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METHOD OF TREATING PHOSPHORUS SULFIDE-ORGANIC COMPOUND - METAL DERIVATIVE LUBRICANT ADDITIVES

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1

This invention relates to lubricants and lubricant additives suitable for use under various conditions, including high temperatures or high pressures, or both, as for example, use in an internal combustion engine operating at higher temperatures and in which the lubricant is in close contact with metallic surfaces, metal compounds and high temperature gases. Lubricating oils, particularly when used under such conditions, are subject to breakdown resulting in lacquer and varnish deposition, sludge and acid formation, and corrosion of the bearing and other materials with which they are in contact.

Phosphorus sulfide-organic reaction products and their metal derivatives have received a great deal of attention during the past twelve years because they impart desirable properties to lubricating compositions, increasing their extreme pressure properties as well as their load-carrying capacity and filming strength. In addition, specific phosphorus sulfide-organic reaction products may inhibit corrosion, check oxidation and prevent sludge, carbonization and lacquer formation on cylinder and piston walls of internal combustion engines and various other types of engines operating under severely high temperatures and pressures. The metal derivatives in particular of these reaction products are said to possess the property of acting as detergents, helping to maintain in suspension as finely-divided particles insoluble substances present in the oils and thus keep the various engine parts free from deposits.

All of this is well known to the art, and is fully set forth in an article by George G. Pritzker, which appeared in the National Petroleum News, December 5, 1945 (volume 37, No. 49) starting at page R-1001.

It has now been found that metal derivatives of phosphorus sulfide-organic reaction products can be markedly improved as to their color or odor or lubricant characteristics or combinations thereof.

It is an object of the invention to provide a process for improving the characteristics of metal derivatives of phosphorus sulfide-organic reaction products useful as lubricants and lubricant additives.

It is another object of the invention to provide a process of mixing metal derivatives of a phosphorus sulfide-organic reaction product with a

2

solvent having selective solvent power for at least one component thereof and separating the mixture into two phases, one of which contains a preponderance of components having better lubricant or additive properties than those of the starting material.

It is another object of the invention to provide improved metal derivatives of phosphorus sulfide-organic reaction products useful as lubricants and lubricant additives.

Other objects of the invention will be apparent as is more fully disclosed hereinafter.

In accordance with the invention, a metal derivative of a phosphorus sulfide-organic reaction product type of lubricant or lubricant additive is treated with a selective solvent to form two phases, an extract phase and a raffinate phase. The phases are separated and from the raffinate phase is recovered a fraction having a preponderance of the characteristics desired for a metal derivative of a phosphorus sulfide-organic reaction product useful as a lubricant or lubricant additive. The solvent in this phase is also recovered and may be reused in the process. The extract is separated and discarded, with recovery of solvent if desired.

Organic compound-phosphorus sulfide reaction products and their metal derivatives are well known to the art and form no part of the present invention, which relates merely to the treatment thereof with a selective solvent. However, the following brief description is given of these reaction products in order to make clear the scope of the invention and for the aid and convenience of those skilled in the art in understanding the reaction products to which the present invention is applicable.

Phosphorus sulfide-organic reaction products may be made with direct admixture of the reactants or, if desired, in the presence of a diluent which may or may not be subsequently removed. A heavy oil, such as white oil, or a lubricating oil may be used as the diluent. The reaction is usually complete in about 10 hours or less, generally 1 to 2 hours. The reaction time is a function of temperature, the amount of the sulfide that is to react, the degree of subdivision of the reactants, the efficiency of mixing, etc.

The organic compound or mixtures thereof may be reacted with the phosphorus sulfide or a

mixture of phosphorus sulfides in ratios from 5 to about 60% by weight of the phosphorus sulfide. Generally about 10 to about 50% is the usual amount that will be used, depending upon the molecular weight of the organic compound, and about 10 to 20% is especially desirable.

Phosphorus pentasulfide is preferred, although other phosphorus sulfides, such as phosphorus sesquisulfide and phosphorus trisulfide or mixtures thereof with phosphorus pentasulfide, may be employed. Phosphorus pentasulfide is least expensive and readily available, and for this reason is used in the illustrative examples.

The organic compound of course must be reactive with phosphorus sulfide, and is characterized by a boiling point above the reaction temperature under the conditions at which the compound reacts with phosphorus sulfide. A large number of organic compounds can be employed, including oxygen-containing organic compounds which contain oxygen in the form of a hydroxyl, carbonyl, carboxyl or ether group, and may have one or more of the various types of these oxygen-containing groups, as well as amines, amides, nitriles, saturated and unsaturated hydrocarbons, and unsaturated hydrocarbon polymers.

Preferably the organic compound reactive with phosphorus sulfide has 6 or more carbon atoms. Generally compounds having not over 20 carbon atoms are employed, although compounds of up to 52 carbon atoms or more are suitable. The compounds may be aliphatic, aromatic or cycloaliphatic in structure, and may contain substituents such as halogen groups, i. e., chlorine, bromine or iodine, nitro groups and the like.

Oxygen-containing carboxyl compounds, i. e., organic acids and esters, which may be employed are beeswax, other waxes, butyl stearate, ethyl lactate, methyl oleate, methyl palmitate, butyl ricinoleate, butyl phthalate, methyl stearate, methyl dichlorostearate, methyl chloro-naphthenate, dichloropalmitic acid, coconut oil, palm oil, babassu oil, hydrogenated linseed, coconut and other vegetable oils, other fatty oils, palmitic acid, abietic acid, rosin, modified rosin, myristic acid, naphthalic acid, naphthoic acid, benzoic acid, naphthenic acids, hydroxystearic acid, dihydroxybenzoic acids, hydroxynaphthenic acids, dihydroxystearic acid, chlorobenzoic acid, dichlorodihydroxystearic acid, lactones, oxidized petroleum fatty acids or other oxygen-containing or acidic petroleum products, as oxidized wax, kerosene, gas oil or other oxidized petroleum oil.

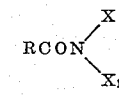
Illustrative of organic ethers are di-(dodecyl) ether, methyl stearyl ether, ethylene glycol monoethers, ethylene glycol chlorohydrin.

Typical oxy and thio alcohols which may be used include lauryl alcohol, stearyl alcohol, alcohols derived from coconut oil, palm oil and cottonseed oil, oleyl alcohol, octyl alcohol, octadecyl mercaptan, decyl mercaptan and oleyl mercaptan.

A large variety of carbonyl compounds, particularly ketones, are suitable for the reaction, including polyketones, methyl-dodecyl, xylyl-heptadecyl, dioctadecyl, diheptadecyl, ethyl-heptadecyl, propyl-heptadecyl, and hydroxy-phenyl-heptadecyl ketones.

The ketone stock may be a mixture of the ketones of different types of different molecular weights or both. Generally, the aliphatic or mixed aliphatic-aromatic, including aliphatic-hydroxyaromatic, ketones are preferred. Of the ketones containing aliphatic radicals, those with saturated aliphatic radicals are preferred. However, those with unsaturated radicals are useful. The ketone stock should contain at least 50.0% ketonic ingredients and preferably 75.0% by weight of the stock.

A large variety of aliphatic amides are suitable. The aliphatic amides having at least 12 carbon atoms in a molecule are preferred. The preferred amides are those which contain either an amido hydrogen (a hydrogen directly connected to the nitrogen), or an olefinic double bond, or both. The choice may be controlled by the desired lubricant, solubility characteristics of the primary sulfide-amide or the final derivative product. The amide should not be so highly unsaturated or conjugated as to give reaction products which are not oil-dispersible. Diamides and compounds containing several amide groups may be used. Typical amides are those which correspond to a carboxylic acid having from 12 to about 20 carbon atoms in the molecule obtainable from natural products, such as dodecanoyl amide, tetradecanoyl amide, octadecanoyl amide, eicosanoyl amide and the corresponding unsaturated amides containing one or more olefinic double bonds in the molecule. The amides may contain a lower aliphatic substituent for one or both of the amido hydrogens in many instances. These may be represented by the formula



where R is an aliphatic hydrocarbon radical and X and X_1 are hydrogen and/or a lower aliphatic substituent, such as methyl and ethyl up to amyl. The amide stock used may be a mixture of amides of different molecular weight or different degrees of saturation. It need not be pure and amounts of other amides may be present provided that the above amides form the major or essential components. An inherent property of such amides is their freedom from sulfurized radicals.

Amines of high molecular weight may be used, such as primary and secondary saturated and unsaturated amines and unsaturated tertiary amines, such as octadecyl amine, dioctadecyl amine, octadecynyl amine, hexadecyl amine, octadecynyl dimethyl amine and didecyl amine. Preferably the amine has an aliphatic radical of at least 10 carbon atoms, the other substituent, in the case of a secondary or tertiary amine, having from 1 to 5 carbon atoms.

A large variety of nitriles are suitable, for example, aliphatic, aromatic or heterocyclic nitriles, saturated or unsaturated; and those having at least 12 carbon atoms in a molecule are preferred. The choice may be controlled by the desired lubricant solubility characteristics of the primary sulfide-nitrile reaction product or the final derivative product. The nitrile should not be so highly unsaturated or conjugated as to give reaction products which are not oil dispersible. Polynitriles may be used. Typical readily available nitriles are those which correspond to the carboxylic acids having from 12 to about 20 carbon atoms in the molecule obtainable from natural products, such as dodecanoic nitrile, tetradecanoic nitrile, octadecanoic nitrile, eicosanoic nitrile and the corresponding unsaturated nitriles containing one or more olefinic double bonds in the molecule. The nitrile stock may be a mixture of nitriles of different molecular weight or different degrees of unsaturation. It need not be pure provided that the above nitriles form the major or essential components.

Unsaturated hydrocarbons having from 6 to 25 carbon atoms and one or more pairs of double or triple bonded carbon atoms are particularly useful. High molecular weight olefin polymers having a molecular weight above 150 up to about 50,000 are preferred. Such an olefin polymer is the so-called "motor polymer" or "reduced motor polymer" which is usually made from C_3 and C_4 olefins by nonselective polymerization, e. g., with a phosphorus acid type catalyst. Motor polymer boils in the range from 80 to 500° F. with a major portion boiling in the range from 120 to 400° F. A polymer gasoline fraction may be removed therefrom by fractional distillation to the 250° F. cut point, and this fraction is called reduced motor polymer. Its average molecular weight is about 145, and it preferably contains a major amount of branched chain olefins boiling below 600° F.

Another polyolefin which is especially useful is one which improves the viscosity index of lubricating oil, which has a molecular weight of about 2,000 to 100,000 and which is substantially saturated. A commercially available material of this type is known as "Paratone." This is a polyisobutylene polymer having a molecular weight from 10,000 to 20,000, in solution in a lubricating oil in an amount to give a viscosity of about 3,000 SSU at 210° F.

The reaction of the individual reactants selected from the above classes may be carried out in the presence or absence of air or in an inert atmosphere such as nitrogen or hydrogen sulfide. It may also be carried out under pressure.

The reaction temperature varies with the organic compound and is readily ascertained. The optimum is in the range of 225 to 600° F., although a higher temperature which is below that at which the reaction product would be decomposed could be used. A temperature of at least 250 to 350° F. is preferred in many cases.

The final reaction mass is preferably centrifuged, filtered or settled and decanted in order to remove the by-product, sludge or other insoluble material. Any excess of a volatile diluent may be removed by distillation. If desired, the final product may be contacted with an absorbent, such as activated charcoal, silica gel, activated clay and the like.

An element of the sulfur family can be incorporated into the reaction product. This sulfur can be incorporated by adding elemental sulfur or a compound which yields sulfur, such as by treating the reaction product therewith or treating a derivative of the reaction product therewith.

If additional reacted sulfur is to be present in the additive, about 0.01 to 2.0 and preferably 0.1 to 1.0 gram atomic weights of sulfur per mole of the phosphorus sulfide is used. Additional reacted sulfur may be incorporated simultaneously with or after the formation and cooling of the primary reaction product. If added afterwards, the mass is maintained at about 200 to 300° F. for from a few minutes to several hours, and preferably about one hour. Selenium and tellurium function much in the same way as sulfur in this respect. Alternatively, the sulfur can be added to the metal derivative.

As is well known, phosphorus sulfide-organic compound reaction products may be utilized in the form of their metal derivatives, or mixtures of this derivative with the original reaction product. The metal derivatives are formed from metal compounds capable of replacing an acid

hydrogen atom in the phosphorus sulfide-organic reaction product.

The metal derivatives may be formed from one or more metal compounds, such as their sulfides, oxides, hydroxides, carbides and cyanamides. The preferred metals are those of groups I, II and III of the periodic table, such as potassium, sodium, calcium, magnesium, beryllium, zinc, barium and aluminum. For some purposes, the heavier metals are especially useful, such as chromium, cadmium, tin, lead, antimony, bismuth, arsenic and the like.

The metal derivatives may be formed by reacting the phosphorus sulfide-organic reaction product with the corresponding metal compound at temperatures in the range of about 100 to about 350° F., a temperature in the range of about 180 to 250° F. being preferred.

When a metal derivative containing subsequently added reacted sulfur is desired, there are two alternative ways of producing it: (1) the original or primary reaction product can be reacted with an element of the sulfur family and this reaction product then converted into the metal derivative, or (2) the primary reaction product can first be converted into the metal derivative and this derivative then reacted with an element of the sulfur family.

From about 0.2 to about 6.0 equivalents of a metal compound may be used per mole of the sulfide used in the sulfide-derived reaction product, preferably about 1.0 to about 3.0 equivalents.

The metal additive compounds, especially those fully saponified so as to have a high metal content, may be mixed with oils to form greases, with or without conventional soaps, and in such cases the metal additive compounds serve to thicken the oil as well as to stabilize it and impart a detergent action.

Obviously the description herein of the preparation of phosphorus sulfide-oxygen-containing organic compound reaction products cannot be exhaustive in view of space limitations. Further details of the preparation of these reaction products will be found in the following patents, which are well known to those skilled in the art: 2,142,998, Chittick; 2,211,231, Henderson; 2,211,306, Whittier; 2,235,860, Williams; 2,242,260, Prutton; 2,257,750, Lincoln; 2,257,751, Lincoln; 2,261,047, Asseff; 2,303,427, Roehner; 2,316,080, Loane et al.; 2,329,426, Cook; 2,337,868, Burwell; 2,355,106, Prutton; 2,356,074, May; 2,357,346, Musselman; 2,358,305, Cook; 2,361,746, Cook; 2,361,957, Musselman; 2,362,624, Gaynor; 2,364,283, Freuler; 2,364,284, Freuler; 2,365,209, Musselman; 2,368,000, Cook; 2,373,094, Berger; 2,375,060, Williams; 2,375,061, Williams.

The above as well as other patents will be found briefly discussed in the article "Use of phosphorus sulfide organic reaction products as 'lube' oil additives," by George G. Pritzker, appearing in National Petroleum News, December 5, 1945 (volume 37, No. 49).

It is to be understood that the process of the invention is applied to metal derivatives of phosphorus sulfide-organic compound reaction products which have previously been subjected to the usual treatments for separation of unreacted starting materials, sludge and precipitable by-products therefrom. Such separations, as set forth heretofore, involve filtration of the reaction product, or centrifuging, or settling and decanting. If desired, prior to the solvent extraction process of the invention the reaction product may

be contacted with an absorbent, such as activated charcoal, silica gel, activated clay and the like.

Solvent extraction processes involve contacting a substrate, i. e., crude or starting material, with a solvent substance in which the solubilities of the various components of the substrate which are to be separated are different such that one of the components of the substrate is soluble at least to some extent and the other or others relatively insoluble. The extraction process of the invention follows this general principle.

In the process of the invention, there is employed a solvent in which at least some of the components of the substrate are so insoluble that two phases are formed, the extract phase containing the solvent and being richer in the less desirable inhibitory components of the original lubricant additive substrate which are soluble in the solvent, and the raffinate phase being substantially free, or at least containing only a minor portion of the solvent, and being richer in the more desirable inhibitory components of the original lubricant additive substrate which are insoluble or less soluble in the solvent. By separating the two phases, new lubricant additive compositions are recovered in the raffinate. Insofar as we are aware, it has never been proposed heretofore to apply these extraction principles to lubricant additives, and it has never been shown that they could be advantageously applied thereto.

Several general instructions can be given to enable those skilled in the art to select a solvent which will meet the above requirements.

As those skilled in the art are aware, a substance is most soluble in that solvent to which it is most closely related in structure and least soluble in a solvent to which it is quite unrelated in structure. Moreover, as one goes higher in a given homologous series, the members become more and more like the hydrocarbons from which they may be considered to have been derived, as regards solubility in organic solvents, and compounds of very high molecular weight exhibit decreased solubility in the inert nonpolar solvents.

The more desirable components of the substrate, metal derivatives of phosphorus sulfide-organic material reaction products treated in accordance with the invention are relatively insoluble in nonpolar organic solvents. In many cases, however, depending upon the organic compound employed in preparing the reaction product, they may also be insoluble in polar organic solvents.

In general, it may be said that the more desirable components have a solubility which is the exact opposite of what would be predicted from a knowledge of its structure, as set forth in the above-stated solubility rules.

The less desirable components of the substrate which it is desired to extract are most soluble in a solvent closely analogous in structure to the organic compound employed as reactant with phosphorus sulfide, and closely follow the above-stated solubility rules. It would not be expected that such a marked difference in solubility would be evidenced between the more desirable and the less desirable components, all of which are derived from the same organic component as reactant.

Applying now these rules to the selection of a solvent for treatment of the various metal derivatives of phosphorus sulfide reaction products of organic compounds, it may be stated that where the reactant with phosphorus sulfide is of the type listed in the following table, the solvents listed in the second column of the table would be preferred; as the solvents in which the more desirable (for lubricating at additive purposes) components of such reaction products are immiscible or least soluble, and the less desirable components miscible and most soluble:

Reactant With Phosphorus Sulfide	Preferred Selective Solvents
Acids	Aldehydes, hydrocarbons, chlorinated hydrocarbons, esters, acids.
Alcohols	Thio- and oxyethers, esters, aldehydes, hydrocarbons, chlorinated hydrocarbons, alcohols.
Amides	Oxy- and thicketones, esters, aldehydes, hydrocarbons, chlorinated hydrocarbons, acids.
Amines	Alcohols, alcohol ethers, ketones, esters, hydrocarbons, chlorinated hydrocarbons, amines.
Esters	Alcohols, ethers, esters, hydrocarbons, chlorinated hydrocarbons, aldehydes.
Ketones	Ketones, aldehydes, hydrocarbons, chlorinated hydrocarbons, esters, aldehydes, ethers.
Mercaptans	Mercaptans, alcohols, ethers, hydrocarbons, chlorinated hydrocarbons, sulfides.
Nitriles	Ketones, hydrocarbons, chlorinated hydrocarbons, aldehydes, ethers, alcohols, esters, nitriles.
Olefins	Alcohols, esters, ethers, acids, ketones, aldehydes, hydrocarbons, chlorinated hydrocarbons.

Thus it will be appreciated that a wide variety of solvents can be employed in the process of the invention. It is important, however, whether the solvent be polar or nonpolar, that the metal derivative of the phosphorus sulfide-organic reaction product be immiscible or insoluble in the solvent employed, and that the solvent have a selective solvent power for components of the reaction product impairing its optimum characteristics as a lubricating oil additive.

The organic solvents or mixtures thereof which meet these requirements and can be employed are selected from the class of solvents consisting of aliphatic, cycloaliphatic and aromatic hydrocarbons, halogenated hydrocarbons, alcohols, mercaptans, sulfides, ethers, ketones, amines, esters, aldehydes and acids. Exemplifying the various classes of solvents which may be employed are carbon disulfide, diethyl sulfide, carbon tetrachloride, chloroform, tetrachloroethylene, dichloroethylene, benzene, bromobenzene, chlorobenzene, mesitylene, the xylenes, toluene, methyl alcohol, ethyl alcohol, isobutyl alcohol, isoamyl alcohol, hexane, pentane, isopentane, ethyl acetate, methyl propionate, acetone, thioacetone, methyl ethyl ketone, dioxane, mesityl oxide, ethyl ether, dibutyl ether, methyl butyl ether, nitroethane, isophorone, furfural, propionaldehyde, acetaldehyde, liquid sulfur dioxide, methyl Cellosolve, diethylene glycol, propyl mercaptan, acetic acid and propionic acid.

The new extraction process may be conveniently carried out in a continuous countercurrent or in a batch operation or in a sequence of batch operations. Generally the solvent will be a liquid and employed at temperatures and pressures at which it will have a maximum solvent effect. Generally this will be at or near its boiling point. However, higher temperatures above its boiling point at atmospheric pressure may, of course, be employed if superatmospheric pressures are employed.

The improved lubricants and lubricant additives obtained in accordance with the invention are, as stated, found in the raffinate phase obtained as a result of the extraction. The extract phase containing the solvent and undesirable ma-

terial ordinarily is treated to recover the solvent, while the extracted material is discarded.

The improved lubricant and lubricant additives may be used similarly to the substrate or crude lubricant or lubricant additive as disclosed heretofore. Generally, however, a lower concentration of the additive may be used with improved results because of the improved properties of the raffinate.

In order to compare the efficiencies of different additives, lubricating oil compositions containing the improved additives were made up and tested according to laboratory test procedures for evaluating the service stability of oils, as described in a paper by R. E. Burk, E. C. Hughes, W. E. Scovill and J. D. Bartleson presented at the Atlantic City Meeting of the American Chemical Society in September, 1941, and in another paper by the same authors presented at the New York City meeting of the American Chemical Society in September, 1944. The latter paper also correlates the results of such laboratory tests with the so-called "Chevrolet Engine Test."

Essentially the laboratory test equipment consists of a vertical, thermostatically heated, large glass test tube, into which is placed a piece of steel tubing of about one-third the length of the glass tube and of much smaller diameter. A piece of copper-lead bearing strip is suspended within and from the upper end of the steel tube by a copper pin, and an air inlet is provided for admitting air into the lower end of the steel tube in such a way that, in rising, the air will cause the oil present to circulate. The test tube is filled with an amount of the oil to be tested which is at least sufficient to submerge the metals.

The ratios of surface-active metals to the volume of oil in an internal combustion test engine are nearly quantitatively duplicated in the test equipment. In the "Standard" test the temperature used is approximately the average temperature of the crankcase. The rate of air flow per volume of oil is adjusted to the same as the average for a test engine in operation. Catalytic effects due to iron are empirically duplicated by the addition of a soluble iron salt and those due to lead-bromide by its addition. The duration of the test is adjusted to that usually used in engine type tests. As is shown by the data in the papers referred to, the laboratory tests have been correlated with engine tests and the properties of the oil in an engine may be determined from the result of the laboratory tests.

The results given in the following tables were obtained from tests using:

A 160 cubic centimeter sample of the lubricant composition
70 liters of air per hour
100 square centimeters of steel surface
4.4 square centimeters of copper-lead surface
1.0 square centimeter of copper surface
0.10% by weight of lead-bromide powder
0.012% soluble iron calculated as Fe_2O_3 (ferric 2-ethyl hexoate in C. P. benzene)

The "Standard" tests were run at 280° F. for 36 hours.

The lacquer is deposited on the steel tube and is determined by difference in weight of the tube after washing with chloroform and drying to constant weight. The oil-insoluble sludge remaining in the glass tube is thought to be related to similar sludge deposits in engines, and was rated visually against color photographic standards, an appearance rating scale ranging from F (worst) through A (best) being used. The corrosion was determined by difference in weight of the copper and heavy metal pieces after scrubbing with chloroform. The used oil was sufficient to enable the determination of all of the usual oil tests, viz., isopentane insolubles, viscosity, acid number, etc.

The following are typical of the various embodiments of the invention:

EXAMPLE 1

(*a*) 600 grams of neutral grade degras and 150 grams of P_2S_5 were mixed and heated to 330° F. for 3 hours with agitation and then maintained at this temperature for an additional hour without agitation. 5.4 grams of gas was evolved. The reaction mass was filtered and the filtrate blown with nitrogen while maintained at 212° F. for one hour. 557.0 grams of a black P_2S_5-degras reaction product and 187.5 grams of sludge were obtained. The reaction product analyzed 3.48% by weight ash, and 13.31% S.

(*b*) 37.15 grams of the above product was extracted with 4,000 cc. of boiling acetone in steps using 20 to 200 cc. at a time. The acetone extract phase was filtered and the acetone distilled off. The raffinate or acetone-insoluble material was a very viscous black resin which analyzed 36.05% S. It weighed 4.25 grams, that is, 12.5% by weight of the charge.

(*c*) 32.8 grams of extract of acetone-soluble material was obtained. This is 87.5% by weight of the charge. It was a nonviscous light red colored oil which analyzed 10.5% S.

(*d*) 84 grams of P_2S_5-degras product (*a*) and 16 grams of barium hydroxide octahydrate were mixed and heated to 190° F. with agitation for four hours and then to 250° F. for one hour. The reaction product was centrifuged hot, 76 grams of very viscous orange oil was obtained as the product (barium-P_2S_5degras). It analyzed 8.57% by weight ash, and 11.52% S.

(*e*) The product obtained in (*d*) was extracted with 2,200 cc. of boiling acetone in a series of extractions using 200 cc. portions at a time. The acetone extract was filtered hot and the acetone distilled off from the filtrate. 27.0 grams of raffinate or acetone-insoluble material was obtained. This was an orange waxy odorless solid which analyzed 36.94% by weight of ash, 22.90% Ba and 15.24% S. This represents 35.5% by weight of the charge, or substrate.

(*f*) 49.0 grams of extract or acetone-soluble material which analyzed 1.31% by weight, 0% Ba, and 7.16% S was obtained. This is 64.5% by weight of the charge. It was a light red oil having an unpleasant odor.

(*g*) 25.45 grams of the above extract from (*c*) and 6.36 grams of barium hydroxide octahydrate were mixed and heated with agitation for four hours at 190° F. and then to 250° F. for one hour. The reaction product was dissolved in ether and filtered hot. The ether was distilled off from the filtrate. 25.25 grams of a very viscous light red colored oil which analyzed 24.36% by weight Ba and 11.33% S was obtained.

"Standard" tests were run on a conventional Mid-Continent acid treated lubricating oil base stock blended with Pennsylvania bright stock (S. A. E. 30) and compositions containing this oil and the additives of the foregoing compositions. These tests indicated that the desirable part of the primary P_2S_5-degras substrate (*a*)

is concentrated in the extract phase (*c*). The extract gives a better used oil rating and engine appearance rating than the substrate when used in the same amount. The extract is a clear red color as compared with the opaque blackness of the substrate.

The desirable part of the barium P_2S_5-degras substrate (*d*) is concentrated in the raffinate phase (*e*). About the same engine appearance rating and used oil rating can be obtained with only two-thirds of the raffinate concentrate as compared with the barium-P_2S_5-degras substrate.

Preparation of a metal derivative from extracted P_2S_5-degras (*c*) is illustrated at (*g*), and when this is used as an addtitve in only one-third the amount of the barium-P_2S_5-degras substrate (*d*), a result of about the same general order is obtained.

The following additional examples on the preparation of the improved materials in accordance with the invention, and tables of results of tests of lubricants comprising some of such improved compositions, will serve to further illustrate and point out some advantages, but none of the examples or embodiments are to be in any wise construed as limiting the scope of the invention as otherwise disclosed and claimed herein.

EXAMPLE 2

(*a*) A commercially available additive, believed to be the potassium salt or soap of the reaction product of P_2S_5 and the polyisobutylene referred to above was obtained and tested for ash. It analyzed 5.13% by weight ash.

(*b*) 14.6 grams of this material was extracted with 200 cc. of liquid propane, in two steps, using 100 cc. per step. 4.4 grams of raffinate was obtained. It analyzed 8.30% by weight ash.

(*c*) After removing the solvent from the extract phase, 10.1 grams of extract remained; it was discarded.

"Standard" tests were run on a blend of conventionally acid treated Mid-Continent oil and acid treated Mid-Continent bright stock, and compositions containing this oil and the additives of Example 2; the results given in Table I are representative.

Table I

Additive from Example No.	None	2(*a*)	2(*b*)
Concentration of Additive (in percent by weight)	0	1.0	1.0
Lacquer deposit (in milligrams)	21.9	3.3	0.1
Sludge (isopentane insoluble, in milligrams)	531.9	127.8	8.4
Corrosion (milligrams per sq. cm. weight loss):			
Cu	1.2	2.3	0.3
Cu-Pb	7.3	18.8	8.4
Acid No.	6.6	2.7	1.4
Viscosity Increase (SSU)	635 0	144.0	104.0

The above example and table demonstrate the remarkable improvement of the additive by its treatment in accordance with the invention. Every tested characteristic of the raffinate (2(*b*)) was markedly better than the untreated additive (2(*a*)), and the known disadvantageous characteristics of this additive were substantially absent in the raffinate. This is of immense practical importance.

EXAMPLE 3

(*a*) 348 grams of commercial dioctadecylamine (a mixture of about three parts of dioctadecylamine and one part of trioctadecylamine) and 89 grams of phosphorus pentasulfide were mixed and heated with agitation for four hours at 300° F. 304 grams of barium hydroxide octahydrate was added and the mass was heated for four hours at 200° F.; it was blown with air for one hour at 250° F. and then insoluble materials were removed from the product by centrifuging the hot mixture and separating the precipitate. The product was a waxy brown solid at room temperature. It analyzed 36.85% by weight ash.

(*b*) 21.7 grams of this product was extracted with 300 cc. of boiling isopropanol in a series of extractions using 50 cc. at a time. 12.0 grams of raffinate was obtained. It analyzed 52.20% by weight ash.

(*c*) 9.7 grams of extract was obtained by evaporating the solvent from the extract phase. It was discarded.

The materials of Example 3 were tested similarly to those of Example 1, except that the base stock used consisted of a conventional Mid-Continent lubricating oil base stock blended with Pennsylvania bright stock (S. A. E. 30). The results given in Table II are representative.

Table II

Additive from Example No.	None	3 (*a*)	3 (*b*)
Concentration of Additive (in percent by weight)	0	1.0	1.0
Lacquer deposit (in milligrams)	11.4	1.9	0.5
Sludge (isopentane insoluble, in milligrams)	193.3	31.0	3.5
Corrosion (milligrams per sq. cm. weight loss):			
Cu	1.3	0.9	0.2
Cu-Pb	7.4	14.7	9.3
Acid No.	2.8	1.6	1.3
Viscosity Increase (SSU)	642.0	80.0	75.0

The data of the above example and table show improved additives prepared in accordance with the invention. All of the indicated characteristics of the raffinate (3(*b*)) show improvement over the untreated additive (3(*a*)), and the important lacquer and sludge characteristics are very markedly improved.

EXAMPLE 4

(*a*) A commercially available additive, believed to be the potassium salt or soap of the reaction product of P_2S_5 and polyisobutylene, was obtained and tested for ash. It analyzed 5.13% by weight ash.

(*b*) 25.3 grams of this material was extracted with 300 cc. of boiling methyl ethyl ketone in a series of extractions using 50 cc. at a time. 5.2 grams of raffinate was obtained. It analyzed 14.65% by weight ash.

(*c*) 18.1 grams of extract was obtained by evaporating the solvent from the extract. It was discarded.

The materials of Example 4 were tested similarly to those of Example 3, using similar base stock. The results given in Table III are representative.

Table III

Additive from Example No.	None	4(*a*)	4(*b*)
Concentration of Additive (in per cent by weight)	0	1.0	1.0
Lacquer deposit (in milligrams)	11.4	1.7	0.2
Sludge (isopentane insoluble, in milligrams)	193.3	40.8	0.0
Corrosion (milligrams per sq. cm. weight loss):			
Cu	1.3	0.2	0.5
Cu-Pb	7.4	80.1	29.5
Acid No.	2 8	1.8	0.6
Viscosity Increase (SSU)	642.0	110.0	63.0

The data of this example and table show a very striking improvement in the sludge characteristic of the raffinate (4(*b*)) of a commercial additive (4(*a*)) treated in accordance with the invention. The inherently high bearing alloy corrosion characteristic of this additive is also very substantially improved. Substantial improvements in the viscosity increase, acidity and lacquer characteristics are also achieved by the treatment. The improved additive (4(*b*)) is far superior to the substrate or original additive (4(*a*)).

EXAMPLE 5

(*a*) A commercially available additive, the potassium salt or soap of the reaction product of P_2S_5 and polyisobutylene was obtained and tested for ash. It analyzed 5.13% by weight ash.

(*b*) 25.6 grams of this material was extracted with 300 cc. of boiling isopropanol in a series of extractions using 50 cc. at a time. 6.2 grams of raffinate was obtained. It analyzed 10.05% by weight ash.

(*c*) 18.1 grams of extract was obtained by evaporating the solvent from the separated extract phase. It was discarded.

The materials of Example 5 were tested similarly to those of Example 3, using similar base stock. The results given in Table IV are representative.

Table IV

Additive from Example No.	None	5 (*a*)	5 (*b*)
Concentration of Additive (in percent by weight)	0	1.0	1.0
Lacquer deposit (in milligrams)	11.4	1.7	0.5
Sludge (isopentane insoluble, in milligrams)	193.3	40.8	2.9
Corrosion (milligrams per sq. cm. weight loss):			
Cu	1.3	0.2	0.0
Cu-Pb	7.4	80.1	26.7
Acid No.	2.8	1.8	0.7
Viscosity Increase (SSU)	642.0	110.0	63.0

The data of this example and table show the improvement of every indicated characteristic of the raffinate (5(*b*)) obtained by a treatment in accordance with the invention of a commercially available additive (5(*a*)). The improvement in the sludge characteristic of the raffinate (5(*b*)) as compared to the substrate (5(*a*)) is particularly striking. It is noteworthy that copper corrosion is entirely removed. Viscosity increase, acidity and lacquer characteristics are also substantially improved.

EXAMPLE 6

Powdered phosphorus pentasulfide is added to octyl alcohol in a glass or ceramic container in the proportion of one gram mole to four gram moles, respectively. The mixture is then agitated at from 250 to 300° F. until the phosphorus pentasulfide has been dissolved. To this material there is added powdered zinc or zinc oxide at from 250 to 300° F. until no more of the metallic compound is dissolved. The product is the zinc derivative of phosphorus pentasulfide-octyl alcohol reaction product. This material analyzes about 18.1% sulfur and 9.3% phosphorus.

Thirty grams of this material is extracted with 300 cc. of boiling dioxane in a series of extractions using 50 cc. at a time. Approximately half this weight of raffinate is recovered. The remainder of the additive is extracted by the solvent and is discarded after recovery of the solvent for reuse.

EXAMPLE 7

2,040 grams of turpentine are placed in a flask equipped with a stirrer, a thermometer and a funnel and heated therein to 240° F. To the turpentine there is then added 1,110 grams of phosphorus pentasulfide at such a rate that the temperature of the reaction mixture does not rise above 275° F. When all of the phosphorus pentasulfide has been added, the temperature of the reaction mixture is increased to 300° F. and the mixture held at this temperature for two hours with stirring. At the end of this period, all of the phosphorus pentasulfide is dissolved and the product is a viscous amber colored liquid. The mixture is then cooled to 230° F. and 1,230 grams of paratertiary amyl phenol added to the mixture, stirred for one hour, at the end of which time 225 grams of zinc oxide is added and the mixture stirred for an additional hour. Thereafter the temperature is increased slowly to 280° F.

In order to facilitate filtration, the resulting product is thinned by intimately mixing therewith 4,380 grams of a light petroleum lubricating oil fraction. The mixture is then filtered and the filtrate is found by analysis to contain 3.19% phosphorus, 8.64% sulfur and 0.48% zinc.

The above reaction product is extracted with 3 times its weight of mesityl oxide in a series of 5 extractions, using equal volumes of solvent each time. The raffinate is recovered and contains the improved additive. The solvent-containing extracted material is recovered by distillation and the solid extract material discarded. The recovered solvent may be reused.

EXAMPLE 8

(*a*) 132 grams of commercial octadecane nitrile (analysis: 94% by weight of octadecanoic nitrile and 6% hexadecanoic nitrile), 55 grams of phosphorus pentasulfide and 396 grams of No. 225 Red Oil (a conventional acid treated Mid-Continent lubricating oil base stock of S. A. E. 20) were mixed and heated at 400° F. in an inert nitrogen atmosphere for 30 minutes, with agitation. The reaction mass was filtered hot. This filtrate product was used as an additive in the test reported hereinafter. It analyzed 2.92% phosphorus and 5.91% sulfur.

(*b*) 188 grams of the above reaction product 8 (*a*) was mixed with 11.2 grams of potassium hydroxide and 21.5 grams of water and heated on a steam bath for two hours with agitation, and then blown with air at 250° F. for two hours. The reaction mass was then filtered hot. The filtrate product analyzed 3.64% ash.

(*c*) This additive is extracted with 3 times its volume of ethane in 4 equal portions. The raffinate contains the valuable components of the additives and has improved engine use properties. The solvent-containing extracted material is recovered by distillation for reuse and the extracted material discarded.

EXAMPLE 9

(*a*) 620 grams of reduced motor polymer and 380 grams of phosphorus pentasulfide were mixed and heated at 350° F. in a pressure vessel at 100 p. s. i. for two hours. A 100% yield was obtained.

(*b*) 500 grams of the above reaction product (*a*) was mixed with 33 cc. of water and the mixture heated at about 200° F. on a steam bath for two hours, with agitation. It was then blown with nitrogen for one and one-half hours at 250° F. to dry the product.

(c) 200 grams of the above water treated product (b) and 14.6 grams of calcium cyanamide were mixed and the mixture heated for one hour at 500° F. with agitation. The reaction product was filtered hot. 144 grams of product was obtained as a filtrate. It analyzed 3.42 weight per cent ash.

(d) This additive is extracted with 5 times its weight of methyl Cellosolve. The raffinate contains the valuable portion of the additive. The extract which is removed by the solvent is discarded.

EXAMPLE 10

(a) Hydrogenated sperm oil is reacted with 20% phosphorus sulfide at a temperature of about 300° F. This hydrogenated sperm oil is available under the trade name of "Spermafol No. 52." It has an iodine value of 6–7, a melting point of 50–52° C., a free fatty acid content (as oleic) of 1.0–2.0%, a saponification value of 135–138, and about 36% of unsaponifiables. After the reaction is complete, which under the reaction conditions takes 4 hours, the material is permitted to stand, after which the by-product residue settles and the reaction product is decanted; following this, it is filtered with the use of a filter aid. The yield of the reaction product based upon hydrogenated sperm oil raw material is 100%.

(b) 360 grams of the above sulfide-spermafol reaction product (a) was mixed with 40 grams of water and the mixture heated at about 200° F. on a steam bath for one and one-quarter hours, with agitation. It was then blown with nitrogen for three hours at 250° F.

(c) A quantity of this reaction product (b) was mixed with 15 weight per cent thereof of calcium cyanamide and the mixture heated for four hours at 500° F., with agitation. The reaction product was filtered hot. A 40 weight per cent yield of product was obtained as a filtrate. It analyzed 0.4 weight per cent ash.

(d) The above additive is extracted with 4 times its volume of methyl ethyl ketone. The raffinate contains the valuable portion of the additive and has superior engine use properties to the unextracted additive. Upon distillation the solvent can be recovered for reuse. The extracted material remaining after distillation of the solvent is discarded.

EXAMPLE 11

(a) 48 grams of commercial "Palmitone," 11.1 grams of phosphorus pentasulfide and 144 grams of No. 225 Red Oil (a commercial acid treated Mid-Continent lube oil with an S. S. U. viscosity of 225 at 100° F.) were mixed and heated to a temperature of 500° F. with stirring for thirty minutes in an inert atmosphere. The reaction mass was filtered hot and 190 grams of a dark colored oily material was obtained.

(b) To 189 grams of the above product was added 31.5 grams of barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$). The mixture was reacted for 3 hours at a temperature of 200° F. with agitation. The mixture was then blown with air for 2 hours at a temperature of 250° F. and filtered. 182 grams of an oil solution of the barium derivative of the P_2S_5-Palmitone reaction product was obtained. The product analyzed 3.86% ash.

(c) The reaction product is extracted with 5 times its weight of methyl isobutyl ketone in 4 equal portions. The raffinate which is recovered contains the portion of the additive having the most valuable engine use properties. The material extracted by the solvent can be discarded when the solvent is recovered for reuse.

EXAMPLE 12

Lauric acid was reacted with 25% phosphorus pentasulfide for one hour at 300° F. The reaction product, after separation from the sludge, was converted into the metal derivative thereof by reaction with 10% (based on the reaction product) of lime to which was added an equal amount of water. This reaction was continued at a temperature of about 180° F. for several hours and then at a temperature of about 250° F. for about one hour. The reaction product was filtered and then extracted with 4 times its volume of propionaldehyde in 4 portions. The valuable portion of the additive is found in the raffinate. The material extracted by the solvent is discarded after recovery of the solvent for reuse.

EXAMPLE 13

Palmitic acid was mixed with an equal proportion of a neutral lubricating oil having a viscosity of 225 S. S. U. at 100° F. and reacted with 38% phosphorus pentasulfide, based on the weight of the palmitic acid. The reaction was continued at a temperature of about 300° F. until complete, as in the previous examples, and the reaction product was separated from a sludge and then converted to the corresponding calcium derivative by reaction with 10% of lime containing an equal amount of water. The latter reaction was carried out at 300° F. under 60 pounds of pressure for about 1 hour.

The above oil solution was extracted with 5 times its volume of ethyl acetate in 4 equal portions. The raffinate is separated from the solvent and the solvent recovered from the extract for reuse. The extracted material is discarded.

EXAMPLE 14

A mixture of 25% stearic acid and 75% oleic acid is reacted with 35% phosphorus pentasulfide at a temperature of 300° F. for approximately one hour. The reaction product is separated from the sludge and converted to the corresponding metal derivative by reaction with 10% of lime containing an equal amount of water. The latter reaction is carried out at 300° F. for about 1 hour under 50 pounds of pressure. The reaction product was filtered during which time an equal amount of oil was added to aid in the filtration.

This reaction product is extracted with 4 times its volume of nitroethane in 4 equal portions. The raffinate is recovered and is an improved lubricating oil additive compared to the unextracted material. The material extracted by the solvent is discarded when the solvent is recovered for reuse.

EXAMPLE 15

p-Tert. octyl phenol was reacted with 20% phosphorus pentasulfide for 4 hours at 300° F. Sludge was separated from the reaction mixture by centrifuging and thereafter the reaction product was converted into the potassium derivative by reaction with 10%, based on the reaction product of potassium hydroxide, to which was added an equal amount of water. This reaction was continued at a temperature of about 250° F. for several hours under pressure. The reaction product was again filtered to separate sludge and unreacted materials.

This metal derivative was then extracted with 4 times its volume of isopentane in 4 portions. The valuable portion of the additive having improved properties is found in the raffinate. The solvent is recovered from the extracted material and the extracted material is then discarded.

EXAMPLE 16

Cyclohexanol is reacted with 25% by weight of phosphorus pentasulfide for 3½ hours at 350° F. The reaction product is then centrifuged to separate unreacted materials and the sludge, and then reacted with zinc chloride (10% by weight) in the presence of an equal amount of water. The reaction was carried out at a temperature of about 180° F. for several hours and then at a temperature of about 250° F. for two hours. The reaction product was filtered and then extracted with 6 times its volume of isopropyl alcohol in 4 portions. The raffinate has improved properties when employed as an additive in a lubricating oil. The solvent is recovered from the extract, which is discarded.

EXAMPLE 17

A commercial terpene mixture containing mixed noncyclic, monocyclic and bicyclic terpenes, including p-cymene, α-pinene and β-pinene, was reacted with 25% by weight of phosphorus pentasulfide at 350° F. for 4 hours under 100 p. s. i. The product was filtered to separate sludge and unreacted material, and then reacted with 10% of lime, to which was added an equal amount of water. The reaction was carried out at about 180° F. for 3 hours and then at 250° F. for 1 hour. The reaction product was filtered and extracted with 4 times its volume of chloroform in 5 portions.

The raffinate which is recovered has improved properties as an additive for lubricating oils. The solvent is recovered from the extract, which is discarded.

The following table illustrates additional types of materials which can be reacted with a phosphorus sulfide to obtain a substrate which can be improved by extraction. In the left hand column is illustrated the additive made by reacting the listed materials with phosphorus sulfide and in the right hand column is listed the selective solvent which may be used in extracting the substrate. In all instances, the relative amounts, temperatures, etc., will be selected so as to give the amount of the raffinate having the desired properties.

Reactant With Phosphorus Sulfide	Selective Solvents
Cetyl Palmitate	Ether.
Dodecane Nitrile	Isophorone.
Alpha Pinene	N-butane.
Tetradecanol	Diethyl Sulfide.
Tetradecaneamide	Isopentane.
Xylylheptadecyl Ketone	Sulfur Dioxide.
Octadecene-1	Isopropanol.
Lauryl Mercaptan	Propyl Mercaptan.

In view of the foregoing disclosures, variations and modifications will be apparent to those skilled in the art. The invention contemplates all such variations and modifications except as do not come within the appended claims.

This application is a continuation-in-part of application Serial No. 18,296, now U. S. Patent No. 2,587,621, which is a continuation-in-part of application Serial No. 578,122, filed February 15, 1945, now abandoned.

We claim:

1. A method of treating lubricant additives which are phosphorus sulfide-organic compound-metal derivatives to remove therefrom material contained therein impairing their optimum characteristics as corrosion-inhibiting additives for mineral lubricating oil which comprises mixing said derivative with a solvent having a selective solvent power for said material with formation of an extract phase and a raffinate phase, separating the raffinate phase from the extract phase and recovering said metal derivative from the raffinate phase.

2. A method in accordance with claim 1 in which the solvent is a liquid polar material.

3. A method in accordance with claim 2 in which the polar material is an oxygenated material.

4. A method in accordance with claim 3 in which the solvent is acetone.

5. A method in accordance with claim 1 in which the solvent is a liquid non-polar material.

6. A method in accordance with claim 1 in which the phosphorus sulfide-organic compound-metal derivative is a phosphorus sulfide-organic ester-metal derivative.

7. A method in accordance with claim 1 in which the phosphorus sulfide-organic compound-metal derivative is a phosphorus sulfide-organic amine-metal derivative.

8. A method in accordance with claim 1 in which the phosphorus sulfide-organic compound-metal derivative is a phosphorus sulfide-olefin polymer-metal derivative.

9. A method in accordance with claim 1 in which the phosphorus sulfide-organic compound-metal derivative is a phosphorus sulfide-organic amide-metal derivative.

10. A method in accordance with claim 1 in which the phosphorus sulfide-organic compound-metal derivative is a phosphorus sulfide-organic ketone-metal derivative.

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