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LUBRICATING COMPOSITION

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This invention relates to novel reaction products having properties of greatly improving and stabilizing lubricants, such as mineral lubricating oils, synthetic lubricants of hydrocarbon or non-hydrocarbon origin, and the like. The invention also pertains to such lubricants containing these reaction products which act as a multifunctional 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, when used in modern engines and machines whether operating under ordinary conditions or at high speeds, elevated temperatures, heavy loads and/or other adverse conditions, tend to oxidize and to form corrosive bodies and sludges. Some of the deterioration products of lubricants formed during their use are hard, carbonaceous materials which adhere to metal surfaces and cause scratching and scuffing of movable metal parts and the clogging of valves and piston rings in engines. In addition, the lubricants are usually incapable of maintaining a continuous lubricating film between movable metal parts, resulting in gradual or rapid wearing away of metal parts. The damage thus caused requires replacement of such parts and/or even the complete overhauling of the engines.

In the case of the highest quality non-corrosive lubricating oils, which have been highly refined for specific uses, or synthetic lubricants developed for specific or special uses, it has been observed that they are generally highly susceptible to oxidation and deterioration.

To improve the lubricating properties of oils and synthetic lubricants, it has become the practice to incorporate into such lubricants, one (and in most cases more than one) addition agents, which have the effect or property of inhibiting deterioration of such lubricants and to impart to them certain beneficial properties.

The development of numerous additives has been due to the fact that most, if not all, such additives are capable of functioning in substantially 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 act as a detergent or corrosion inhibitor. In many cases it is found that an additive possesses very good properties in one respect, but is the cause of harmful effects and, therefore, detrimental as an additive in another respect. This requires the use of still other additives in order to overcome such defects and to obtain a good stable lubricant. The combination of additives in lubricants wherein each additive exerts its influence without interfering with the function

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of other additives is a difficult matter to attain. In most cases additives co-react or interfere with each other. To prevent this, 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 lubricating properties of various lubricating bases by the addition thereto of a minor amount of certain multi-functional materials, which material is novel. 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. Still another object is to add to oleaginous materials, e. g. mineral lubricating oils, synthetic lubricants, and the like, a multi-functional compound which inhibits oxidation and corrosion and helps to prevent the formation of sludge, varnish and lacquer even under adverse operating conditions, and also prevents ring-sticking 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 oleaginous materials, e. g., in lubricating compositions, a multi-functional material which inhibits wear, scuffing, scratching and other damage to engine parts. Furthermore, it is an object of this invention to provide a novel class of compounds particularly suitable as multi-functional improving and enhancing additives for lubricants. Other objects will appear from the following description of the present invention.

Broadly stated, the invention is directed to products obtained by first reacting an organic carbonyl compound with a polyamine, and treating said reaction product with a sulfurizing (or compound of the sulfur family) phosphorizing or sulfo-phosphorizing agent, such as elemental sulfur, sulfur halides, alkali polysulfides, phosphorus, phosphorus halides and phosphorus oxyhalides, phosphorus sulfides, phosphorus acids, reactive organic phosphorus compounds and the like; the invention is also directed to oleaginous materials, particularly lubricating oils, containing minor amounts of the aforesaid reaction products.

The organic carbonyl compound may be saturated or unsaturated ketones or aldehydes; the following are representative examples:

I. Aliphatic ketones, such as: acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl n-amyl ketone, dipropyl ketone, ethyl amyl ketone, diisobutyl ketone, diethyl ketone, mesityl oxide and condensation products thereof, 3-methyl-heptanone, methyl vinyl ketone pentanedione, palimitone, laurone, stearone, pentadecanone, etc.

II. Aromatic ketones, such as: acetophenone, benzophenone, benzyl phenyl ketone, dibenzyl ketone, etc.

III. Cyclic ketones, such as: isophorone and higher homologues thereof, isophorone bottoms and fraction thereof, cyclobutanone, cyclopentanone, cyclohexanone, methyl cyclohexanone, menthone, camphor, beta decalone, pulegone, piperitone, eucarvone, carvenone, etc.

IV. Other types of ketones, such as: diacetyl, acetylacetone, acetonylacetone, cyclohexandione, quinone, benzoyl-acetone, etc.

V. Aliphatic aldehydes, such as: acetaldehyde, propionaldehyde, butyraldehyde, caproaldehyde, acrolein, croton aldehyde, ethyl butyraldehyde, ethyl propylaldehyde, heptaldehyde, 2-ethyl hexanal, chloral, butyl chloral, etc.

VI. Aromatic aldehydes, such as: benzaldehyde, paratoluic aldehyde, cinnamaldehyde, salicylaldehyde, naphthaldehyde, vanillin, phenylacetaldehyde, laurylbenzaldehyde, etc.

Among the preferred compounds are the higher molecular weight organic carbonyl compounds, particularly the higher molecular weight ketones. Of these ketones, preferred are the cyclic ketones, such as isophorone bottoms.

Isophorone bottoms are primarily high molecular weight unsaturated ketones having at least twelve and preferably more than eighteen carbon atoms in the molecule. These products may be obtained by condensation of acetone in a caustic solution under elevated temperature and pressure. Specifically, the product is obtainable by condensing acetone in a 30% to 60% caustic solution at a temperature ranging between about 130° C. and about 170° C., and under a pressure of from about 300 to about 500 pounds per square inch. The resultant product is subjected to distillation to remove distillable ketones and other constituents and impurities. The product remaining in the still is preferably 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 to herein, is usually a complex mixture of high molecular weight unsaturated cyclic ketones containing at least twelve and preferably more than eighteen carbon atoms in the molecule. These crude isophorone bottoms can be used as such or fractionated and/or chemically treated as disclosed in U. S. Patent 2,489,249.

The polyamines which can be used to react with the above organic carbonyl compounds in order to form the initial reaction product of this invention are alkylene polyamines such as: ethylene diamine, diethylene triamine, triethylene tetra-amine, tetraethylene pentamine, tetramethyl methylene diamine, propylene diamine, dipropylene triamine, tripropylene tetramine, N-n-dodecyl diethylene triamine, N-octyl ethylene diamine, hydroxyethyl-ethylene diamine, hydroxy isopropyl propylene diamine, hydroxy ethyl diethylene triamine, N-beta-hydroxypropyl propylene diamine, N-n-hexadecyl diethylene triamine, 3-diethyl amino propylamine, 1,3, diamino butane, 1,10 decylene diamine, phenyl ethylene diamine, di-o-tolyl ethylene diamine and the like.

The initial reaction product of this invention, namely, a reaction product obtained by reacting organic carbonyl compounds with polyamines disclosed above is carried out by admixing the reacting materials in a suitable reaction vessel with or without an inert solvent such as benzene, toluene, light hydrocarbons and the like, preferably

in the mole ratio of 2 to 6 moles of the carbonyl compound to 1 to 3 moles of the polyamine. The reaction can be carried out at reflux temperature, and generally varies from 50° C. to 250° C., and preferably 80° C. to 180° C., and is continued for a period of time until water formation ceases. The water formed is generally removed as it is formed by distillation and any polyamine which is carried over with the water is replaced and the reaction continued until completed. Generally, the time required to complete the initial reaction varies from 4 to 24 hours. The initial reaction product can be freed of unreacted materials, impurities and solvent such as benzene, if used, by heating the reaction product at around 100° C. in a stream of natural gas.

The final reaction product is obtained by treating an initial reaction product (as described in the preceding paragraph) with a sulfurizing, phosphorizing and/or sulfo-phosphorizing agent preferably in the mole ratio of from 1:1 to 1:8, respectively, and the preferred mole ratio of the reactants is from 1:2 to 1:4.

Among the sulfurizing, phosphorizing and/or sulfo-phosphorizing agents which can be used to treat the initial reaction product may be included sulfur, H_2S, SCl_2, S_2Cl_2, sodium tetrasulfide, sodium pentasulfide; $POCl_3$, PCl_3, PCl_5, P_2S_5, P_4S_3, selenium, P_2Se_5 and the like.

The final reaction is carried out under varying temperature conditions which can range from below zero to above 200° C. and higher. The temperature primarily depends on the phosphorizing, sulfurizing and/or sulfo-phosphorizing agents used to form the final product of this invention. For example, if phosphorus chloride is used the final reaction should be carried out at between —10° C. and zero degrees centigrade, while when sulfur halides are used the temperature ranges from zero to about 100° C. On the other hand, when sulfur or sodium polysulfide is used to form the final reaction product, the temperature reaction conditions generally vary between 115° C. and 200° C. and preferably between 125° C. and 170° C.; while if phosphorus sulfides are used the reaction temperature is generally in the range of from 100° C. to 180° C. In essence the sulfur, phosphorus and/or sulfo-phosphorus materials used to treat the initial reaction product govern the final reaction temperature. Reaction products of this invention can be added to various bases in amounts of from 0.01 to 10% and preferably from about 0.1 to 5%.

To more clearly illustrate the present invention, the following examples are presented.

EXAMPLE I

A. *Initial reaction product of topped, crude isophorone bottoms with ethylene diamine*

About two moles of topped, crude isphorone bottoms fraction containing at least eighteen carbon atoms in the molecule and about one mole of ethylene diamine were dispersed in benzene, and the entire mixture was heated at 75°–80° C. under a short distillation column bearing a phase separating stillhead. Water was drawn off overhead as lower layer in the benzene-water azeotrope. When water formation ceased, the water layer was titrated with standard acid in order to determine the amount of ethylene diamine that had distilled over. This quantity of the diamine was then added to the reaction vessel, and heating and stirring was resumed until water evolution again ceased. The reaction product was

freed from benzene, and small amounts of unchanged ethylene diamine by heating at about 100° C. in a stream of natural gas. The product obtained was a dark brown transparent mass, which was non-flowing at room temperature and on analysis contained 3.0(8) % nitrogen.

B. *Final reaction product obtained by treating I(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product I(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 130° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered, and the filtrate evaporated. The resultant product was a brittle, dark brown solid, which on analysis contained:

Sulfur, per cent wt.	9.8
Phosphorus, per cent wt.	7.8
Nitrogen, per cent wt.	1.6(7)

The product was oil soluble and imparted extreme pressure properties to base oil.

EXAMPLE II

A. *Initial reaction product of di-isobutyl ketone bottoms with ethylene diamine*

About two moles of diisobutyl ketone bottoms containing at least eighteen carbon atoms in the molecule and about one mole of ethylene diamine were dispersed in benzene, and the mixture reacted and processed under the same conditions as in Example I(A). The product obtained was a dark brown viscous liquid, which on analysis contains 4.4(4) % nitrogen.

B. *Final reaction product obtained by treating II(A) with phosphorus pentasulfide*

About one mole of the above initial reaction product II(A) and about four moles of P_2S_5 were admixed, and the mixture was reacted under constant agitation at a temperature of from about 110° to 150° C. The nitrogen, phosphorus and sulfur-containing reaction product was worked up as in Example I(B) and was a viscous, brown mass, which analyzed as follows:

Sulfur, per cent wt.	9.7
Phosphorus per cent weight.	7.6(5)
Nitrogen, per cent wt.	1.7

EXAMPLE III

A. *Initial reaction product of a saturated cyclic ketone fraction containing eighteen carbon atoms and obtained from mesityl oxide condensation with ethylene diamine*

About two moles of a C_{18} saturated cyclic ketone (derived from mesityl oxide condensation) and about one mole of ethylene diamine were reacted under substantially the same conditions as disclosed in Example I(A). The product obtained was a dark brown transparent mass, virtually non-flowing at room temperature and on analysis contained 3.3(3) % nitrogen.

B. *Final reaction product obtained by treating III(A) with sulfur monochloride*

To approximately two moles of the above reaction product, about one mole of sulfur monochloride was added dropwise at ice temperature, and the mixture was stirred vigorously and warmed

slowly to room temperature over a period of about twenty-four hours. The reaction product was then heated for about three hours on a steam bath and thereafter separately solvent treated, first with a non-aromatic hydrocarbon and then with methyl ethyl ketone as in Example I. The non-aromatic hydrocarbon portion was a dark brown viscous mass, and on analysis contained:

Carbon, per cent wt.	68.8(9)
Hydrogen, per cent wt.	9.9(7)
Nitrogen, per cent wt.	2.1(9)
Chlorine, per cent wt.	5.2(2)
Sulfur, per cent wt.	9.8(5)
Oxygen, per cent wt. (by difference)	3.8(8)

while the methyl ethyl ketone portion on analysis contained:

Carbon, per cent wt.	60.4(7)
Hydrogen, per cent wt.	8.5(0)
Nitrogen, per cent wt.	3.4(1)
Chlorine, per cent wt.	7.7(9)
Sulfur, per cent wt.	13.5
Oxygen, per cent wt. (by difference)	6.3(3)

Both the hydrocarbon- and ketone-soluble fractions were oil soluble and imparted good extreme pressure properties to base mineral oil.

EXAMPLE IV

About one mole of the initial reaction product of Example II and about four moles of sulfur monochloride were reacted under the conditions described in Example III(B) and the reaction product formed was solvent treated with the non-aromatic hydrocarbon as described above. The soluble portion of the reaction product was a dark brown, extremely viscous mass, which on analysis contained:

Nitrogen, per cent wt.	2.7(6)
Chlorine, per cent wt.	4.4(1)
Sulfur, per cent wt.	23.9

while the insoluble portion of the reaction product was a black, brittle solid, which on analysis contained:

Nitrogen, per cent wt.	2.1(3)
Chlorine, per cent wt.	4.6(2)
Sulfur, per cent wt.	36.7

EXAMPLE V

About one mole of the initial reaction product of Example I(A) was admixed with two moles of flower of sulfur, and the mixture was heated for about three hours with vigorous agitation at 125°–170° C. The reaction product was solvent treated with a light hydrocarbon, filtered and on removing the solvent a dark brown viscous material, which was non-flowing at room temperature, was obtained, which on analysis contained:

Nitrogen, per cent wt.	2.0(6)
Sulfur, per cent wt.	7.3(2)

EXAMPLE VI

About one mole of the initial reaction product of Example III(A) and four moles of flower of sulfur were admixed and reacted under the same conditions as described in Example V. The solvent-treated product was a dark brown, semi-solid mass, which on analysis contained:

Nitrogen, per cent wt.	2.3(0)
Sulfur, per cent wt.	4.4(8)

EXAMPLE VII

A. *Initial reaction product of topped, crude isophorone bottoms with propylene diamine*

About two moles of topped, crude isophorone bottoms fraction containing at least eighteen carbon atoms in the molecule and about one mole of propylene diamine were dispersed in benzene and reacted under the condition of Example I(A). The product obtained was a dark brown transparent mass, which was non-flowing at room temperature and on analysis contained over 3% nitrogen.

B. *Final reaction product obtained by treated VII(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product VII(A) about two moles of phosphorus pentasulfide was slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 130° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered and the filtrate evaporated. The resultant product on analysis contained sulfur, phosphorus and nitrogen in the molecule and was oil soluble.

EXAMPLE VIII

A. *Initial reaction product of diisobutyl ketone bottoms with di-o-tolyl ethylene diamine*

About two moles of diisobutyl ketone bottoms containing at least eighteen carbon atoms in the molecule and about one mole of di-o-toyly ethylene diamine were dispersed in benzene, and the mixture reacted and processed under the same conditions as in Example I(A). The product obtained was a dark brown, viscous liquid, which on analysis contained over 4% nitrogen.

B. *Final reaction product obtained by treating VIII(A) with phosphorus pentasulfide*

About one mole of the above initial reaction product VIII(A) and about four moles of P_2S_5 were admixed and the mixture was reacted under constant agitation at a temperature of from about 110° to 150° C. The nitrogen phosphorus- and sulfur-containing reaction product was worked up as in Example I(B) and was a viscous, brown mass, which on analysis contained sulfur, phosphorus and nitrogen in the molecule.

EXAMPLE IX

A. *Initial reaction product of benzophenone with ethylene diamine*

About two moles of benzophenone and about one mole of ethylene diamine were dispersed in benzene, and the entire mixture reacted and processed under the same condition as in Example I(A). The product obtained was a dark brown transparent mass, which was non-flowing at room temperature and on analysis contained over 3% nitrogen.

B. *Final reaction product obtained by treating IX(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product IX(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 150° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered, and the filtrate evaporated. The resultant product contained sulfur, phosphorus and nitrogen in the molecule and was oil soluble and possessed extreme pressure properties.

EXAMPLE X

A. *Reaction product of butyraldehyde with ethylene diamine*

About two moles of butyraldehyde and about one mole of ethylene diamine were dispersed in benzene, and the entire mixture reacted under the conditions of Example I(A). The product obtained was a dark brown, transparent mass, which was non-flowing at room temperature and on analysis contained 3% nitrogen.

B. *Final reaction product obtained by treating X(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product X(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 130° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered and the filtrate evaporated.

The product was oil soluble and possessed extreme pressure properties.

EXAMPLE XI

A. *Reaction product of lauryl benzaldehyde with ethylene diamine*

About two moles of lauryl benzaldehyde and about one mole of ethylene diamine were dispersed in benzene, and the entire mixture was heated under conditions of Example I(A). Water was drawn off overhead as lower layer in the benzene-water azeotrope. When water formation ceased, the water layer was titrated with standard acid in order to determine the amount of ethylene diamine that had distilled over. This quantity of the diamine was then added to the reaction vessel, and heating and stirring was resumed until water evolution again ceased. The reaction product was freed from benzene, and small amounts of unchanged ethylene diamine by heating at about 100° C. in a stream of natural gas. The product obtained was non-flowing at room temperature and on analysis contained over 3% nitrogen.

B. *Final reaction product obtained by treating XI(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product XI(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 150° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered and the filtrate evaporated.

The product was oil soluble and possessed extreme pressure properties.

EXAMPLE XII

A. *Reaction product of phenylacetaldehyde with ethylene diamine*

About two moles of phenylacetaldehyde and

about one mole of ethylene diamine were dispersed in benzene, and the entire mixture was reacted as in the above initial reactions. The product obtained on analysis contained over 3% nitrogen.

B. *Final reaction product obtained by treating XII(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product XII(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 150° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered and the filtrate evaporated and found to be oil soluble and possessed extreme pressure properties.

EXAMPLE XIII

A. *Reaction product of benzophenone with propylene diamine*

About two moles of benzophenone and about one mole of propylene diamine were dispersed in benzene, and the entire mixture was reacted as in the above initial reaction. The product obtained on analysis contained over 3% nitrogen.

B. *Final reaction product obtained by treating XIII(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product XIII(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 150° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233° F. The product was filtered, and the filtrate evaporated, and found to be oil soluble and possessed extreme pressure properties to said oil.

EXAMPLE XIV

A. *Reaction product of lauryl benzaldehyde with diethylene triamine*

About two moles of lauryl benzaldehyde fraction containing at least eighteen carbon atoms in the molecule and about one mole of diethylene triamine were dispersed in benzene, and the entire mixture was heated at 75–80° C. under a short distillation column bearing a phase-separating stillhead. Water was drawn off overhead as lower layer in the benzene-water azeotrope. When water formation ceased, the water layer was titrated with standard acid in order to determine the amount of diethylene triamine that had distilled over. This quantity of the triamine was then added to the reaction vessel, and heating and stirring was resumed until water evolution again ceased. The reaction product was freed from benzene, and small amounts of unchanged diethylene triamine by heating at about 100° C. in a stream of natural gas. The product obtained was a dark brown, transparent mass, which was non-flowing at room temperature and on analysis contained over 3% nitrogen.

B. *Final reaction product obtained by treating XIV(A) with phosphorus pentasulfide*

To approximately one mole of the above initial reaction product XIV(A) about two moles of phosphorus pentasulfide were slowly added, and the mixture was reacted under constant agitation for about three hours at a temperature of from about 125° to 130° C. The product was extracted with a mixture of equal volumes of methyl ethyl ketone and a non-aromatic hydrocarbon having a boiling range of between 164° F. and 233 F. The product was filtered and the filtrate evaporated, and found to be oil soluble and possess extreme pressure properties to said oil.

EXAMPLE XV

A. *Initial reaction product of benzophenone with ethylene diamine*

About two moles of a benzophenone and about one mole of ethylene diamine were reacted under substantially the same conditions as disclosed in Example I(A). The product obtained was a dark brown, transparent mass, virtually non-flowing at room temperature and on analysis contained 3.3(3) % nitrogen.

B. *Final reaction product obtained by treating XV(A) with sulfur monochloride*

To approximately two moles of the above reaction product about one mole of sulfur monochloride was added dropwise at ice temperature, and the mixture was stirred vigorously and warmed slowly to room temperature over a period of about twenty-four hours. The reaction product was then heated for about three hours on a steam bath and thereafter separately solvent-treated, first with a non-aromatic hydrocarbon and then with methyl ethyl ketone as in Example I.[1]

[1] The final product contained nitrogen and sulfur in the molecule and was oil soluble.

To illustrate the pronounced improvement obtained in lubricating compositions by the addition of small amounts of reaction products of this invention, compositions as indicated in the table below were subjected to Oxygen Absorption and Thrust Bearing Corrosion Tests as described in the National Petroleum News, September 17, 1941, pp. R–294–296, and the results as noted are self-explanatory.

Composition	Oxidation Test—Refined, undoped, lubricating oil, SUS at 210° F. of 64–67 was employed, oxidation at 150°C.—Catalyst: 1 cm.² Cu/g. oil		Thrust Bearing Corrosion—Estimated approximate critical corrosion temperature, ° C.
	sulfate ash (percent)	1,500 ml. oxygen time (hrs.)	
Mineral Oil	----------	5.9	115
Composition Ex. I	0.1	79.7	>160
Composition Ex. II	0.1	79.4	>160
Composition Ex. III	0.1	53.0	>160
Composition Ex. V	0.1	60.0	>160

In addition to the above properties the addition of reaction products of this invention to mineral lubricating oils inhibits lacquer formation in engines operating under the most adverse conditions. Also reaction products of this invention can be used as valuable constituents of heavy duty oils, motor oils, diesel oils, aviation oils, turbine oil, synthetic oils, dioctyl sebacate, alkylated naphthalene and the like because of their anti-corrosion, antioxidation, and antiwear properties. Besides their utility as lubricating oil additives, reaction products of this invention are useful as anti-oxidants for natural and synthetic rubber and other organic materials which are subject to

oxidation deterioration. The amount of additive used can be varied over 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 the bases.

Because of its synergistic effect the reaction product of this invention can be combined with other additives in lubricants, such as, blooming agents, pour point depressants or 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 those 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 disulfides, methylene bis alkylphenols; 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 diesters, including the corresponding thio phosphoric, arsonic and antimony acids; phosphonic and arsonic acids and the like.

Additional detergents are the alkaline earth phosphate diesters, including the thiophosphate diester; the alkaline earth diphenolates, specifically the calcium and barium salts of diphenol mono and poly sulfides.

Non-metallic detergents include compounds such as the phosphatides such as lecithin and cephalin, certain fatty oils and rapeseed oils, voltolized 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, penta methyl-phenol, 2,4 dimethyl-6-tertiary-butyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-di-tertiary-butyl-4-methyl-phenol, 2,4,6 tri-tertiary-butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl amine, phenyl-beta-naphthylamine, phenyl - alpha - naphthylamine, 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 or 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 tri-sulfides, 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 phosphorus 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 thiourea 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 reaction products of this invention.

The novel reaction products of this invention, in addition to being excellent lubricating oil improving agents, are potent oxidation inhibitors for fuels, natural and synthetic rubber, wax coating compositions and other organic materials.

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.

The invention claimed is:

1. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said lubricant against deterioration, of a reaction product obtained by reacting an organic carbonyl compound selected from the group consisting of ketones and aldehydes with an alkylene polyamine in the mole ratio of 2 to 6:1 to 3, respectively, and at a temperature of from 50 to 250° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a temperature ranging from below zero degree to about 175° C. and for a period of from 3 to 24 hours.

2. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said lubricant against deterioration, of a reaction product obtained by reacting a ketone with an alkylene polyamine in the mole ratio of 2 to 6:1 to 3, respectively, and at a temperature of from 50 to 250° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a tempera-

ture ranging from below zero degree to about 175° C. and for a period of from 3 to 24 hours.

3. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said lubricant against deterioration, of a reaction product obtained by reacting an aldehyde with an alkylene polyamine in the mole ratio of 2 to 6:1 to 3, respectively, and at a temperature of from 50 to 250° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a temperature ranging from below zero degree to about 175° C. and for a period of from 3 to 24 hours.

4. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting a cyclic ketone having at least twelve carbon atoms with alkylene polyamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a temperature ranging from below zero degree to about 175° C. and for a period of from 3 to 24 hours.

5. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting a cyclic ketone having at least twelve carbon atoms with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a temperature ranging from below zero degree to about 175° C and for a period of from 3 to 24 hours.

6. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting an isophorone bottoms fraction having at least twelve carbon atoms with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a temperature ranging from below zero degree to about 175° C. and for a period of from 3 to 24 hours.

7. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting diisobutyl ketone with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with an inorganic carbon-free sulfur compound selected from the group consisting of phosphorus sulfide, sulfur halide, and sulfur in the mole ratio of from 1:1 to 1:8, respectively, at a temperature ranging from below zero degree to about 175° C. and for a period of from 3 to 24 hours.

8. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting isophorone bottoms fraction having at least twelve carbon atoms with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with phosphorus sulfide in the mole ratio of from 1:1 to 1:4, respectively, and at a temperature of 125° to 175° C. and for a period of from 3 to 24 hours.

9. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting diisobutyl ketone with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with phosphorus sulfide in the mole ratio of from 1:1 to 1:4, respectively, and at a temperature of 125° to 170° C. and for a period of from 3 to 24 hours.

10. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting isophorone bottoms fraction having at least twelve carbon atoms with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with sulfur in the mole ratio of from 1:1 to 1:4, respectively, and at a temperature of 125° to 175° C. and for a period of from 3 to 24 hours.

11. A lubricant comprising a major amount of mineral oil and a minor amount, sufficient to stabilize said oil against deterioration, of a reaction product obtained by reacting isophorone bottoms fraction having at least twelve carbon atoms with ethylene diamine in the mole ratio of 2 to 6:1 to 3, respectively, at a temperature of from 80 to 180° C. until water formation ceases and treating the resulting reaction product with sulfur halide in the mole ratio of from 1:1 to 1:4, respectively, and at around room temperature and for a period of from 3 to 24 hours.

12. A lubricating composition of claim 4 wherein the cyclic ketone is isophorone bottoms having at least 12 carbon atoms and the alkylene polyamine is propylene diamine and the carbon-free sulfur compound is phosphorus pentasulfide.

13. A lubricating composition of claim 8 wherein the reactants, isophorone bottoms having at least twelve carbon atoms and ethylene diamine, are in the mole ratio of 2:1, respectively, and the phosphorus sulfide is phosphorus pentasulfide.

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