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LUBRICATING OIL COMPOSITION

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13 Claims. (Cl. 252—49.8)

This invention relates to improved lubricating compositions and a class of organic compounds particularly adapted to improve the properties of liquids and/or solids which are suitable for use as fluid lubricants, greases, coolants, rust- and/or corrosion-inhibiting compositions, coating compositions, and the like. More particularly, this invention pertains to lubricants such as natural or synthetic lubricants, emulsions, aqueous solutions, and organic and/or inorganic materials which can be adapted for lubricating purposes, which lubricants possess improved chaarcteristics due to the addition thereto of a class of multifunctional organic compounds capable of stabilizing and imparting extreme pressure, anti-wear, and anti-fouling properties to lubricating compositions, 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, low or elevated temperatures, under heavy loads and/or 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 as well as sticking of valves and piston rings in engine. Many lubricants are generally incapable of maintaining a continuous lubricating film between movable parts, which results in a 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 highly 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 at least one addition agent, which additive has the effect or property of inhibiting deterioration of lubricants and imparting to them certain beneficial properties. Thus, additives have been specifically designed which have the property of inhibiting the corrosion of alloyed bearings, such as copper-lead, cadmium-silver, and like bearings developed for automotive, diesel, and aircraft engines, due to acidic oxidation or decomposition components formed in lubricants during use. The additive inhibits or prevents such attack by the formation of a protective film on the bearing surface. Additives have also been developed which possess the property of modifying the carbonaceous materials formed by deterioration of lubricants on piston rods, rings, valves, and other metal parts in internal combustion engines, 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 decreased so that the ringsticking, piston scuffing, scratching, and wearing away of engine parts 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 peptization of soot, sludge, varnish, or lacquer formed from deterioration of the oil when subjected to high operating temperatures. Detergents, due to their cleaning and dispersing action, prevent the deposition of these deleterious materials and assist in their removal. Anti-wear additives have the property of reducing the wear of movable metal parts.

The use of a plurality of additives in a single lubricant has been due to the fact that most such additives are capable of functioning in substantially only one specific manner. Thus, a good antioxidant may 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 an additive possesses very good properties in one respect, but is detrimental as an additive in another respect. Therefore a second additive may be required to counteract a detrimental effect of an otherwise desirable additive. The combination of additives in lubricants wherein each additive exerts its desired influence without adversely interfering with the functions of other additives is a difficult goal to attain.

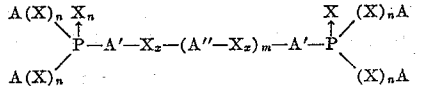
Additives which are used in lubricants for industrial purposes such as in cutting, drawing, quenching, and rolling operations must impart to said lubricants film strength, corrosion-inhibiting, and detergent properties, as well as aid the base lubricant to cool and lubricate the base metal or other surfaces under the most adverse conditions of lubrication and the like.

It is a principal object of this invention to provide improved lubricating compositions comprising various fluid lubricating media and a multifunctional additive material. Another object of this invention is to add to compounded or doped lubricants a multifunctional 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, organic and inorganic liquid lubricants, including mineral lubricating oils, synthetic lubricants of various types, and the like, a multifunctional material so as to inhibit oxidation, at both low and high temperatures, and corrosion and also 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 multifunctional 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 multifunctional material which inhibits wear, scuffing, scratching, and other damage normally caused to engine parts. Also, it is an object of this invention to improve the lubricating and cooling properties of base materials adapted for use in cutting, quenching, drawing, and rolling operations by addition to said base materials a multifunctional material of this invention. Furthermore, it is an object of this invention to provide novel multifunctional lubricating agents, which may be used as lubricants, per se, as well as for improving and enhancing the properties of lubricating base stocks. 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.

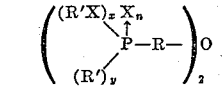
Broadly stated, this invention is concerned with lubricating compositions comprising a class of polyphospho organic compounds having the general formula:



I

wherein each A can be independently selected from the same or different hydrocarbyl radicals or polar-substituted hydrocarbyl radicals, preferably having at least three (3) carbon atoms, wherein the polar group can be amino, nitro, cyano, sulfo, keto, carboxyl, hydroxyl, thiol, etc., and wherein the P—A′ group contains the P—C linkage; X can be the same or different divalent radicals —O—, —S—, —Se—, —Te—, and —NA‴— and preferably are selected from the group having elements of the chalkogen family of which those with atomic numbers of 8 and 16, namely, oxygen and sulfur are preferred; A′ can be the same or different, but preferably the same, polar substituted or unsubstituted divalent hydrocarbyl radicals (hydrocarbylene or hydrocarbylidene), the polar group being selected from those which may be present in A, A″ can be the same as A′ and preferably is an alkylene, arylene, or cycloalkylene radical, A‴ can be hydrogen or the same as A, *n* is zero or 1, *m* can be zero or an integer varying from 1 to about 20, and *x* is an integer of 1 or 2. By a hydrocarbyl radical is meant a radical obtained by removing one or more hydrogen atoms from the same or different carbon atoms of a hydrocarbon.

A preferred class of compounds for use in the practice of the invention, and coming within the broader class defined before, is the class which is representable by the general formula



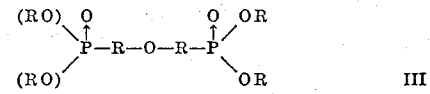
II

wherein each R′ is selected independently from functionally saturated organic radicals, preferably functionally saturated hydrocarbyl radicals, i. e., radicals devoid of olefinic or acetylenic unsaturation, but including aromatic radicals; R is a divalent organic radical containing essentially a hydrocarbon or oxahydrocarbon radical connecting the phosphorus atom (P) and the oxygen atom (O) by an unbroken chain of carbon atoms or an unbroken chain of oxygen and carbon atoms, R being joined directly to P by a P—C linkage, wherein the C atom thereof is joined by three separate single valences to three different atoms or groups of atoms, and R is joined to the oxygen atom (O) by a C—O linkage. Except for the foregoing limitations, R can be a corresponding substituted hydrocarbon or substituted oxahydrocarbon radical consisting essentially of hydrocarbon or oxahydrocarbon bearing minor proportions of substituents such as halogen, oxy, hydroxy, amino, hydrocarbyloxy, nitro, sulfonate, and the like atoms or groups. The term "oxahydrocarbon" is meant to include polyoxahydrocarbons and is illustrated by such divalent radicals as methyleneoxymethylene (2-oxapropylene-1,3), ethyleneoxyethylene (3-oxapentylene-1,5); ethyleneoxyethyleneoxyethylene (3,6-dioxaoctylene-1,8); (polyethyleneoxy) ethylene; propyleneoxy propylene (2,5-dimethyl-3-oxapentylene-1,5); trimethylene-oxytrimethylene (4-oxaheptylene-1,7). The R′ radicals preferably should have a carbon content of from one to about 12 carbon atoms each and the R preferably should have a chain length of from one to about 15 atoms, including oxygen atoms in an oxahydrocarbon chain. Compounds as represented by Formula II wherein the R′ radicals as defined have at least 3 carbon atoms are particularly preferred as additive agents in compositions of this invention and furthermore constitute a new class of compounds having valuable properties as noted hereinafter.

Some illustrative compounds which are representative of the class defined by Formula II and which are suitable for use in the practice of the invention are:

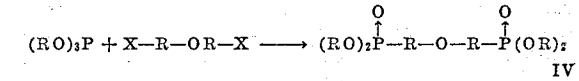
Bis[(diamyl phosphono)methyl]ether,
Bis[(dilauryl phosphono)ethyl]ether,
Bis[(dibutyl-5-phosphono)3-oxapentyl]ether,
Bis[(dipropyl-5-phosphono)1,4 - dimethyl-3-oxapentyl]-ether,
Bis[(dihexyl-8-phosphono)3,6-dioxaoctyl]ether,
Bis[(butyl benzenephosphinico)ethyl]ether,
Bis[-2(butyl p-chlorobenzenephosphinico)ethyl]ether,
Bis[(diamyl 3-phosphono)2-oxa-propyl]ether,
Bis[(dibutyl 3-phosphono)2-hydroxy-propyl]ether.

The polyphospho organic compounds of this invention can be prepared in a number of ways. For example, a bis(dihydrocarbyl phosphonohydrocarbyl) ether, which can be represented by the general formula



III

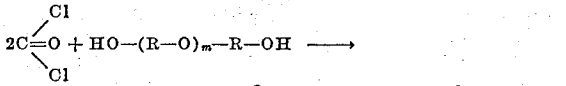
can be prepared by reacting a trihydrocarbyl phosphite with bis(halohydrocarbyl) ether; bis(dihydrocarbyl phosphonoöxomethyl) ether. The reaction is representable as follows:



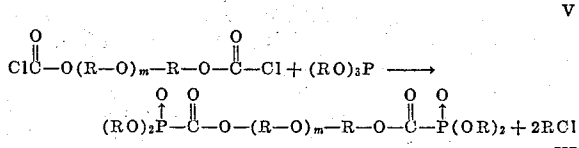
IV

wherein the R's are hydrocarbyl radicals.

Another method of preparing compounds of the class as represented by Formula V is by reacting polyalkylene glycol with phosgene to form the bis(chloroformyloxy poly-alkyleneoxy) alkylene and thereafter treating the resultant product with an organic phosphite. The reaction proceeds as follows:



V



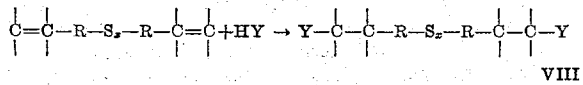
VI

wherein the R's are the same as in Formula III and *m* is the same as in Formula I.

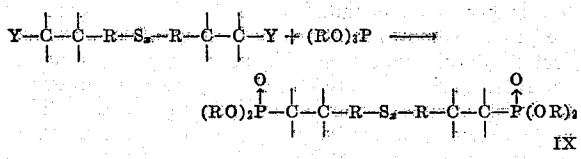
To illustrate the present invention further, the following examples are presented, with the understanding, however, that various modifications can be resorted to without departing from the spirit and scope of the invention. The thioether and amino derivatives of compounds under discussion can be prepared by hydrobromination of diallyl sulfide or diallyl amine and reacting these brominated materials with an organic phosphite. The peroxygen or polychalkogen analogs of polyphospho compounds of this invention can be prepared by reacting, for example, sodium polysulfide with a halo unsaturated hydrocarbon compound, hydrohalogenating the resulting polysulfide, and thereafter treating said halo polysulfide with an organic phosphite. The reaction proceeds as follows:



VII



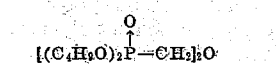
VIII



IX

(R is a hydrocarbyl radical, Y is a halogen atom, and S_x represents mono-, di-, tri-, and other poly-sulfides.)

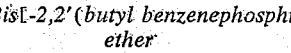
Example I.—Bis[(dibutyl phosphono)methyl]ether



A mixture of 100 grams (0.87 mole) of sym-dichloromethyl ether and 500 grams (2.00 moles) of redistilled tributyl phosphite were heated and the butyl chloride formed was continuously removed by means of a fractionating column. The reaction started when the kettle temperature was about 140° C. and was completed when the temperature reached about 202° C. The residue was topped to 200° C. kettle temperature at 1 mm. pressure to remove unreacted tributyl phosphite. The crude product was agitated with 1M KOH at 50° C., washed with water, dried and distilled in a falling-film molecular still at 155° C. under 10^{-5} mm. pressure. This product, bis[(dibutyl phosphono)methyl]ether had the following properties:

	Found	Calc. or Theory
Percent C	50.8	50.2
Percent H	9.5	9.3
Percent P	14.1	14.1
Percent N	0	0
Br. No.	0	0
Acid No.	1.5	0
Mol. wt.	430	430
B. P. at 1 mm. ° C.	200–215	
Visc. (cs.) at 100° F.	11.92	
V. I. (D and D)	104	
Pour Point, °F.	<−65	

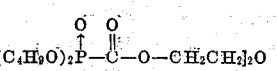
Example II.—Bis[-2,2'(butyl benzenephosphinico)ethyl]-ether



Into a flask containing 305 grams (1.2 moles) of dibutyl benzenephosphonite heated at 165° C. was slowly added 116 grams (0.5 mole) of 2,2'-dibromodiethyl ether. The butyl bromide formed was removed and the reaction mixture was stabilized by distilling off materials boiling below 100° C. under 1 to 2 mm. Hg pressure and then distilled in a molecular still. The purified bis[-2,2'(butyl benzenephosphinico)ethyl]ether had the following properties:

	Found	Calc. or Theory
Percent P	13.9	13.1
Mol. wt.	450	466
Acid No.	.07	

Example III.—Bis[(dibutyl phosphono)formoxyethyl]-ether



About 120 grams (0.518 mole) of dichloroformate of ethylene glycol, obtained by the interaction of ethylene glycol and phosgene, was reacted with 325 grams (1.30 moles) of tributyl phosphite at reflux temperature and thereafter the reaction product was topped by distilling off materials boiling below 160° C. at 1 mm. Hg pressure. The residue had a refractive index of $n_D^{20}=1.4508$ and had the following properties:

	Found	Calc. or Theory
Percent C	48.3	48.3
Percent H	8.1	8.05
Percent Cl	0.3(5)	0.0
Percent P	11.2	11.35
Mol. wt.	544	546
V. I.	141	

Example IV.—Bis[(diisopropyl phosphono)ethyl]ether

This product was produced by heating for about 20 hours at 125° C. a solution composed of abouf 500 grams of triisopropyl phosphite and about 100 grams of sym-dichloroethyl ether. The tetraester was recoverable by fractional distillation.

Example V.—Bis[2-(di-n-butyl phosphono)ethyl]ether

Bis[2-(di-n-butyl phosphono)ethyl]ether was prepared by heating 3 moles of tributyl phosphite to 160° C. at 40 mm. pressure and slowly adding thereto about 1 mol of bis(2-bromoethyl)ether. The reaction mixture was heated until no further butyl bromide was liberated and thereafter stabilized by heating to 156° C. at 5.0 mm. pressure. The crude product was purified by heating under reflux with 1.2 N sodium hydroxide; the aqueous phase was removed and the product water-washed and thereafter dried by heating at 150° C. and 5 mm. pressure.

The purified bis[2-(di-n-butyl phosphono)ethyl]ether had the following properties:

Acid Neut. No.	0.09
Pour point, ° F.	<−65
Visc., 100° F. (cs.)	13.31
Viscosity index	113

Example VI.—Bis[4-(di-n-butyl phosphono)butyl]ether

Bis[4-(di-n-butyl phosphono)butyl]ether was prepared substantially in accordance with the procedure set forth in Example V using 3 moles of tributyl phosphite and 1 mole of dichlorobutyl ether, said ether compound being prepared in accordance with the method of Alexander and Schniepp; J. Am. Chem. Soc., 70, 1839 (1948). The dichlorobutyl ether and tributyl phosphite were very slowly reacted below 250° C. and then rapidly heated to 265°–275° C.

The purified product had the following properties:

Acid Neut. No.	0.04
Pour point, ° F.	−80
Visc., 100° F. (cs.)	20.60
Viscosity index	140

Example VII.—Bis[2-(dinonyl phosphono)ethyl]ether

This product was prepared by reacting tri(nonyl) phosphite with bis(2-bromoethyl)ether at 180°–200° C. and 17 mm. pressure. The product had the following properties:

Acid Neut. No.	0.10
Pour point, ° F.	−30
Visc., 100° F. (cs.)	64.82
Viscosity index	117

Other examples of polyphospho ether compounds of this invention for use in the practice of the invention are:

Bis[(dicyclohexyl phosphono)ethyl]ether
Bis[(diisopropyl phosphono)methyl]ether
Bis[(diisopropyl phosphono)ethyl]ether
Bis[(dibenzyl phosphono)methyl]thio ether
Bis[(dibutyl phosphono)methyl]ether
Bis[(dicresyl phosphono)methyl]ether
Bis[(dioctyl phosphono)ethyl]ether
Bis[(dihexyl phosphono)ethyl]ether
Bis[(butyl benzenephosphino)methyl]ether

Bis[(butyl chlorobenzenephosphino)methyl]ether
Bis[(butyl trichloromethanephosphino)methyl]ether
Bis[(dibutyl phosphono)formyl]oxide
Bis[(dibutyl 1-phosphono)phthaloyl]oxide
Bis[(dibutyl 1-phosphono)succinyl]oxide
Bis[(dioctyl 2-phosphono)-2-aminoethyl]ether
Bis[(dibutyl phosphono)ethoxyethyl]ether
Bis[(dibutyl phosphono)ethoxy]ethane
Bis[(diisopropyl 2-phosphono)-2-methylolethyl]ether
Bis[(dibenzyl 2-phosphono)-2-methylolethyl]ether
Bis[(benzyl butyl phosphono)methyl]ether
Bis[(phenyl butyl phosphono)methyl]ether
Bis[(dibutyl phosphono)propyl]amine
Bis[(dihexyl 2-phosphono)-2-chloroethyl]ether
Bis[2-(di sec. butyl phosphono)ethyl]ether
Bis[(dibutyl phosphono)n-propyl]dithio ether

Vehicles to which the phosphorus-containing substances of this invention may be added, for purposes of improving the lubricating qualities of said vehicles or for purposes of producing corrosion-preventing compositions and the like, may be divided into several groups.

The vehicles should preferably be substantially neutral, although they may be weakly acidic or weakly basic, preferably having dissociation contants not above about 10^{-8}. Both polar and non-polar vehicles may be employed. Among the former are water, monohydric alcohols, such as propyl, isopropyl, butyl, amyl, hexyl, cyclohexyl, heptyl, methylcyclohexyl, octyl, decyl, lauryl, myristyl, cetyl, stearyl, oleyl, allyl, benzyl, etc., alcohols, polyhydric alcohols, such as ethylene glycol, propylene glycol, butylene glycol, cetene glycol, glycerol, methyl glycerol, 2-methylpentane-2,4-diol, trimethylene glycol, tetramethylene glycol, etc.; phenols and various alkyl phenols and thiophenols; ketones, such as acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl butyl ketone, dipropyl ketone, cyclohexanone, and higher ketones; keto alcohols; ethers such as diethyl ether, diisopropyl ether, B,B'-dichlorodiethyl ether, diphenyl oxide, chlorinated diphenyl oxide, diethylene glycol, triethylene glycol, mono- and di-butyl ethers of ethylene glycol and diethylene glycol, and the like; neutral esters of carboxylic and other acids such as ethyl, propyl, butyl, amyl, octyl, stearyl, oleyl, phenyl, cresyl, and higher hydrocarbyl acetates, propionates, butyrates, lactates, laurates, myristates, palmitates, stearates, oleates, ricinoleates, phthalates, salicylates, carbonates, and phosphates; natural waxes such as carnauba wax, candelilla wax, Japan wax, jojoba oil, sperm oil; fats such as tallow, lard oil, olive oil, cottonseed oil, Perilla oil, linseed oil, tung oil, soya bean oil, flaxseed oil, castor oil, etc.; as well as fractions and derivatives thereof.

Vehicles of little or no polarity comprise hydrocarbons such as liquid butanes, pentanes, hexanes, heptanes, octanes, octenes, benzene, toluene, xylene, cumene, indene, hydrindene, alkyl naphthalenes, and mixtures thereof as well as well known mixtures such as gasoline, kerosene, fuel oil, turbine oil, motor oil, mineral spirits, aromatic solvents, lubricating oils (which may be soap-thickened to form greases), petrolatum, paraffin waxes, albino asphalts, etc. Generally, when petroleum oils are used it is preferable that they be purified, as by solvent treatment, so as to remove foreign matter.

Also, synthetic oils may be used as the vehicles such as polymerized olefins, copolymers of alkylene glycols and alkylene oxides; organic esters, e. g., di-2-ethylhexyl sebacate, allyl laurate, and polymers thereof; dioctyl phthalate, trioctyl phosphate, polymeric tetrahydrofuran, polyalkyl silicon polymers, alkyl methacrylate polymers and copolymers and the like. Mixtures of synthetic and natural lubricants and oils can be used. In addition, resinous materials such as petroleum resins, natural resins such as rosin, resins formed by polymerization of drying fatty oils, phenol-formaldehyde resins, and glyptal-type resins formed by esterification of polyhydric alcohols with polycarboxylic acids can be used.

Still another class of vehicles to which condensation products of this invention can be added are water-in-oil and oil-in-water emulsions suitable for various uses such as lubricating, cooling, rust inhibiting, and the like.

If the phosphorus compounds of this invention are not sufficiently soluble in some of the mediums indicated above, solubilizers can be used.

The amount of additive of this invention which can be used depends upon the vehicle to which it is added and the intended purpose to which the composition is to be subjected. Generally, the additive can be used in amounts varying from 0.01% to 20% and higher, preferably between 0.1% and 5%. Various ones of the phosphorus compounds of the invention are useful as lubricants per se, or where they constitute a major proportion of the lubricating medium.

Organic phospho compounds of this invention in addition to being good lubricant-improving agents can be used for improving greases, fuel compositions, hydraulic fluids, insecticidal compositions, coating compositions, rubber compositions, resinous compositions and the like.

The utility of the described phosphono compounds for lubrication is demonstrated by an evaluation of compositions thereof by the Dornte Oxidation Stability Test as described in the National Petroleum News, September 17, 1941, pages R–294–296 and in the High-Temperature Oxidation Apparatus of H. Diamond et al. which is fully described in the general papers presented before the Division of Petroleum Chemistry at the meeting of the American Chemical Society (September 18–23, 1949, Atlantic City, New Jersey) on pages 31–45 of the Preprints. Representative results are given in Table I.

TABLE I

[Base: Mineral lubricating oil.]

Additive	Dornte Oxidation Test (150° C.) 1,500 cc., Time (hours)			High Temperature Oxidation Test (260° C.) 250 cc., Time (minutes)			
	Conc., Percent	Catalyst		Conc.		Catalyst	
		Copper	Crankcase	Percent	None	Copper	Crankcase
None	-------	23	4.6	-------	31	5.1	6.6
Example I: Bis[(dibutyl phosphono)-methyl] ether.	1	37	16	1.25	46	34	42
Example III: Bis[(dibutyl phosphono)-formoxyethyl] ether.	2.1	51	59	2.1	36	23	35
Dimethyl tetradecanephosphonate	1.2	7	4.2	1.2	42.5	4.2	5.7
Dibutyl octanephosphonate	1.75	3.9	3.9	1.2	30.4	3.6	19.1
Lauryl benzyl sulfide	1	24.3	6.2	1	40	12	5.0
Dibenzyl sulfide	1	26.3	5.8	1	24	14	16

(The base mineral oil was a refined mineral lubricating oil.)

Representative compositions of this invention were evaluated neat and compared with other types of phosphorus compounds, as noted by Examples 6, 7 and 8, by subjecting them to a modification of the corrosion-oxidation resistance test in the presence of various metals as described in Federal Specification VV-L-791d, Test 530.81.

The results were as follows:

[Corrosion test: Wt. loss (mg./cm.²).]

	Cu	Mg	Fe	Cd	Al
1. Tetrabutyl bis(phosphonoethyl)-ether	2.90	0.64	0	5.84	0.04
2. Bis[-2,2'(butyl benzene-phosphinico)ethyl]ether	3.84	3.54	0.04	0.16	0
3. Bis[(dibutylphosphono)-butyl]-ether	1.12	0.04	0	0	0
4. Bis[(dinonylphosphono)-ethyl]-ether	0.72	0.36	0.04	0.04	0
5. Bis[2,2'-(butyl p-chlorobenzene-phosphinico)-ethyl]ether	5.28	0.72	0	0.08	0.04
6. Diallyl benzenephosphonite	141.7	77.8	0.24	11.9	0.12
7. Dibutyl 2-ethylhexanephosphonate	48.3	8.20	0	7.56	0.08
8. Butyl n-octanephosphinate	(1)	(1)	(1)	(1)	(1)

[1] Very corrosive and unstable.

A hydraulic fluid consisting of the following materials was subjected to the corrosion test as described above and the results are tabulated below:

Composition A:	Per cent
Alkyl(C_4–C_{12})methacrylate polymer	5
Glycidyl phenyl ether	1
Wax disulfide	0.1
Bis[2-(dioctylphosphono)ethyl]ether	Balance

[Corrosion test: Wt. loss (mg./cm.²).]

	Cu	Mg	Fe	Cd	Al
Composition A	0	+0.08	0	0.08	0

Compositions of this invention can be combined with other additives such as blooming agents, pour-point depressors, and/or viscosity improvers, anti-foaming agents, and the like. Among the specific additives for lubricating purposes which can be used are oil-soluble detergents which include oil-soluble salts of various bases with detergent-forming acids. Such bases include metal-containing as well as organic bases. Metallic bases include those of alkali metals, Ca, Mg, Cu, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary amines and quaternary ammonium compounds, e. g., benzyl trimethyl ammonium hydroxide.

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

Additional detergents are the alkaline earth phosphate diesters, including the thiophosphate di-esters; 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 (lecithin and cephalin), certain fatty oils such as rapeseed oils, "Voltolized" fatty or mineral oils and the like.

An excellent 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 products are excellent detergents.

Antioxidants which are suitable for use in combination with the phosphono compounds comprise several types, for example, alkyl phenols such as 2,4,6-trimethylphenol, pentamethylphenol, 2,4-dimethyl-6-tertiary-butylphenol, 2,4-dimethyl-6-octylphenol, 2,6-ditertiary-butyl-4-methylphenol, 2,4,6-tritertiary-butylphenol, and the like; aminophenols such as benzylaminophenols; aromatic amines, such as N,N'-dibutyl-p-phenylenediamine, diphenylamine, phenyl-beta-naphthylamine, phenyl-alpha-naphthlyamine, and dinaphthylamine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 or 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-cyanostearic acid), glycidyl phenyl ether, wax disulfide, etc.

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 additional 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.

We claim as our invention:

1. A composition of matter comprising a major amount of mineral oil and a minor amount, sufficient to inhibit oxidation, of bis[(dibutyl phosphono)methyl] ether.

2. A composition of matter comprising a major amount of mineral oil and a minor amount, sufficient to inhibit oxidation, of bis[(dibutyl phosphono)ethyl] ether.

3. A composition of matter comprising a major amount of mineral oil and a minor amount, sufficient to inhibit oxidation, of bis[(dibutyl phosphono)formoxyethyl]-ether.

4. A composition of matter comprising a major amount of mineral oil and a minor amount, sufficient to inhibit oxidation, of bis[-2,2'(butyl benzenephosphinico)ethyl]-ether.

5. A composition of matter comprising a major amount of mineral oil and a minor amount, sufficient to inhibit oxidation, of bis[(diisopropyl phosphono)ethyl]ether.

6. A composition of matter comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to inhibit oxidation, of bis[(dibutyl phosphono)methyl]-ether.

7. A composition of matter comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to inhibit oxidation, of bis[(dibutyl phosphono)-ethyl]ether.

8. A composition of matter comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to inhibit oxidation, of bis[(dibutyl phosphono)-formoxyethyl]ether.

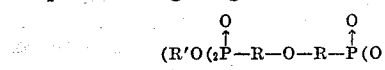
9. A composition of matter comprising a major amount of a mineral lubricating oil and a minor amount, sufficient to inhibit oxidation, of bis[-2,2-(butyl benzenephosphinico)ethyl]ether.

10. A composition of matter comprising a major amount of mineral lubricating oil and a minor amount, sufficient to inhibit oxidation of said oil, of a bis[(di-(C_{1-12})alkyl phosphono) C_1 to C_{15} alkyl]ether.

11. A composition of matter comprising a major amount of mineral lubricating oil and a minor amount,

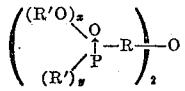
sufficient to inhibit oxidation of said oil, of a bis[(C1 to C12 alkyl benzene phosphinico) C1 to C15 alkyl]ether.

12. A composition of matter comprising a major amount of a mineral lubricating oil and a minor amount sufficient to inhibit oxidation of said hydrocarbon of a compound having the general formula



wherein each R is a saturated hydrocarbon radical of from 1 to 15 carbon atoms and R′ is a hydrocarbyl radical of from 1 to 12 carbon atoms.

13. A composition of matter comprising a major amount of a mineral lubricating oil and a minor amount sufficient to inhibit oxidation of said hydrocarbon of a compound having the general formula:



wherein R is a divalent organic radical selected from the group consisting of hydrocarbon and oxahydrocarbon radicals of from 1 to 15 carbon atoms and free of heterocyclic groups; R′ is a saturated hydrocarbyl radical of from 1 to 12 carbon atoms; x is a whole number from 1 to 2, and y is a whole number from 0 to 1 and the sum of x and y is 2.

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