in the range of from about 200 to about 500° F., with from about 0.5 to about 2.5 mols of boric acid per mol of phosphorus in said reaction product, from about 4 to about 15 parts by weight of petroleum sulfonic acid per part by weight of phosphorus in said reaction product and from about 1.5 to about 4.0 mols of an inorganic basic barium compound per mol of phosphorus in said reaction product at a temperature in the range of from about 120° F. to about 400° F. in the presence of an alcohol-containing reaction solvent wherein the alcohol is an aliphatic alcohol having from 1 to 7

carbon atoms, said solvent being present in an amount sufficient to provide from about 2 to about 15 mols of aliphatic alcohol per mol of said barium compound.

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