United States Patent Office

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EXTREME PRESSURE LUBRICANT

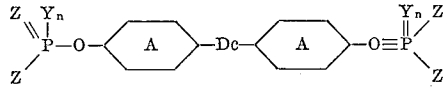
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4 Claims. (Cl. 252—46.6)

The present invention relates to novel compounds having particular utility as extreme pressure and antiwear agents in oleaginous base lubricants.

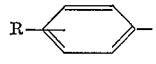
Mineral oil and synethetic lubricants, in the form of greases or free-flowing liquids, are called upon to ease friction and prevent damage to machinery operated at temperatures to as high as about 450° F. At elevated temperatures an internal combustion engine using these lubricants is an ideal oxidizing machine since the lubricant is violently agitated in the presence of air for long periods of time. In addition the stability of the lubricants is further drastically reduced due to contact with metallic surfaces which give up metallic particles to the lubricant that act as powerful oxidation catalysts. Furthermore, water also causes corrosion of metallic surfaces and accentuates oxidation of the lubricant. Aside from being stable under conditions of use the lubricant must exhibit antiwear and load-carrying or extreme pressure characteristics.

It has now been discovered that the novel compounds of the present invention when added in small effective amounts to oleaginous base lubricating oils provide a lubricant composition with improved antiwear and extreme pressure characteristics. Many of the novel compounds, in addition, endow lubricants with improved oxidation resistance. The novel compounds of the present invention can be represented by the following general formula:

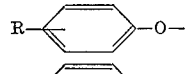


wherein P is phosphorus; O is oxygen; D is a divalent aliphatic hydrocarbon radical of 1 to 5 carbon atoms and $c=0$ to 1; Z is a radical selected from the group consisting of

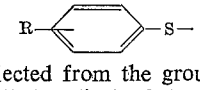
(a)



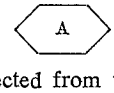
(b)



(c)



in which R is selected from the group consisting of hydrogen and an alkyl radical of 1 to 20 carbon atoms.



is a cyclic radical selected from the group consisting of phenyl and cyclohexyl; Y is a Group VIA atom of up to 52 atomic number, such as oxygen, selenium, tellurium and sulfur; and n is 0 to 1. At least one of the Z radicals on each phosphorus atom should contain an R group to give solubility to the compound and preferably the R group will average 5 or more carbon atoms. When both sulfur and oxygen are present in the compound it is

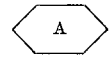
preferred that the R group average 12 or more carbon atoms.

In general the novel compounds of the present invention are the condensation products of bisphenol or bisphenol or hydrogenated bisphenol, the particular phospane or the corresponding cyclohexyl compounds such as 2,2-bis(4-hydroxycyclohexyl) propane with

(I) a monophenol or thiophenol and a phosphorous halide; or
(II) a phenyl phosphorous halide; or
(III) a phenyl phosphorus halide and a monophenol or thiophenol.

Thus, depending upon whether the reactants of I, II or III are selected for condensation with the particular bisphenol or hydrogenated bisphenol, the particular phosphorous halide or benzene phosphorous chloride employed, the compounds of the present invention can be diphosphites, diphosphates, dithiophosphates, diphosphonites, diphosphonates, dithiophosphonates, disphosphinates, disphosphinates or dithiophosphinates.

The cyclic



radicals can be substituted, if desired, with non-interfering groups and it is preferred that they be halogenated for instance, with from 1 to 4 halogens of atomic number of 17 to 35, such as chlorine, bromine or iodine. Particularly preferred bisphenols are the bis(3,5-dichloro) compounds such as 2,2-bis(3,5-dichloro-4-hydroxyphenyl) propane.

The monophenol and/or thiophenol reactants of the present invention can be alkylated as with an alkyl group of 1 to 20 carbon atoms, preferably 4 to 12 carbon atoms; the alkyl group being preferably located in a para position to the —SH or OH group. Particularly suitable alkylated phenols and thiophenols are, for example, cresols, para tertiary butyl phenol, para tertiary octylphenol, para tertiary butyl thiophenol, thioxylenol and the like.

Examples of appropriate phosphorous halides are phosphorous trichloride, phosphorous, oxychloride, thiophosphoryl chloride. Suitable phenyl phosphorous halides are, for instance, phenyl phosphoric dichloride, phenyl phosphorous thiodichloride, preferably wherein the phenyl group is alkylated as with alkyl groups of 1 to 20 carbon atoms, preferably 4 to 12 carbon atoms.

The compounds of the present invention can be conveniently prepared in a hydrocarbon solvent, for instance toluene, xylene, etc. at atmospheric pressure at temperatures of from about 100 to 250° C., generally from about 100 to 150° C., using an amine such as pyridine, triethylamine, etc. as a hydrogen halide acceptor. The diphosphates and diphosphites can be prepared, for instance, by first slowly adding 2 moles of a monophenol or thiophenol to 1 mole of the appropriate phosphorus halide, for example, PCl_3 or $POCl_3$, to replace two of the halide atoms. Two of the resulting monohalide molecules are then coupled with the bis hydroxy reactant such as 2,2-bis(4-hydroxyphenyl) propane or 2,2-bis(4-hydroxycyclohexyl) propane. The diphosphonites and diphosphonates can be prepared respectively by reacting equimolecular proportions of a benzene phosphonohalide or a benzene phosphinous halide and the monophenol or thiophenol and then reacting the resulting product with the bis compound

reactant in a molar ratio of about 2:1. The diphosphinites and diphosphinates can be prepared, for instance, by reacting directly in equimolar proportions a dibenzylphosphonohalide or a dibendylphosphinous halide and the bis compound reactant. The dithiophosphates, dithiophosphonates and dithiophosphinates of the present invention can be prepared by employing the appropriate phosphorous thiohalide or alternatively by sulfurizing, as with flowers of sulfur, the diphosphite, diphosphonite or diphosphinite compounds.

The lubricating oil base stock used in the present invention is of lubricating viscosity and can be, for instance, a solvent extracted or solvent refined oil obtained in accordance with conventional methods of solvent refining lubricating oils. Generally, lubricating oils have viscosities from about 20 to 250 SUS at 210° F. The base oil may be derived from paraffinic, naphthenic, asphaltic or mixed base crudes, and if desired, a blend of solvent-treated Mid-Continent neutrals and Mid-Continent bright stocks may be employed. The oils may be thickened to grease consistency.

The base oil of the fluid lubricant or grease may be a synthetic oil of lubricating viscosity. One type of synthetic oleaginous base used is an ester synthetic oil of lubricating viscosity which consists essentially of carbon, hydrogen and oxygen, e.g. di-2-ethylhexyl sebacate. Various of these lubricating materials have been described in the literature and generally their viscosity ranges from the light to heavy oils, e.g. about 50 SUS at 100° F. to 250 SUS at 210° F. and preferably 30 to 150 SUS at 210° F. These esters are of improved thermal stability, low acid number and high flash and fire points. The complex esters, diesters, monoesters and polyesters may be used alone or to achieve the most desirable viscosity characteristics, complex esters, diesters and polyesters may be blended with each other or with naturally-occuring esters like castor oil to produce lubricating compositions of wide viscosity ranges which can be "tailor-made" to meet various specifications. This blending is performed, for example, by stirring together a quantity of diester and complex ester at an elevated temperature, altering the proportions of each component until the desired viscosity is reached.

These esters are prepared fundamentally by the action of acids on alcohols. The mere mixture of an alcohol and acid at the proper temperature will react to produce an equilibrium mixture which includes the monoester. The same is true for the reactions of organic dibasic acids and glycols to produce synthetic lubricant polyester bright stock. The diesters are frequently of the type alcohol-dicarboxylic acid-alcohol, while complex esters are generally of the type X–Y–Z–Y–X in which X represents a monoalcohol residue, Y represents a dicarboxylic acid residue and Z represents a glycol residue and the linkages are ester linkages. These esters have been found to be especially adaptable to the conditions to which turbine engines are exposed, since they can be formulated to give a desirable combination of high flash point, low pour point, and high viscosity at elevated temperature, and need contain no additives which might leave a residue upon volatilization. In addition, many complex esters have shown good stability to shear. Greases which use these esters as the oleaginous base also have most of these characteristics.

Suitable mono- and dicarboxylic acids used to make synthetic ester lubricant bases can be branched or straight chain and saturated or unsaturated and they frequently contain from about 2 to 12 carbon atoms. The alcohols usually contain from about 4 to 12 carbon atoms. In general, the useful glycols include the aliphatic monoglycols of 4 to 20 or 30 carbon atoms, preferably 4 to 12.

The compositions of this invention incorporate a small, minor amount of the above described additives sufficient to provide the base oil of lubricating viscosity which is the major portion of the composition with improved antiwear and extreme pressure properties. This amount is generally about 0.01 to 15 or 20% or more depending on the particular base oil used and its application. The preferred concentration should be the minimum amount to give the desired properties for the particular application and usually will be about 0.2 to 5%. In some cases where oil solubility might limit the amount of additive employed, dispersants may be used to increase the concentration. In these cases, it has been found that increased solubility is best obtained in highly refined oils by dissolving the dispersant in the oil before dissolving the additive.

Materials normally incorporated in lubricating oils and greases to impart special characteristics can be added to the composition of this invention. These include corrosion inhibitors, additional extreme pressure agents, antiwear agents, etc. The amount of additives included in the composition usually ranges from about 0.01 weight percent up to about 20 or more weight percent, and in general they can be employed in any amounts desired as long as the composition is not unduly deleteriously affected.

The following examples are included to illustrate the preparation of the condensation products of the present invention but are not to be considered limiting. Any method apparent to one skilled in the art can be employed in preparing the compounds.

EXAMPLE I

2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl phosphite)phenyl]propane

A flask was flushed with nitrogen to remove the air and a nitrogen blanket was employed to prevent hydrolysis of the PCl_3 and/or PH_3 formation, during the monophenol addition. To 257 g. (3.25 moles) of pyridine and 137 g. (1 mole) of PCl_3 in 800 g. toluene, while stirring vigorously, were slowly added, over about one hour, 412 g. (2 moles) para-tertiary octylphenol dissolved in 600 g. toluene. The temperature rose from 28° C. to 53° C. during the addition. Heat was then applied to the flask via a heating mantle, the nitrogen turned off and a reflux condenser was attached, which was protected from the air with a drying tube. After about one-half hour 200 g. toluene were added and fifteen minutes later the toluene started to reflux at a pot temperature of 113° C. The mixture was stirred at reflux for 6 hours and then allowed to stand and cool overnight. The next morning 183 g. 0.5 mole) 2,2-bis(3,5-dichloro-4-hydroxyphenyl) propane dissolved in 1000 g. toluene was added and the flask contents stirred and heated to reflux temperature of 112° C. It was maintained at 112° C. for 7 hours and then allowed to stand and cool overnight. The next day the pyridine hydrochloride was filtered off and washed with toluene. The filtrate was washed with water, dilute $NaHCO_3$, and then twice with water again. Methanol was used to break the emulsions formd. Finally it was allowed to dry over anhydrous calcium sulfate over the weekend. The mixture was then filtered and the filtrate topped to 226° C. at 10 mm. pressure. The bottoms product weighed 575 g. (92.5% theory) and was an off-white soft solid. It analyzed 4.24% phosphorus and 10.5% chlorine.

EXAMPLE II

2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl thiophosphate)phenyl]propane

Into a suitably sized flask were charged 400 g. of the diphosphite prepared in Example I above, 20 g. of sulfur flowers and 150 g. toluene. The mixture was heated and stirred at reflux temperature of 129° C. for 22.5 hours. It was then topped to 186° C. at 6 mm. The bottoms weighing 420 g. were a dark yellow color and analyzed 4.07% phosphorus, 6.21% sulfur and 9.93% chlorine.

EXAMPLE III

2,2-bis[4-(di para tertiary octylphenyl phosphite) cyclohexyl]propane

This compound was made in a similar manner as Example I. The para tertiary octylphenol in toluene was added to PCl_3 in pyridine and toluene over 50 minutes while the reaction temperature rose from 28° C. to 66° C. It was heated and stirred for 6.5 hours at 114° C. 2,2-bis (4-hydroxycyclohexyl)propane partially dissolved in ether was added at 28° C. The ether was removed by distillation, toluene added and the mixture stirred at 112° C. for 4.5 hours. After filtering off the pyridine hydrochloride at room temperature, the filtrate was washed 3 times with water using methanol to break the emulsion. After drying, the mixture was topped to 203° C. at 4 mm. An appreciable amount of unreacted para tertiary octylphenol was removed during topping. The pale yellow plastic product, obtained in 82.5% yield, analyzed 5.65% phosphorus and acid number 2.0.

EXAMPLE IV

2,2-bis[4-(di para tertiary octylphenylthiophosphate) cyclohexyl]propane

The diphosphite of Example III was sulfurized for 24 hours at 125° C. After drying the mixture was topped to 180° C. at 5 mm. The product analyzed 5.39% phosphorus and 3.65% sulfur.

EXAMPLE V

2,2-bis[4-(di para tertiary octylphenyl phosphate) cyclohexyl]propane

This compound was made similar to Examples I and III. Two moles of para tertiary octylphenol in 600 g. of toluene were added to one mol of phosphorus oxychloride in 3.25 moles of pyridine and 500 g. toluene over one hour. After stirring at 114° C. for 8 hours and cooling to room temperature, 0.5 mole of 2,2-bis (4-hydroxycyclohexyl)propane, slurred in 1000 g. ether and 300 g. acetone, and about one gram of anhydrous $MgCl_2$ were added. After removing the ether and acetone by distillation, the mixture was stirred at 113–115° C. for 4½ hours during which time about one gram each of anhydrous $MgCl_2$ and $AlCl_3$ were added. The filtered mass was washed with water and dilute $NaHCO_3$ followed by 3 water-methanol washes and dried. It was topped to 200° C. at 4 mm. The yield was 63.3% theory. The product analyzed 7.0% phosphorus and 0.0% chlorine.

EXAMPLE VI

2,2-bis[3,5-dichloro-4 (di para tertiary octylphenyl phosphate)phenyl]propane

Two preparations of this compound were made in the same manner employed in Example V except that 2,2-bis (3,5-dichloro-4-hydroxy phenyl)propane was employed instead of 2,2-bis (4-hydroxy cyclohexyl) propane. The two preparations differed in the use of solvent, toluene was used in one designated (a) and xylene in the other designated (b). (a) was topped to 215° C. at 8 mm. and (b) to 208° C. at 4 mm. The products were dark green hard solids and analyzed as follows:

	Percent P	Percent Cl
(a)	4.95	11.1
(b)	4.42	9.3

EXAMPLE VII

2,2-bis[3,5-dichloro-4-(para tertiary octylphenyl benzene-phosphonate)phenyl]propane

The flask was flushed with nitrogen to remove the air. The N_2 was continued into the flask. Eighty grams of pyridine and 390 g. (2 moles) phenylphosphonic dichloride weighed into 400 g. xylene were charged at room temperature. Stirring was started and heat was applied to the flask. Over the next 40 minutes 412 g. (2 moles) para tertiary octyl phenol dissolved in 500 g. xylene was added dropwise or in a small stream. The N_2 inflow was discontinued, the flask stopped at that neck and the heat was turned up. Forty-five minutes later at 144° C. the xylene started refluxing. Then 250 g. xylene were added for better mixing and the reaction allowed to continue for 4 hours and 10 minutes before being shut down for the night. The next morning the stirrer and heat were turned on. After 25 minutes and at a flask temperature of 35° C., 166 g. pyridine, 366 g. (1 mole) tetrachlorobis-phenol A dissolved in 1000 g. xylene at 75° C. and 1 g. anhydrous $AlCl_3$ were added. After one hour refluxing started at 140° C. After about 1½ hours the material turned green and 1 g. $AlCl_3$ was added. After 1¾ hours later another gram of $AlCl_3$ was added. It was then allowed to react for about 3½ hours before being shut down for the night. The next day the pyridine hydrochloride was filtered off using a Buechner funnel and vacuum. The filtrate was washed with water, H_2O—MeOH and $NaHCO_3$ solution until basic. An additional H_2O wash turned it acid again. It was then stirred with Drierite and solid $NaHCO_3$ for 1 hour and after adding Attapulgas fines, 30 minutes longer. It filtered clear and was still green. It was then evaporated down on a steam bath overnight. The next morning a precipitate was visible and it was filtered again. A portion (500 g.) was again evaporated down to 365 g. but no more precipitation occurred. The mass was then topped to 225° C. at 7 mm. A green product was obtained in a yield of 86% of theory, which analyzed 5.79% phosphorus, 13.3% chlorine and Acid No. 44.9.

EXAMPLE VIII

2,2-bis[3,5-dichloro-4-(para tertiary octylphenyl-benzene-thiophosphonate)phenyl]propane

This compound was prepared in essentially the same manner as in Example VII above. Both were one mole runs. Three weights differed in that an extra 80 g. pyridine was used at the start of the reaction and 412 g. (2 moles) phenyl-phosphorous thiodichloride were weighed into 600 g. xylene, instead of 390 g. (2 moles) phenylphosphonic dichloride into 400 g. xylene, with 250 g. added after the octyl phenol.

The filtrate was not washed with $NaHCO_3$ solution after water and H_2O—MeOH washing. It was dried the same way. No precipitate occurred on steam bath removal of the toluene. A black product was obtained in 85% yield (theory) and analyzed 5.98% phosphorus, 12.3% chlorine, 6.25% sulfur and Acid No. 44.9.

EXAMPLE IX

2,2-bis[3,5-dichloro-4-(di para tertiary butyl-phenyl-phosphate)phenyl]propane

This compound was prepared in the same manner as the compound of Example V except that butyl phenol was employed instead of octyl phenol. The product was a dark green solid and analyzed 5.81% phosphorus, 12.0% chlorine and Acid No. 59.9.

To demonstrate the advantages of the compounds of the present invention in lubricant compositions, 1% of some of the compounds of Examples I to IX were incorporated in an oil blend (identified in Table I below) and the lubricant compositions were subjected to an oxidation test and the Shell 4-Ball Extreme Pressure and Wear

Tests. The oxidation test comprised charging 350 cc. of the oil to a large tube maintained at 285° F. in an oil bath for 144 hours while introducing 5 liters of oxygen per hour at the bottom of the tube in the presence of a copper on lead coupon measuring 1" x 3". For comparison, the base oil (identified in Table I) without the additives of the present invention was also tested. The results of the tests are shown in Table I.

TABLE I

Compound	Oil Blend		Oxidation Test			
	Percent Conc.	KV/100	KV/100	Percent Vis. Rise	Catalyst Wt. Change (mg.)	Acid No.
Base Oil [1]		28.03	38.60	38	−20.3	10.6
2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl phosphite) phenyl] propane (Ex. I)	1.0	28.74	26.20	−8	+18.0	2.9
2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl thiophosphate) phenyl] propane (Ex. II)	1.0	28.46	27.18	−5	+8.8	2.7
2,2-bis[4-(di para tertiary octylphenyl phosphite) cyclohexyl] propane (Ex. III)	1.0	28.89	24.2	−16	+21.0	2.6
2,2-bis[4-(di para tertiary octylphenyl thiophosphate) cyclohexyl] propane (Ex. IV)	1.0	27.17	25.9	−5	+18.5	2.1
2,2-bis[4-(di para tertiary octylphenyl phosphate)cyclohexyl] propane (Ex. V)	1.0	29.75	26.3	−11	−363	2.2
2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl phosphate) phenyl] propane (Ex. VI(a))	1.0	30.47	28.82	−5	−262.1	2.9
2,2-bis[3,5-dichloro-4-(para tertiary octylphenyl-benzene-phosphonate) phenyl] propane (Ex. VII)	1.0	28.18	34.16	21	−5	6.8
2,2-bis[3,5-dichloro-4-(para tertiary octylphenyl-benzene-thiophosphonate) phenyl] propane (Ex. VIII)	1.0	27.69	234.1	745	−5.3	8.5
2,2-bis[3,5-dichloro-4-(di para tertiary butyl-phenyl-phosphate) phenyl] propane (Ex. IX)	1.0	28.44	32.59	15	−106	6.0

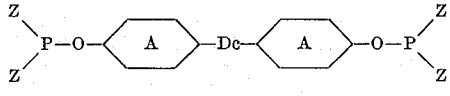
Compound	Oxidation Test (continued)				Shell 4-Ball		
	Pentane Insol., Percent	Initial pH	Condition		Mean Hertz Load	Weld, kg.	Ave. Wear Diam., mm.
			Copper	Tube			
Base Oil	4.24	2.4	Blotched	Lt. sludges	13.1	141	0.55
2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl phosphite) phenyl] propane (Ex. I).	0.00	2.3	Clean	Clean	33.6	141	0.30
2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl thiophosphate phenyl] propane (Ex. II).	0.02	2.5	Black	do	26.1	141	0.30
2,2-bis[4-di para tertiary octylphenyl phosphite cyclohexyl] propane (Ex. III).	0.00	2.4	Clean	do	32	141	0.29
2,2-bis[4-(di para tertiary octylphenyl thiophosphate) cyclohexyl] propane (Ex. IV).	0.01	2.4	do	do	21.2	141	0.31
2,2-bis[4-(di para tertiary octyphenyl phosphate) cyclohexyl] propane (Ex. V).	0.01	2.3	do	do	32.6	158	0.20
2,2-bis[3,5-dichloro-4-(di para tertiary octylphenyl phosphate) phenyl] propane (Ex. VI(a)).	0.02	3.1	do	do	26.3	141	0.30
2,2-bis[3,5-dichloro-4-(para tertiary octylphenyl-benzene-phosphonate) phenyl] propane (Ex. VII).	1.88	1.7	Bronze	do	24.8	141	0.49
2,2-bis[3,5-dichloro-4-(para tertiary octylphenyl-benzene-thiophosphonate)phenyl]propane (Ex. VIII).	3.94	1.4	Black	Heavy sludge.	25.6	126	0.35
2,2-bis[3,5-dichloro-4-(di para tertiary butyl-phenyl-phosphate) phenyl] propane (Ex. IX).	0.17	1.7	Dark	Clean	31.3	141	0.28

[1] Base oil is a blend of 70% of a naphthenic base raw lube distillate having a viscosity of 55 to 60 at 100° F. and 30% of a solvent refined Mid-Continent neutral oil having a viscosity of 600 SUS at 100° F. to which has been added 3% of an ashless detergent consisting of a copolymer of 95 parts lauryl methacrylate and 5 parts dimethyl aminoethyl methacrylate.

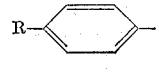
The data of Table I demonstrate the advantageous extreme pressure and antiwear properties possessed by the compounds of the present invention. In addition, many of the compounds are also shown to be excellent antioxidants.

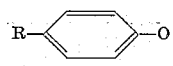
It is claimed:

1. An oleaginous lubricant composition consisting essentially of a base oil of lubricating viscosity and an amount sufficient to give improved extreme pressure properties to the composition of an oil-soluble compound respresented by the general formula:



wherein P is phosphorous; O is oxygen; D is a divalent hydrocarbon radical of 1 to 5 carbon atoms and *c* is 0 to 1; Z is a radical selected from the group consisting of:

(a) 

(b) 

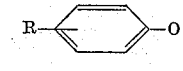
(c) 

in which R is selected from the group consisting of hydrogen and alkyl radical of 1 to 20 carbon atoms; and



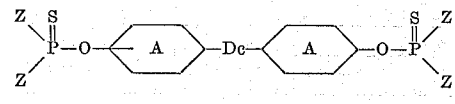
is a cyclic radical selected from the group consisting of phenyl and cyclohexyl; said amount is being about 0.01 to 20% by weight.

2. The composition of claim **1** wherein Z is the radical:



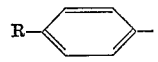
in which R is an alkyl radical of 1 to 20 carbon atoms.

3. An oleaginous lubricant composition consisting essentially of a base oil of lubricating viscosity and an amount sufficient to give improved extreme pressure properties to the composition of an oil-soluble compound represented by the general formula:

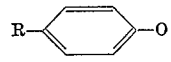


wherein P is phosphorus; O is oxygen; D is a divalent hydrocarbon radical of 1 to 5 carbon atoms and *c* is 0 to 1; Z is a radical selected from the group consisting of:

(a)



(b)



(c)

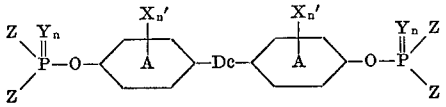


in which R is selected from the group consisting of hydrogen and an alkyl radical of 1 to 20 carbon atoms; and



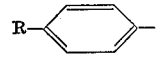
is a cyclic radical selected from the group consisting of phenyl and cyclohexyl; said amount being about 0.01 to 20% by weight.

4. An oleaginous lubricant composition consisting essentially of a base oil of lubricating viscosity and an amount sufficient to give improved extreme pressure properties to the composition of an oil-soluble compound represented by the general formula:

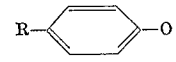


wherein P is phosphorous; O is oxygen; D is a divalent hydrocarbon radical of 1 to 5 carbon atoms and *c* is 0 to 1; Z is a radical selected from the group consisting of:

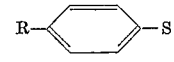
(a)



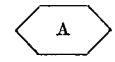
(b)



(c)



in which R is selected from the group consisting of hydrogen and an alkyl radical of 1 to 20 carbon atoms;



is a cyclic radical selected from the group consisting of phenyl and cyclohexyl; X is a halogen atom of atomic number 17 to 52 and *n'* is an integer of 1 to 4; Y is a Group VIA atom of up to 52 atomic number an *n* is 0 to 1, said amount being about 0.01 to 20% by weight.

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