

## UNITED STATES PATENT OFFICE

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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. This invention also pertains to lubricants, such as mineral lubricating oils, synthetic lubricants of hydrocarbon or non-hydrocarbon origin and character, and the like, containing therein 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 to form corrosive bodies and sludge when used in modern engines and machines operating under ordinary conditions or at high speeds, elevated temperatures, heavy loads and other adverse conditions. 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 sticking of valves and piston rings in engines. In addition, presently known lubricants are generally 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 or even the complete overhauling of engines and machines, resulting in expensive loss of production and time.

In the case of the highest quality non-corrosive, stable lubricating oils, which have been highly refined for specific uses, or synthetic lubricants developed for specific or special uses, it has been observed that such oils or lubricants are generally high susceptible to oxidation and deterioration, becoming progressively 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 with various lubricants one, and in most cases more than one, additional agent, which additives have the effect or 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 readily attack these bearings but are inhibited or prevented from doing this by the formation of a corrosion-protective film formed on the bearing surface with the aid of additives. Additives have

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also been developed which 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, such as automotive and truck engines, aviation engines, high speed diesel engines and the like. Such 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 so that ringsticking, piston scuffing, scratching and wearing away of other engine parts and material reduction of engine efficiency are prevented or materially inhibited.

Other additives have been developed for the purpose of acting as detergents in lubricants in order to assist in the removal of soot or sludge, varnish and lacquer formed from deterioration of the oil when subjected to high operating temperatures. Detergents due to their cleaning 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 to withstand extreme pressures, disperse impurities, solubilize certain additives and the like.

The development of numerous additives has been due to the fact that most, if not all, additives are capable of functioning in substantially only one specific manner. Very few lubricant additives have the ability to improve 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 formations and, therefore, detrimental as an additive in another respect. Therefore, other additives are frequently required 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 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.



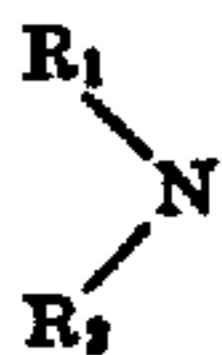
It is an object of this invention to improve the lubricating properties of various lubricating bases by the addition thereto of a minor amount of a multi-functional material. Another object of this invention is to add to compounded or doped lubricants a multi-functional material whereby a synergistic effect is produced, resulting in a product of accentuated and improved properties. Another object of this invention is to add to oleaginous materials, such as mineral oils, vegetable and animal oils, synthetic lubricants and the like, a multi-functional 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 multi-functional 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 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 novel multi-functional improving and enhancing additives for lubricating bases. Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention consists of features which will be hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain embodiments of the invention, these being illustrative of but a few variations in which the principle of the invention may be employed.

Broadly stated, this invention is directed to the use, in lubricants, of a reaction product obtained by treating with a phosphorizing reagent an organic five and/or six-membered heterocyclic ring compound represented by the general formula:



wherein Q is a five or six-membered heterocyclic carbon-containing ring in which the hetero atom or atoms are not solely oxygen, R' and R may be alkyl, aryl, alkaryl, aralkyl, alkoxy, aroxy radicals; Z is a polar radical, e. g. NH<sub>2</sub>, NO<sub>2</sub>, NO, N-NO,



CN, SCN, SO<sub>2</sub>, SO<sub>3</sub>H, —OSO<sub>3</sub>H, XR<sub>3</sub>, CXXR<sub>3</sub> where one or both of the X's may be O, S, Te and/or Se, R<sub>1</sub> and R<sub>2</sub> may be hydrogen, alkyl, aryl and/or cyclic radicals and R<sub>3</sub> is hydrogen, alkyl or aryl group; as well as the phosphates, phosphites, phosphonites, and the thioderivatives; m may be zero or an integer of 1 and 2; n may be zero or 1; and y may be an integer of 1, 2 or 3. Among the heterocyclic compounds which can be used to form reaction products of this invention are:

#### Thiophene and derivatives thereof

Thiophene, 2-methyl thiophene, 3-methyl thiophene, 2-acetyl thiophene, 2-acyloxyacetyl thiophene, lauryl thiophenes, dicyclo hexyl thiophenes, phenyl thiophenes, methyl phenyl thiophenes, benzothiophene, aminobenzothiophenes, dibenzothiophene, dihydroxy dibenzo thiophenes, diamino dibenzothiophene, chlorothiophene, di-

amylamino thiophene, dibutylaminothiophene, alkyl thiophene carboxylic acid, alkyl thiophene dicarboxylic acid, alkyl thiophene mono and disulfonic acid, 2-propyl thiophene-3,4 dicarboxylic acid, dithienyl methane, thienyl triphenyl methane, 2,2-di-2 thienyl-1,1,1 trichlorethane, 2,2 bis(2,5 - dichloro-3 - thienyl) - 1,1 dichloro ethylene, etc.

#### Pyrrole and derivatives thereof

Pyrrole, dimethyl pyrrole, N - (p - hydroxy phenyl) - 2,5 dimethyl pyrrole, 2-carboxy pyrrolidone-5,2,2,4 trimethyl 2-carboxy pyrrolidone-5,2-pyrrolidone, 2-pyrrolone, 1,2 diethyl pyrrole, 3-nitro pyrrole, 2-amino pyrrole, 2,4 dimethyl-3-carbethoxy-5-nitropyrrole, pyrrole dicarboxylic acid, 2,4 diphenyl pyrroline, 2 - (p - methoxy phenyl) - pyrroline, 2-phenyl-4-beta-naphthyl-pyrroline, 2,4 diphenyl pyrrole mono sulfonic acid, 5-nitroso-2,4 diphenyl pyrrole, isoamyl pyrrole, phenyl-pyrrole, methyl phenyl pyrrole, indole, indoleine, indole carboxylic acid, 2-methyl indole, carbazoles, nitrocarbazoles, poly pyrrol compounds and the like.

#### Azoles and their derivatives

The term "azole," as used herein, comprises the penta heterocyclic compounds containing at least two hetero atoms in the ring, one of which is nitrogen. Examples of such compounds are: pyrazole, dimethyl pyrazole, n-octyl pyrazole, phenyl pyrazole, phenyl dimethyl pyrazole, amino pyrazole, amino trimethyl pyrazole, phenyl ethoxy pyrazole, chloro pyrazole, pyrazole carboxylic acids, dithiodiazole, dithiozolidine benzothiazole, mercapto benzothiazole, benziminazole, methyl mercapto benzothiazole, phenyl mercapto benzothiazole, di(phenyl benzothiazyl) disulfide, thiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, amyl thiazole, dihexyl thiazole, phenyl thiazole, 4-propyl 2-amino thiazole, 5 phenyl 2-mercapto thiazole, 2-butyl 4,5 dihydroxy thiazole, amyl thiazoline, phenyl thiazoline, anthranil, octyl benzothiazole, benzothiazole thiobenzoic acid, mercapto naphthathiazole, hexyl naphthathiazole.

#### Diozines and related compounds

Amino quinolines, alpha, alpha-dipyridyl, hydroxy pyridyl ethers and thioethers, diazines, e. g. pyridazine, pyrimidine, pyrazine, cinnoline, phthalazine, quinoxaline, quinoxaline, phenazone, said diazines preferably containing at least one polar group and/or an alkyl group; methyl pyridazines, phenyl pyridazines, methyl phenyl pyridazines, methyl pyrimidines, dimethyl amino pyrimidines, chloro octyl pyrimidines, thiomorpholine, N-amylthiomorpholine, 2-methyl-peri-naphtho-m-thiazine, 2-(m-hydroxy phenyl) - peri-naphtho-m-thiazine, phenthiazine, N-amyl phenthiazine, dihydroxy phenthiazine, thialdine, etc.

#### Other heterocyclic-sulfur containing compounds

Trithioacetone, 1,3,5 trithiane, trithiobenzaldehyde, 1,4 - dithiane, thianthrene, dioctadecyl thianthrene, hydroxy thianthrene, thiomorpholine, and the like.

The above heterocyclic compounds and mixtures thereof are reacted with phosphorus and sulfur compounds and/or a phosphorizing agent at a temperature varying from room temperature to above 400° F. depending upon the base material being reacted and the phosphorizing agent selected to form the final reaction product.



Among the phosphorus or phosphorus and sulfur reagents which can be used to form reaction products of this invention are:  $P_2S_5$ ,  $P_4S_3$ ,  $P_2S_5$ ,  $P_2S_5$ ,  $P_2Te_3$ , P,  $P_2O_5$ ,  $POCl_3$ ,  $PCl_3$ ,  $PCl_5$ ,  $PSCl_3$ , etc. Also the heterocyclic compounds can be first reacted with a sulfurizing agent of the sulfur family, e. g., sulfur,  $SCl_2$ ,  $S_2Cl_2$ , sodium polysulfides, ammonium hydrosulfide-  $H_2S$ ,  $SeCl_2$ ,  $SeCl_4$  and the like and thereafter retreated with a phosphorizing agent, such as  $P_2O_5$ ,  $P_2S_5$ , phosphoric acids, etc., so that the final reaction product contains both sulfur and phosphorus. If desired, the reaction can be carried out in the reverse order, namely, the heterocyclic compound can be first treated with a phosphorizing agent, e. g.,  $P_2O_5$  and thereafter retreated with sulfur, ammonium hydrosulfide and hydrogen sulfide, metal polysulfides, sulfur chloride and the like. The reaction can be carried out in an inert diluent such as light hydrocarbons, or in a base oil to which the reaction product is intended to be added.

When the reaction products of this invention are produced in a two-step process, namely, by first sulfurizing and then phosphorizing the sulfurization temperature can vary from 200 to 400° F. and the phosphorization step can be carried out at the reflux temperature of the reactants. With phosphorus sulfides the reaction can be made to proceed at room temperature or higher temperatures depending upon the heterocyclic starting material thus treated.

The mole ratio of the heterocyclic compounds to the phosphorus and sulfur or phosphorizing reagent may vary over wide limits, such as 1 to 10:2 and preferably 1 to 3:0.5 to 4 moles of the above-mentioned reagents, respectively.

The preparation of the phosphorized or phosphorized-sulfurized heterocyclic compound reaction product of this invention is relatively simple and requires no elaborate or special equipment. The reactants may be simply admixed, if desired, in an inert diluent and in an inert atmosphere in a suitable reaction vessel and refluxed for from 2 to 8 hours, or the reaction temperature may be much higher by carrying out the reaction under pressure in a closed system. At the completion of the reaction the reaction product containing phosphorus or phosphorus and sulfur in the molecule may be extracted with a suitable solvent such as a non-aromatic hydrocarbon or ethyl acetate. The reaction product thus produced may be added to various lubricants in order to improve their lubricating properties or to fuels, greases and other compositions.

If desired, the above reaction product can be neutralized and the neutralized product used as an oil additive. The neutralization of reaction products of this invention may be attained by dispersing or dissolving the reaction product in a larger quantity of a suitable hydrocarbon oil and to this mixture a calculated amount of lime or any other desired neutralizing agent may be added and the mixture agitated at an elevated temperature of about 250° F. for about 2 or more hours. The neutralized reaction product is then filtered to recover the product from the oil and may be refiltered to remove excess lime and other impurities.

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

### Example I

Approximately one mole proportion of thiophene was refluxed with about 0.5 mole proportion of  $P_2S_5$ . The reaction mixture reacted slowly forming a brown mush-like material, containing both phosphorus and sulfur in the molecule. The reaction product was extracted by means of ethyl acetate and the resultant product therefrom gave a very viscous brown liquid which on analysis contained:

Per cent sulfur	20.0-21.2
Per cent phosphorus	18.3-18.6

The reaction product was soluble in mineral oil.

### Example II.— $P_2S_5$ treated reaction product of thiophene with ammonium-hydrosulfide and hydrogen sulfide

(a) *Initial reaction product.*—Isopropyl alcohol was saturated with dry ammonia followed by dry hydrogen sulfide. To this product thiophene in isopropyl alcohol was added and the mixture saturated with hydrogen sulfide. The mixture was allowed to stand in an enclosed flask for a week. The reaction mixture was filtered and the alcohol removed by evaporation. The residue was dissolved in a hydrocarbon solvent and thereafter the solvent was removed leaving behind the initial reaction product of this invention.

(b) *Final reaction product.*—To approximately one mole of the initial reaction product about 0.5 mole of  $P_2S_5$  was added and the reaction was allowed to proceed as in Example I. The final reaction product contained both sulfur and phosphorus in the molecule with the sulfur being present in a predominant amount. The reaction product was oil soluble.

### Example III

Approximately in equal mole ratio, alpha, alpha, dipyrindyl and  $P_2S_5$  were admixed and reacted at a temperature ranging from 250° to 400° F. until a homogeneous product was obtained which contained both phosphorus and sulfur in addition to the nitrogen already present in the molecule. The product was oil soluble.

### Example IV

Approximately one mole of benzothiazole was refluxed with about 0.5 mole of  $P_2S_5$ . The reaction mixture reacted slowly forming a material containing phosphorus in the molecule. The product was oil soluble.

Other phosphorized-sulfurized and/or phosphorized heterocyclic reaction products of this invention which are formed in the manner indicated above and which represent working examples of this invention are:

- Methyl thiophene treated with phosphorus pentasulfide
- Lauryl thiophene treated with phosphorus pentasulfide
- Dicyclohexyl thiophene treated with phosphorus pentasulfide
- Benzothiophene treated with phosphorus pentasulfide
- Dihydroxy dibenzothiophene treated with phosphorus pentasulfide
- Alkyl thiophene carboxylic acid treated with phosphorus pentasulfide
- Diamino dibenzothiophene treated with phosphorus pentasulfide



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Oleyl thiophene treated with phosphorus pentasulfide

Benzothiophene treated with phosphorus pentoxide

Thiophene treated with phosphorus oxychloride

Thiophene treated with phosphorus pentoxide

Thiophene treated with sodium pentasulfide and phosphorus pentasulfide

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Ca salt of thiophene sulfonic acid treated with phosphorus sulfide

Ca salt of wax substituted thiophene sulfonic acid treated with phosphorus sulfide

All of the above working examples are suitable oil improving agents.

Other compositions of this invention are illustrated in the table below:

Components <sup>1</sup>	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
<b>Primary Additives:</b>																				
P <sub>2</sub> S <sub>5</sub> treated thiophene.....	x							x			x			x		x	x			
P <sub>2</sub> S <sub>5</sub> treated alpha, alpha dipyridyl.....									x											
P <sub>2</sub> S <sub>5</sub> treated benzothiazole.....		x																		
P <sub>2</sub> O <sub>5</sub> treated thiophene.....										x						x				
P <sub>2</sub> O <sub>5</sub> treated N-amyl thiomorpholine.....				x																
P <sub>2</sub> S <sub>5</sub> treated N-amyl phenthiazine.....							x													
POCl <sub>3</sub> treated thiophene.....			x															x		
P <sub>2</sub> S <sub>5</sub> +SCl <sub>2</sub> treated hydroxy pyrrole.....												x								x
P <sub>2</sub> O <sub>5</sub> +S treated benzothiophene.....						x														x
P <sub>2</sub> S <sub>5</sub> treated Ca salt of thiophene sulfonic acid.....					x								x						x	
<b>Secondary Additives:</b>																				
Ca petroleum sulfonate.....	x	x		x					x	x	x		x			x		x		x
Ca octyl phenol-formaldehyde condensation product.....		x			x					x					x				x	
Phenyl-alpha-naphthylamine.....				x											x		x			
Triethanolamine oleate.....			x																	
Ba alkyl phenol sulfide.....						x	x					x						x		
Sulfurized oleic acid.....																x	x			
Dibutyl trichloromethane phosphonate.....											x									
2,4 dibutyl-6-methyl phenol.....								x												
Zn dibutyl dithiocarbamate.....			x		x									x						
<b>Base:</b>																				
Mineral oil.....	x	x		x	x	x	x			x	x			x	x	x	x			
Fuel oil.....			x									x	x					x	x	
Diethyl sebacate.....								x	x											x

<sup>1</sup> The additives in the above composition comprise less than 5% of the total composition of which the primary additive is about 1% and the remainder being the secondary additive. Generally suitable compositions are obtained when the sum total of the additives does not exceed 2% by weight.

Benzothiophene treated with sodium pentasulfide and phosphorus pentasulfide

Pyrrole treated with phosphorus pentasulfide

Isoamyl pyrrole treated with phosphorus pentasulfide

Hydroxy pyrrole treated with phosphorus pentasulfide

Pyrrole treated with phosphorus pentaoxide

Carbazole treated with phosphorus pentaoxide

Carbazole treated with phosphorus pentasulfide

Carbazole treated with sulfur and phosphorus pentasulfide

Pyrazole treated with phosphorus pentasulfide

Phenyl ethoxy pyrazole treated with phosphorus pentasulfide

Mercapto benzothiazole treated with phosphorus pentasulfide

Mercapto benzothiazole treated with phosphorus oxychloride

Hydroxy pyridyl ether treated with phosphorus pentasulfide

Hydroxy pyridyl ether treated with phosphorus pentoxide

N-amyl thiomorpholine treated with phosphorus pentoxide

N-amyl thiomorpholine treated with phosphorus pentasulfide

N-amyl phenthiazine treated with phosphorus pentasulfide

N-amyl phenthiazine treated with ammonium hydrosulfide, hydrogen sulfide and phosphorus pentasulfide

Mercaptobenzothiazole treated with sulfur chloride and phosphorus pentasulfide

Benzothiophene treated with sulfur and phosphorus pentoxide

Hydroxy pyrrole treated with phosphorus sulfide and sulfur chloride

Oleyl thiophene treated with phosphorus sulfide and selenium chloride

The base for additives of this invention can be any natural or synthetic material having lubricating properties. Thus, the base may be a hydrocarbon oil of wide viscosity range, e. g. 100 SUS at 100° F. to 100 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like, and/or with synthetic lubricants such as polymerized olefins, copolymers of alkylene glycols and oxides; organic esters, e. g. 2-ethylhexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran, polyalkyl silicone polymers, e. g. dimethyl silicone polymer and the like. If desired, the synthetic lubricants may be used as the sole base lubricant or admixed with fixed oils and their derivatives.

To illustrate the pronounced improvement obtained with lubricating compositions containing reaction products of this invention the following test data are given:

TABLE I.—OXIDATION STABILITY DETERMINATION

A refined undoped lubricating oil, 64–67 SUS at 210° F. was employed, temperature, 150° C.

[Catalyst: 1 cm.<sup>3</sup> Cu/gm. oil + 1,500 ml. oxygen]

Additives	Amount, percent	Time, hours
None.....		5.9
P <sub>2</sub> S <sub>5</sub> treated thiophene.....	1	24.2
P <sub>2</sub> S <sub>5</sub> treated alpha, alpha dipyridyl.....	1	30
P <sub>2</sub> S <sub>5</sub> treated benzothiazole.....	1	35

The doped and undoped oils were further tested in the thrust bearing corrosion machine (described in the National Petroleum News, September 17, 1941, pp. R-294–296) and the critical cor-



rosion temperature of the oils tested was estimated. The results were as follows:

TABLE II.—TESTS IN THRUST BEARING CORROSION MACHINE

[Fixed conditions Cu-Pb bearings, 20 hours' duration, 125 p. s. i. Thrust 2,400 R. P. M. A refined, undoped, lubricating oil of 64-67 S. V. at 210° F. was employed.]

Additive	Amount, percent weight	Estimated approximately critical corrosion temperature ° C.
None.....		115
P <sub>2</sub> S <sub>5</sub> treated thiophene.....	1	170

Compositions 1, 3, 6, 12 and 15, identified in the table above and similar compositions 1', 3', 6', 12' and 15', in which the primary additive has been omitted were subjected to the copper strip test. This test comprises in suspending in a vessel containing the test oil a clean copper strip. The oil in the vessel is suspended over a vigorously boiling vessel of water for 3 hours. The copper strip is then removed and its condition observed. If the strip is discolored by the oil it is a sign of failure. The results were as follows:

Composition	Results
Straight mineral oil.....	Failed.
Composition 1'.....	Do.
Composition 3'.....	Do.
Composition 6'.....	Do.
Composition 12'.....	Do.
Composition 15'.....	Do.
Composition 1.....	Passed.
Composition 3.....	Do.
Composition 6.....	Do.
Composition 12.....	Do.
Composition 15.....	Do.

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 oils, synthetic oils, greases, fuels and the like, because of their anti-corrosion, anti-oxidation, and anti-wear 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. They can be used in fuels, hydraulic fluids, rubber compositions, insecticidal compositions, degreasing compositions, greases, etc. 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 base lubricants.

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, oiliness agents, anti-foaming 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, 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 monoesters, aromatic keto acids, aromatic ether acids, diphenols as di-(alkylphenol) 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 monoesters; phosphoric arsenic and antimonie acid mono and diesters, including the corresponding thiophosphoric arsenic and antimonie 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 polysulfides.

Non-metallic detergents include compounds such as the phosphatides such as lecithin and cephalin, certain fatty oils as 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 0.25% to 0.2% sulfate ash. Also alkaline metal salts of alkyl phenol-aldehyde condensation reaction products are excellent detergents.

Anti-oxidants 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-tritertiary butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl - phenylene diamine, diphenylamine phenyl - beta - naphthylamine, phenyl - alpha-naphthylamine, dinaphthylamine.

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.



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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 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.

We claim as our invention:

1. An oleaginous base having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure properties to said base, a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with a heterocyclic ring compound selected from the group consisting of thiophene, benzothiazole, and alpha, alpha-dipyridyl compounds in the mole ratio of 1:5 to 2:1, respectively.

2. An oleaginous base having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure properties to said base, a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with thiophene in the mole ratio of 1:5 to 2:1, respectively.

3. An oleaginous base having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure properties to said base, a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with benzothiazole in the mole ratio of 1:5 to 2:1, respectively.

4. An oleaginous base having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure properties to said base, a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with alpha, alpha-dipyridyl in the mole ratio of 1:5 to 2:1, respectively.

5. A mineral oil having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure properties to said oil, a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with a heterocyclic ring compound selected from the group consisting of thiophene, benzothiazole, and alpha, alpha-dipyridyl compounds in the mole ratio of 1:5 to 2:1, respectively.

6. A mineral lubricating oil having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure to said oil of a metal-free reaction product of phosphorus pentasulfide and alpha, alpha-dipyridyl prepared by reacting said materials at reflux temperature and in the mole ratio of 2:1, respectively.

7. A mineral lubricating oil having incorporated therein an amount sufficient to stabilize against

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deterioration and impart extreme pressure to said oil of a metal-free reaction product obtained by reacting thiophene with a phosphorus sulfide at reflux temperature and in the mole ratio of about 1:2, respectively.

8. A mineral lubricating oil having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure to said oil of a metal-free reaction product obtained by reacting benzothiazole with a phosphorus sulfide at reflux temperature and in the mole ratio of about 1:2, respectively.

9. A mineral lubricating oil having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure to said oil of a metal-free reaction product of phosphorus pentasulfide and thiophene prepared by reacting said materials at reflux temperature and in the mole ratio of 2:1, respectively.

10. A mineral lubricating oil having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure to said oil of a phosphorus pentasulfide and benzothiazole prepared by reacting said materials at reflux temperature and in the mole ratio of 2:1, respectively.

11. As a new product a metal-free phosphorized-sulfurized thiophene prepared by reacting thiophene with a phosphorus sulfide at reflux temperature and in the mole ratio of about 1:2, respectively.

12. As a new product a metal-free phosphorized sulfurized benzothiazole prepared by reacting benzothiazole with a phosphorus sulfide at reflux temperature and in the mole ratio of about 1:2, respectively.

13. As a new compound a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with a heterocyclic compound selected from the group consisting of thiophene, benzothiazole, and alpha, alpha-dipyridyl compounds in the mole ratio of 1:5 to 2:1, respectively.

14. An oleaginous base having incorporated therein an amount sufficient to stabilize against deterioration and impart extreme pressure properties to said base, a metal-free reaction product obtained by reacting at reflux temperature a phosphorus sulfide with alpha, alpha-dipyridyl in the mole ratio of 1:5 to 2:1, respectively.

15. As a new product a metal-free phosphorized-sulfurized alpha, alpha-dipyridyl prepared by reacting alpha, alpha-dipyridyl with a phosphorus sulfide at reflux temperature and in the mole ratio of about 1:2, respectively.

GEORGE G. PRITZKER.  
DAVID E. ADELSON.

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**Certificate of Correction**

Patented January 6, 1953

Patent No. 2,624,707

**GEORGE G. PRITZKER ET AL.**

It is hereby certified that it appears that mistakes have been made in the above numbered patent and a showing has been made that such mistakes occurred in good faith and were not the fault of the Patent Office, said mistakes requiring correction as follows:

Column 11, line 65, column 12, lines 1, 8, 15, and 22-23, after "extreme pressure" insert *properties*.

The said patent should be read as though corrected as specified.

Signed and sealed this 23rd day of June, A. D. 1953.

[SEAL]

THOMAS F. MURPHY,  
*Assistant Commissioner of Patents.*



# Certificate of Correction

Patented January 6, 1953

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