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LUBRICATING COMPOSITION

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This invention relates to new and novel products which have properties of greatly improving and stabilizing lubricants. More particularly, this invention pertains to oleaginous materials, especially lubricants, such as mineral lubricating oils, synthetic lubricants of hydrocarbon and non-hydrocarbon origin and the like, containing a multi-functional additive having detergent and anti-ringsticking properties as well as acting as an inhibitor of oxidation and corrosion.

It is well known that various lubricants, whether doped or undoped, tend to oxidize and form corrosive bodies and sludge when used in modern engines and machines operating under ordinary conditions, and especially at high speeds, elevated temperatures, heavy loads and other adverse conditions. Also as lubricants deteriorate during use, hard carbonaceous materials are formed on engine and machine parts, causing scratching and scuffing of movable metal parts and sticking of valves and piston rings in engines. In addition, known lubricants are generally incapable of maintaining a continuous lubricating film between movable metal parts; this results in a gradual or rapid wearing away of the metal parts. The damage thus caused requires replacement of such parts, or even a complete overhauling of engines and machines, resulting in expensive loss of production and time.

In the case of the highest quality non-corrosive, stable undoped mineral lubricating oils, which are highly refined for specific uses, or synthetic lubricants developed for special uses, it has been found that such oils and lubricants are generally highly susceptible to oxidation and deterioration, becoming progressively more and more corrosive in engines and machines even under ordinary operating conditions.

To improve the lubricating properties of oils and synthetic lubricants, it has become the practice to blend therewith one or more additives which have the effect or the property of inhibiting deterioration of lubricants and impart to them certain beneficial properties. Thus additives have been specifically designed which have the property of inhibiting corrosion of alloyed bearings such as copper-lead, cadmium-silver and the like, developed for automotive, Diesel and aircraft engines. Acidic oxidation or decomposition components formed in lubricants during use can readily attack these bearings, but are inhibited or prevented from doing this by the formation of a corrosion protective film formed with the aid of the additive on the bearing surface. Additives have also been developed which

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possess the property of modifying the carbonaceous materials formed by deterioration of lubricants on piston rods, rings and valves and other metal parts in internal combustion engines, automotive and truck engines, aviation engines, high speed Diesel engines, and the like. These additives serve a very important function because by modifying this carbonaceous material so that it can be removed easily, the tendency of engine parts to become stuck is inhibited; ringsticking, piston scuffing and scratching and wearing away of other parts and material reduction of engine efficiency is thereby prevented.

Other additives have been developed which act as detergents in order to assist in the removal of soot, sludge, varnish, and/or lacquer formed from deterioration of the oil at high operating temperatures. Detergents, due to their cleansing action, prevent the build-up of these deleterious materials and assist in removing those formed. Anti-wear additives have the property of reducing friction of movable metal parts of the same or different metals. Due to the function exerted or property imparted by such additives on lubricants, wear caused by direct frictional contact of metals can be greatly reduced. Also additives have been developed for withstanding extreme pressures, dispersion of impurities, solubilizing of certain other additives, etc.

The large number of additives thus developed has been due to the fact that an additive is capable of functioning mainly in only one specific manner: very few lubricant additives have the ability of improving a lubricant in more than just one respect. Thus, a good anti-oxidant might not be able to inhibit lacquer and varnish formation on piston rods, or to act as a detergent or corrosion inhibitor. In many cases, it is found that whereas an additive possesses very good properties in one respect, this same additive is the cause of harmful deposits in another respect. A second and third additive is therefore frequently required in order to obtain a good stable lubricant. The combination of additives in lubricants wherein each additive exerts its influence without interfering with the function of other additives present is a difficult matter to attain because in most cases additives co-react or interfere with each other. To prevent this from occurring great care must be taken in selecting the additives, mixing them in specific proportions, and continuously watching and replacing additives which have stopped functioning or have deteriorated.

It is an object of this invention to improve the

properties of various oleaginous materials. Another object is to add to compounded or doped lubricants a multi-functional material whereby a synergistic effect is produced, resulting in a product of accentuated and improved properties. Another object of this invention is to add to mineral lubricating oils, synthetic lubricants, and the like, a multifunctional material so as to inhibit oxidation and corrosion and prevent the formation of sludge, varnish and lacquer in said lubricants even under adverse operating conditions. Still another object of this invention is to use in lubricating compositions a material which prevents ringsticking as well as the sticking of other engine parts due to deterioration of the lubricant. Also it is an object of this invention to use in lubricating compositions a material which inhibits wear, scuffing, scratching and other damage to engine parts. It is still another object of this invention to provide novel compounds which possess multifunctional improving and enhancing properties when added to lubricants.

The above and other objects may be attained in accordance with the present invention by adding to oleaginous materials, e. g. various lubricating bases, a minor amount of sulfurized reaction product or sulfurized salt of a reaction product obtained by treating phosphorus sulfide with a saturated and unsaturated cyclic ketone fraction having at least 12 and preferably more than 18 carbon atoms in the molecule, said ketone fraction having been derived from isophorone bottoms during its synthesis from acetone by condensation, as well as from other sources. The phosphorus sulfide-cyclic ketone reaction product may be sulfurized and if desired thereafter treated with a metal or organic base to form the salt of said reaction product. Also the salt of phosphorus sulfide-cyclic ketone may be formed first and thereafter sulfurized. Preferably, the phosphorus sulfides used to produce the reaction products of this invention should be selected from the class consisting of phosphorus pentasulfide, phosphorus heptasulfide and the like. The preferred ketones used to obtain the oil additive of this invention are the unsaturated cyclic ketones which are reacted with these phosphorus sulfides and are normally obtained from isophorone bottoms produced by condensation of acetone under elevated temperature and pressure. The isophorone bottoms thus produced may be fractionated into various cuts each of which may be used to react with phosphorus sulfide to form the compound or oil additive of this invention. Among the specific isophorone fractions which may be used to form the reaction product of this invention are topped, crude isophorone, topped crude hydrolyzed isophorone bottoms, and the like. Although the mol ratio of the phosphorus sulfide and unsaturated cyclic ketones of this invention may be varied over wide limits, it is preferable to keep them within the range of from 1:2 to 1:1.2, respectively. The reaction between these two ingredients is generally carried out under controlled elevated temperature conditions. This reaction product may be treated with any suitable metal such as the alkali metals, alkaline earth metals, heavy metals, nitrogen containing organic bases and the like. Specifically such a compound as a hydroxide, carbonate or oxide of Na, Li, K, Ca, Ba, Sr, Mg, Al, Zn, Cu, Dr, Cd, Fe, Mn, Ni, Sn, etc., or basic reagents such as ammonia alkyl or aryl substituted ammonia, such as amines and the like, or it may be sulfurized, or the phosphorus sulfide-cyclic ketone reaction product may be neutralized and thereafter resulfurized.

The sulfurizing agents which may be used to treat the phosphorus sulfide-cyclic ketone reaction product or its salt may be selected from the class consisting of elemental sulfur, flowers or sulfur, sulfur halides, alkali polysulfide, ammonium hydrogen sulfide-hydrogen sulfide, sulfur dioxide, and the like.

The terms topped crude isophorone bottoms and topped crude hydrolyzed isophorone bottoms, and similar terms, which will be hereinafter used and fully described are generic and are used to identify various unsaturated cyclic ketone fractions of relatively high molecular weight obtained from acetone condensation. Unsaturated cyclic ketone fractions useable in reactions of the kind under consideration may be obtained by condensing acetone in 30% to 60% caustic solution at a temperature ranging between about 130° C. and 170° C., and under pressure of from 300 to 500 pounds per square inch. The resultant product is preferably subjected to distillation to remove distillable ketones and other constituents and impurities. The product remaining in the still is purified by filtration, solvent treatment, and comprises crude unsaturated cyclic ketones of high molecular weight, preferably referred to as crude isophorone bottoms. The term isophorone bottoms as referred herein is thus a complex mixture of high molecular weight unsaturated cyclic ketones containing at least 12 and preferably more than 18 carbon atoms in the molecule. The product formed is not to be confused with straight isophorone which is specifically 3,5,5-trimethyl cyclohexene-2-one-1, an unsaturated cyclic ketone containing only nine carbon atoms in the molecule. Isophorone bottoms produced by condensation of acetone under conditions referred to above includes within its scope any and all unsaturated cyclic ketones containing at least 12 and preferably more than 18 carbon atoms and having generally the chemical structural configuration of isophorone as well as the chemical structural configuration resulting from its condensation.

Crude isophorone bottoms can be fractionated and/or chemically treated and each fraction thereof can in turn be treated with phosphorus sulfide at elevated temperatures to produce a compound containing both phosphorus and sulfur. Among the various fractions which can be obtained from crude isophorone bottoms are topped crude isophorone bottoms which contain at least 15 carbon atoms in the molecule and which are obtained after removal of distillate from crude isophorone bottoms to a still head temperature of 140° C. at 10 mm. Hg pressure. Crude isophorone bottoms can be subjected to hydrolysis with dilute sodium hydroxide and the acetone and isophorone formed removed by distillation. The bottoms can then be filtered and purified and comprise essentially unsaturated cyclic ketones containing at least 12 and more carbon atoms in the molecule and are referred to as crude hydrolyzed isophorone bottoms. This material can be subjected to distillation to split it into two fractions. This distilled hydrolyzed isophorone fraction has a boiling point of about 140° C. at 10 mm. Hg pressure and consists of a mixture of unsaturated cyclic ketones containing between 15 to 18 carbon atoms in the molecule. The residue is referred to as topped crude hydrolyzed isophorone bottoms and is similar to

topped crude isophorone bottoms. They comprise essentially unsaturated cyclic ketones of at least 15 carbon atoms in the molecule. Crude isophorone bottoms can be also subjected to condensation over solid sodium hydroxide to yield two types of resinous materials. The first resinous fraction or soft resin has a viscosity at 210° F. of about 25–26 centistokes and an average molecular weight of 320 to 350. The heavier fraction or medium resin has a viscosity at 210° F. of about 80 to 120 centistokes and an average molecular weight of 370 to 390. All of the various unsaturated cyclic ketone fractions obtained in the manner fully described above can be used for reacting with phosphorous sulfide to form a multi-functional lubricating additive. Other cyclic ketones having at least 12 carbon atoms are obtained by hydrogenating the above unsaturated cyclic ketones to obtain saturated cyclic ketones having at least 12 carbon atoms, alkyl cyclohexanone, i. e. dibutyl cyclohexanone, alkyl substituted carvomenthone, menthone, pulegone, carvone, camphor, and the like having at least 12 carbon atoms.

Phosphorus sulfides generally can be used in producing reaction products of this invention and preferably phosphorus pentasulfide and phosphorus heptasulfide are used because of their availability, cost and desired reactivity. The exact manner in which phosphorus and sulfur enter the reaction is at present not known or understood and the chemical structure of the reaction is also not known, however, it might be possible that thioketones containing phosphorus in the form of ester linkages are produced when phosphorus sulfide is reacted with unsaturated cyclic ketones. This is in contrast to early references of reactions of the type under discussion which stated that phosphorus did not enter the reaction and the products formed were thioketones. Thus A. E. Kretov and Ya P. Komissarov in the Jr. Gen. Chem. U. S. S. R. 5,388–91 (1935), state that the action of phosphorus pentasulfide on aliphatic ketones results in the formation of thioketones. Gatterman in Ber. 28, 2877 disclosed that when benzophenone in benzine solution is heated with phosphorus pentasulfide for several hours at 130° C. in a bomb, thiobenzophenone forms and phosphorus does not enter into the reaction. Also Patents 2,309,829 and 2,402,640 disclose that ketones when reacted with phosphorus sulfide produce thioketones and phosphorus does not enter into the reaction. Unlike any previous teachings reaction products of this invention contain both phosphorus and sulfur, and physically as well as chemically are quite unlike in properties to thioketones.

The phosphorus sulfide-unsaturated cyclic ketone reaction products of this invention can be prepared from any of the ketone fractions obtained in the manner described above, although certain fractions are preferred to others. The kind of phosphorus sulfide used, the ratio of the two reactants, the temperature, time and conditions under which the reaction is carried out, as well as the manner in which the final product is recovered, are also important and controlling factors. The preferred ketone fractions are topped crude isophorone bottoms which are residues remaining after removal of distillate from crude isophorone bottoms to a still head temperature of 140° C. at 10 mm. Hg pressure, and comprise unsaturated cyclic ketones containing at least 15 carbon atoms in the molecule. Another preferred fraction is topped crude hydrolyzed isophorone

bottoms obtained from crude hydrolyzed isophorone bottoms similar to the topped crude isophorone bottoms. The term "topped" used throughout has the same meaning as in the petroleum art, namely, a distillation or fractionation step, whereby certain materials are removed as an overhead fraction.

Phosphorus pentasulfide and phosphorus heptasulfide are preferred although other phosphorus sulfides can be used. The mol ratio of phosphorus sulfide to ketone is a most important factor in obtaining a desired reaction product. When the mol ratio of phosphorus sulfide to ketone is from 1:2 to 1:1.2, superior reaction products are obtained. However, this mol ratio need not be adhered to strictly and may be varied at times to 1:4 and even 1:8 of phosphorus sulfide to ketone, respectively. Generally, when these ratios are used the resultant products are relatively inferior and for some lubricants may prove to be unsatisfactory.

The reaction temperature can be varied between about 130° C. and about 200° C. or higher, and preferably between 150° C. and 170° C. However, the initial or starting temperature should be controlled quite carefully and be restricted within relatively rather narrow limits to obtain a desired controlled reaction. If initially the reaction is allowed to progress at a rapid rate over 100° C., due to the vigor of the resultant reaction, it cannot then be controlled and an undesirable product forms. The initial stage of the reaction should be carefully controlled and heated slowly in a suitable bath or by any suitable means to an initial temperature of between about 60° C. and 80° C., and thereafter heated relatively more rapidly to the desired or optimum temperature.

The reaction should be carried out in substantially inert atmosphere and the two materials can be reacted per se or dispersed in a suitable inert or non-reactive diluent and then reacted under conditions described above. When the reaction is completed, the desired fraction can be extracted with a suitable material, such as non-aromatic hydrocarbons, e. g. one having a boiling range of between 164° F. to 233° F., or an aviation base stock gasoline boiling up to 190° F. and containing little, e. g. not more than about 4%, aromatics.

The reaction of phosphorus sulfide with saturated or unsaturated cyclic ketone to produce the initial reaction products of this invention is relatively simple and requires no elaborate or special equipment, undue precautions or skill. The obtainment of the desired initial reaction products simply requires a mixing and stirring of unsaturated cyclic ketones of this invention with for example dry, powdered phosphorus pentasulfide, in an inert atmosphere, such as nitrogen or carbon dioxide, for 2 to 8 hours. Initially, the reaction is kept at between about 60° C. and about 80° C., the mixture being then rapidly heated to an elevated temperature of 200° C., or higher. At the completion of the reaction the desired fraction may be extracted with a non-aromatic hydrocarbon having a boiling point of 164° F. to 233° F. The non-extractable material is discarded and the solution is filtered, evaporated at steam temperature in a current of inert gas to yield the desired products suitable as lubricant additives. The additives thus produced vary in color from amber to dark brown and in consistency from viscous liquid to brittle solids. They are readily soluble in various petroleum lubricat-

ing oils as well as other types of oleaginous materials, oils and synthetic lubricating bases.

This reaction product of this invention obtained by treating the above phosphorus sulfide-cyclic ketone may be treated with a suitable sulfurizing material to obtain one of the final reaction products of this invention. This can be readily accomplished by sulfurizing the phosphorus sulfide-cyclic ketone either in bulk or in a suitable solvent with sulfur and the like at an elevated temperature of above about 150° C. and preferably above 160° C.

The general procedure for preparing the salts of reaction products obtained by treating phosphorus sulfide-cyclic ketones may be attained by dispersing or dissolving a phosphorus sulfide treated cyclic ketone in a large quantity of a quantity of a suitable hydrocarbon oil by heating to approximately steam temperature. To this composition a calculated amount of neutralizing agent, such as lime or the like, is added and the mixture agitated at an elevated temperature of above about 120° C. for over a period of 2 hours. After the reaction is completed a stream of inert gas is introduced to remove any entrained moisture or other contaminants. The neutralized phosphorus sulfide-cyclic ketone reaction product is then filtered to recover the product from the oil and may be refiltered to remove excess lime and other impurities.

The preparation of salts of phosphorus sulfide with saturated or unsaturated cyclic ketone reaction products of this invention is relatively simple and requires no elaborate or special equipment, undue precautions or skill. The obtainment of the desired reaction products simply requires a mixing and stirring of unsaturated cyclic ketones of this invention with, for example, dry, powdered phosphorus pentasulfide, in an inert atmosphere, such as nitrogen or carbon dioxide, for 2 to 8 hours. Initially, the reaction is kept at between about 60° C. and about 80° C., the mixture being then rapidly heated to an elevated temperature of 200° C., or higher. At the completion of the reaction the desired fraction may be extracted with a non-aromatic hydrocarbon having a boiling point of 164° F. to 233° F. The non-extractable material is discarded and the solution is filtered, evaporated at steam temperature in a current of inert gas to yield the desired products which when treated with a metal or organic base are suitable as lubricant additives. The additives thus produced vary in color from amber to dark brown and in consistency from viscous liquid to brittle solids. They are readily soluble in various petroleum lubricating oils as well as other types of oleaginous materials, oils and synthetic lubricating bases.

If salts are formed they may be if desired sulfurized and this may be prepared by dispersing said salt in a suitable liquid carrier such as a liquid hydrocarbon and treating said mixture with a sulfurizing agent such as sulfur at an elevated temperature, preferably under inert conditions, until the reaction is completed. The sulfurization temperature generally ranges from between about 150° up to about 200° C. and higher and is carried out for a period of 24 hours and longer. The sulfurized salt may be recovered from the liquid diluent by any suitable means such as distillation, evaporation, filtration, etc. If the diluent used is a desirable mineral lubricating oil, the sulfurized salt need not be recovered therefrom but additional oil can be added to the mixture until the sulfurized salt in the oil base is adjusted to a desired concentration.

To more clearly illustrate the present invention, the following examples are presented. It is to be understood, however, that various modifications can be restored without departing from the spirit of the invention as presented in the subjoined claims.

Example IA.—Initial reaction product

A mixture of cyclic unsaturated ketones containing at least 18 carbon atoms in the molecule, obtained by topping bottoms from crude isophorone bottoms at a kettle temperature of 140° C. and 10 mm. Hg pressure and phosphorus pentasulfide were reacted, in the mole ratio of 1.6:0.56 respectively, for about five hours at around 160° C. in an inert atmosphere of carbon dioxide and under constant agitation. The mixture was placed initially in a bath maintained at about 60° C. to 80° C. and then rapidly heated to about 160° C. At the end of the reaction period, the desired product was extracted with a non-aromatic hydrocarbon having a boiling range of between about 164° F. and 233° F. The solution was filtered and the filtrate evaporated at steam temperature in a current of carbon dioxide. The final product on analysis contained 13.8% sulfur and 1.3% phosphorus.

Example IB.—Final reaction product

Approximately 80 gm. of the above initial reaction product and about 16 gm. of sulfur were reacted for between about 2 to 4 hours at between about 150 and 180° C. with constant stirring until the reaction was complete. The resultant product was a hard brown brittle mass, readily soluble in mineral oil and contained 23.9% sulfur, while the phosphorus content remained substantially the same as noted in the initial reaction.

Example IIA.—Initial reaction product

A mixture of about 1.6 mols of ketones as used in Example IA and about 0.54 mol of P_4S_7 were reacted and the reaction product isolated in the manner indicated in Example IA. The reaction product contained 14.3% sulfur and 5.2% phosphorus.

Example IIB.—Final reaction product

Approximately 80 gm. of the reaction product of IA and about 16 gm. of sulfur were reacted for about four hours at between about 158 and 166° C. with constant stirring until the reaction was complete. The resultant product was hard and brittle, but readily soluble in mineral oil and contained 24.1% sulfur, while the phosphorus content remained constant.

Example IIIA.—Initial reaction product

The bottoms from the condensation of diisobutyl ketone containing above 12 and preferably 15 carbon atoms were reacted with P_2S_5 in the mol ratio of 8:5 in the manner described in Example IA. The product on analysis contained about 18.8% sulfur and above 5.0% phosphorus.

Example IIIB

Reacting approximately 80 gm. of the product of IIIA with about 16 gm. of sulfur for 2 hours at between about 157 and 172° C. yielded a reaction product containing 26.6% sulfur. The same materials in the same proportions when reacted for 4 hours at between about 158 to 180° C. yielded a

product containing about 24.6% sulfur. Further heating did not have any effect upon the reaction.

Example IV

A mixture of cyclic unsaturated ketones containing at least 18 carbon atoms in the molecule, obtained by topping bottoms from crude isophorone bottoms at a kettle temperature of 140° C. and 10 mm. Hg pressure and phosphorus pentasulfide in the weight ratio of 8:2, respectively, were stirred and heated in an inert atmosphere of carbon dioxide for approximately five hours to around about 160° C. The mixture was placed initially in a bath maintained at about 60° C. to 80° C. and then rapidly heated to 160° C. At the end of the reaction period, the desired product was extracted with a non-aromatic hydrocarbon having a boiling range of between about 164° F. and 233° F. The solution was filtered and the filtrate evaporated at steam temperature in a current of carbon dioxide. The resultant product on analysis contained 14.3% sulfur and 1.2% phosphorus.

Approximately 10 parts of this reaction product was dissolved in a desirable amount of mineral lubricating oil by gentle heating at about 90° C. to 100° C. If desired, this mixture may be filtered to remove any foreign and oil insoluble matter. To this heated mixture about 15 parts of lime is added and a minor amount of water and the product heated for about two to three hours at about 100° C. The mixture is then filtered to remove excess lime and the filtrate reheated for about two hours at between 120° C. and 130° C. A stream of nitrogen gas is then blown through the mixture to remove entrained foreign matter, moisture and the like. The salt can be recovered by any suitable means from the oil solution. The calcium salt of this reaction product contains both sulfur and phosphorus and is readily soluble in mineral oil. This calcium salt was dissolved in a mineral oil up to about 0.02% sulfate ash and the amount of sulfur in such a blend was approximately 0.46%. To this blend about 15 gm. of sulfur was added under agitation of the mixture heated for 24 hours at between about 150 and 170° C. in an inert atmosphere.

The sulfurized salt was then recovered and on analysis contained 2.0 (8)% sulfur. The product was readily soluble in mineral oil.

Example V

The initial reaction, namely, the reaction of phosphorus sulfide-unsaturated cyclic ketone, was carried out as indicated in Example I, except that the weight ratio of ketone to phosphorus pentasulfide was maintained at 8:4, respectively. On analysis this product contained 15.3% sulfur and 4.6% phosphorus. The calcium salt of this reaction product was formed in the manner described in Example I.

This calcium salt was dissolved in a mineral oil up to about 0.03% sulfate ash, and the amount of sulfur in such a blend was approximately 0.43%. This blend was sulfurized with elemental sulfur under the same conditions as described in Example I. On analysis the sulfurized salt contained 2.58% sulfur and was readily soluble in mineral oil.

To illustrate the pronounced improvement obtained in lubricating compositions by addition of small amounts of reaction products of this invention, the following test data is given on the Oxidation Stability Test and the Thrust Bearing Corrosion Test as described in the National Petroleum News, September 17, 1941, pp. R-294-296.

Oxidation stability and thrust bearing corrosion tests

[A refined undoped lubricating oil, 64-67 S. U. at 210° F. was employed, temperature 150° C.]

Oxidation Stability; Catalyst: 1 cm. 2/gm. oil [1]			Thrust bearing Corrosion, Critical Corrosion Temperature
Additive	Amount, per cent	1500 ml. oxygen, time	
		Hours	° C.
None		5.9	115
Ca Petroleum sulfonate	0.3% sulfate ash	4.0	110
Reaction Product of IIB plus Ca Petroleum sulfonate.	1% S, 0.3% sulfate ash.	39.3	170
Reaction Product of IIIB plus Ca petroleum sulfonate.	1% S, 0.3% sulfate ash.	53.4	170

[1] All oxidation products corrected to 1500 ml. oxygen absorbed per 100 gm. of oil, assuming amount of product is proportional to oxygen adsorbed.

Sulfurized salts of this invention are excellent oil improving agents, imparting to oil film strength and extreme pressure properties as well as stabilizing said oil against oxidation, corrosion, deterioration and the like.

The sulfurized salts of reaction products of this invention can be used as valuable additives to or constituents of heavy duty oils, motor oils, Diesel oils, aviation oils, synthetic oils, and the like, because of their anticorrosion, antioxidation, and anti-wear properties. The amount of additive used can be varied over relatively wide limits but generally it is not necessary to use more than 5% by weight of the reaction product and preferably only between about 0.1% to 2.0% by weight is added to base lubricants.

The reaction product of this invention can be combined with other additives in lubricants, such as, blooming agents, pour point depressants, viscosity improvers, extreme pressure agents, antifoaming agents, and the like. Among the specific additives which can be used are oil-soluble detergents which include oil-soluble salts of various bases with detergent-forming acids. Such bases include metal as well as organic bases. Metallic bases include the hydroxides, etc., of the alkali metals, Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary and quaternary amines.

Examples of detergent forming acids are the various fatty acids of, say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax), chlorinated fatty acids, rosin acids, aromatic carboxylic acids including aromatic fatty acids, aromatic hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicylic acids, phthalic acid mono-esters, aromatic keto acids, aromatic ether acids; diphenols as di-(alkyl phenol) sulfides and di-sulfides, methylene bis alkyl phenols; sulfonic acids such as may be produced by treatment of alkyl aryl hydrocarbons or high boiling petroleum oils with sulfuric acid; sulfuric acid mono-esters; phosphoric, arsonic and antimony acid mono and di-esters, including the corresponding thiophosphoric, arsonic and antimony acids; phosphonic and arsonic acids and the like.

Additional detergents are the alkaline earth phosphate di-esters, including the thiophosphate di-ester; the alkaline earth diphenolates, specifically the calcium and barium salts of diphenol mono and polysulfides.

Non-metallic detergents include compounds such as the phosphatides such as lecithin and cepholin, certain fatty oils as rapeseed oils, volatilized fatty or mineral oils and the like.

An excellent metallic detergent for the present purpose is the calcium salt of oil-soluble petroleum sulfonic acids. This may be present advantageously in the amount of about 0.025% to 0.2% sulfate ash. Also alkaline metal salts of alkyl phenol-aldehyde condensation reaction products are excellent detergents.

Antioxidants comprise several types, for example, alkyl phenols such as 2,4,6-trimethyl phenol, pentamethyl phenol, 2,4-dimethyl-6-tertiary butyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-ditertiary butyl-4-methyl phenol, 2,4,6-tritertiary butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl-amine, phenyl-beta-naphthyl amine, phenyl-alpha-naphthyl amine, dinaphthyl amine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms; alkali metal and alkaline earth salts of sulfonic acids and fatty acids; organic compounds containing an acidic radical in close proximity to a nitrile, nitro or nitroso group (e. g. alpha cyano stearic acid).

Extreme pressure agents which may be used comprise: esters of phosphorus acids such as triaryl, alkyl hydroxy aryl, or aralkyl phosphates, thiophosphates or phosphites and the like; neutral aromatic sulfur compounds of relatively high boiling temperatures such as diaryl sulfides diaryl disulfides, alkyl aryl disulfides, e. g., diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and trisulfides, and the like; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc., in which the sulfur is strongly bonded; sulfurized long chain olefins such as may be obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils or acids, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorous acids with sulfurized hydroxy fatty acids; chlorinated hydrocarbons such as chlorinated paraffin, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc., or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients may comprise oil-soluble urea or thio-urea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc., polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds.

Depending upon the additive used and conditions under which it is used, the amount of additive used may vary from 0.01% to 2% or higher. However, substantial improvement is obtained by using amounts ranging from 0.1% to 0.5% in combination with phosphorus sulfide-unsaturated cyclic ketone reaction products of this invention.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted, except by the prior art and the scope of the appended claims.

I claim as my invention:

1. A composition comprising a major amount of an oleaginous material and a minor amount, sufficient to stabilize said oleaginous material against deterioration and corrosion, of a reaction product obtained by initially treating cyclic ketone fractions having at least 12 carbon atoms with phosphorus sulfide at a temperature not in excess of 200° C. and thereafter treating said reaction product with a sulfurizing agent at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

2. A composition comprising a major amount of an oleaginous material and a minor amount, sufficient to stabilize said oleaginous material against deterioration and corrosion, of a reaction product obtained by initially treating saturated cyclic ketone fractions having at least 12 carbon atoms with phosphorus sulfide at a temperature not in excess of 200° C. and thereafter treating said reaction product with a sulfurizing agent at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

3. A composition comprising a major amount of an oleaginous material and a minor amount, sufficient to stabilize said oleaginous material against deterioration and corrosion, of a reaction product obtained by initially treating unsaturated cyclic ketone fractions having at least 12 carbon atoms with phosphorus sulfide at a temperature not in excess of 200° C. and thereafter treating said reaction product with a sulfurizing agent at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

4. A composition comprising a major amount of an oleaginous material and a minor amount, sufficient to stabilize said oleaginous material against deterioration and corrosion, of a reaction product obtained by initially treating unsaturated cyclic ketone fractions having at least 12 carbon atoms and derived from condensation of acetone to high molecular weight isophorone type fractions with phosphorus sulfide at a temperature not in excess of 200° C. and thereafter treating said reaction product with a sulfurizing agent at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

5. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to stabilize said mineral lubricating oil against deterioration and corrosion, of a reaction product of phosphorus pentasulfide with isophorone bottoms comprising essentially unsaturated cyclic ketone fractions having at least 12 carbon atoms at a temperature below 200° C. and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

6. A lubricating composition comprising a major amount of a mineral lubricating oil and a

minor amount, sufficient to stabilize said mineral lubricating oil against deterioration and corrosion, of a reaction product of phosphorus pentasulfide with crude isophorone bottoms comprising essentially unsaturated cyclic ketone fractions having at least 15 carbon atoms at a temperature below 200° C. and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

7. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to stabilize said mineral lubricating oil against deterioration and corrosion, of a reaction product of phosphorus pentasulfide with a condensation product of diisobutyl ketone containing above 12 carbon atoms at a temperature below 200° C. and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

8. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to stabilize said mineral lubricating oil against deterioration and corrosion, of a reaction product obtained by reacting at below 200° C., one mol of P_2S_5 with from about 1.2 to about 2 mols of unsaturated cyclic ketone fractions having at least 12 carbon atoms and derived from condensation of acetone, and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

9. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to stabilize said mineral lubricating oil against deterioration and corrosion, of a reaction product obtained by reacting at below 200° C., one mol of P_2S_5 with from about 1.2 to about 2 mols of crude isophorone bottoms comprising essentially unsaturated cyclic ketone fractions having more than 18 carbon atoms and derived from condensation of acetone, and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

10. A lubricating composition comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to stabilize said mineral lubricating oil against deterioration and corrosion, of a reaction product obtained by reacting at below 200° C., one mol of P_2S_5 with from about 1.2 to about 2 mols of a condensation product of diisobutyl ketone containing above 12 carbon atoms and derived from condensation of acetone, and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

11. A process of producing a stable, non-corrosive reaction product, obtained by reacting at a temperature below 200° C. phosphorus sulfide with a cyclic ketone fraction having at least 12 carbon atoms and thereafter treating said reaction product with a sulfurizing agent at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

12. A process of producing a stable, non-corrosive reaction product, obtained by reacting at a temperature below 200° C. one mol of P_2S_5 with about 1.2 to 2 mols of a cyclic ketone having at least 12 carbon atoms, and thereafter treating said reaction product with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

13. A lubricant comprising a major amount of a mineral lubricating oil and a minor amount, but sufficient to stabilize said mineral oil against deterioration, of a stable, non-corrosive sulfur treated calcium salt of phosphorus- and sulfur-containing reaction product obtained by reacting at a temperature below 200° C. one mol of P_2S_5 with from about 1.2 to about 2 mols of topped, crude isophorone bottoms comprising essentially unsaturated cyclic ketone fractions having at least 15 carbon atoms per molecule, said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

14. A lubricant comprising a major amount of a mineral lubricating oil and a minor amount, but sufficient to stabilize said mineral oil against deterioration, of a stable, non-corrosive sulfur treated calcium salt of phosphorus- and sulfur-containing reaction product obtained by reacting at a temperature below 200° C. one mol of P_2S_5 with from about 1.2 to about 2 mols of topped, crude hydrolyzed isophorone bottoms comprising essentially unsaturated cyclic ketone fractions having at least 15 carbon atoms per molecule, said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

15. A lubricant comprising a major amount of a mineral lubricating oil and a minor amount, but sufficient to stabilize said mineral oil against deterioration of a stable, non-corrosive sulfur treated calcium salt of phosphorus- and sulfur-containing reaction product obtained by reacting at a temperature below 200° C. one mol of P_2S_5 with from about 1.2 to about 2 mols of crude isophorone bottoms comprising essentially unsaturated cyclic ketone fraction having at least 12 carbon atoms, said reaction being effected at a temperature between about 150° C. and 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

16. A composition comprising a major amount of an oleaginous material and a minor amount, sufficient to stabilize said oleaginous material against deterioration, of a stable, non-corrosion reaction product from the group consisting of sulfurized reaction products obtained by initially treating cyclic ketone fractions having at least 12 carbon atoms with phosphorus sulfide at a temperature below 200° C. and thereafter reacting said product with a sulfurizing agent at a temperature below 180° C., and a sulfurized salt

of phosphorus and sulfur reaction product obtained by reacting phosphorus sulfide and a cyclic ketone having at least 12 carbon atoms, neutralizing said reaction product and thereafter treating said neutralized product with a sulfurizing agent, said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

17. A process of producing a stable, non-corrosive sulfurized salt, which comprises reacting at a temperature below 200° C. a phosphorus sulfide with a cyclic ketone fraction having at least 12 carbon atoms and derived from condensation of acetone to high molecular weight isophorone type fractions, treating said phosphorus- and sulfur-containing ketone with a metal and thereafter reacting said salt with a sulfurizing agent, said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

18. A process of producing a stable, non-corrosive sulfurized salt, which comprises reacting one mol of P_2S_5 with about 1.2 to 2 mols of topped, crude isophorone bottoms comprising essentially of unsaturated cyclic ketone fractions having at least 15 carbon atoms, at around about 160° C. under inert conditions, dispersing said reaction product containing both phosphorus and sulfur in an aliphatic hydrocarbon solvent, removing the extract fraction and after distilling off the solvent, treating said reaction product with a metal from the group consisting of alkali, alkaline earth and heavy metal, and thereafter reacting said salt with sulfur at a temperature below 180° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

19. A process of producing a stable, non-corrosive sulfurized salt, which comprises reacting one mol of P_2S_5 with about 1.2 to 2 mols of topped, crude isophorone bottoms comprised essentially of unsaturated cyclic ketone fractions having at least 15 carbon atoms, at around about 160° C. under inert conditions, dispersing said reaction product containing both phosphorus and sulfur in an aliphatic hydrocarbon solvent, removing the extract fraction and after distilling off the solvent, treating said reaction product with an alkaline earth metal and thereafter reacting said salt with sulfur at a temperature of around about 160° C., said final reaction product containing from about 1.2% to 5.2% phosphorus and from about 32% to 73% increase in sulfur above that present in the initial reaction product.

20. As a composition a resulfurized phosphorus and sulfur containing unsaturated cyclic ketone fractions having at least 12 carbon atoms derived from the condensation of acetone, containing above 1.2% phosphorus and above 23.9% sulfur.

21. As a composition a resulfurized phosphorus and sulfur containing unsaturated cyclic ketone fractions having at least 12 carbon atoms in the molecule, containing above 1.2% phosphorus and above 23.9% sulfur.

22. As a composition a resulfurized metal salt of a phosphorus and sulfur containing unsaturated cyclic ketone fractions having at least 12 carbon atoms in the molecule, containing above 1.2% phosphorus and above 23.9% sulfur.

23. As a composition a resulfurized phosphorus and sulfur containing cyclic ketone fractions having at least 12 carbon atoms in the molecule, containing above 1.2% phosphorus and above 23.9% sulfur.

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The following references are of record in the file of this patent:

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