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PHOSPHORUS DERIVATIVES OF 4,4'-DISUCCINIMIDOBIPHENYLOXIDE AND LUBRICANT COMPOSITIONS CONTAINING SAME

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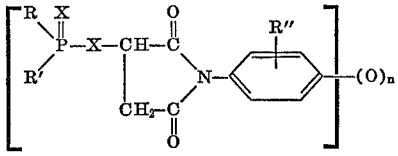
No Drawing. Filed Aug. 30, 1971, Ser. No. 176,270

Int. Cl. C10m *1/48, 1/10*

U.S. Cl. 252—46.7 8 Claims

ABSTRACT OF THE DISCLOSURE

Herein are disclosed phosphorus derivatives of 4,4'-disuccinimidobiphenyls or 4,4'-disuccinimidobiphenyloxides and lubricant compositions containing same. Said phosphorus derivatives having the structural formula:



wherein R and R' are individually selected from the group consisting of hydrocarbyl and hydrocarbyloxy, R'' is selected from the group consisting of hydrogen, R and R^1, *n* is 0 or 1 and X is oxygen or sulfur.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to new compositions of matter, and in particular it relates to cerain phosphorus derivatives of 4,4'-disuccinimidobiphenyls or 4,4'-disuccinimidobiphenyloxides and to compositions comprising a lubricant and an antiwear amount of such materials.

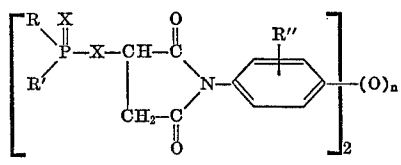
Description of the prior art

It is known in this art that many lubricants are subject to localized failure when being used to lubricate moving metal parts which are in contact with each other. This is true to a limited extent even under mild conditions, but may become particularly severe when the lubricated parts are subjected to high temperatures, high loads and/or high speeds. When failure occurs, the thin film of lubricant ruptures, thus allowing a direct metal-to-metal contact. Scoring of the metal results, and if the condition causing this is not remedied, heavy damage or even destruction of the device is a consequence.

There is extensive art relating to efforts to solve the wear problem, and phosphorus-containing compounds occupy a prominent place among those which have been used. These are well known to those skilled in the lubricant art, and it would thus serve no useful purpose to set them forth here. Suffice to say that no publications are known that disclose or suggest the compounds of this invention or their use as antiwear agents in lubricants.

SUMMARY OF THE INVENTION

In accordance with the invention, there are provided compounds of the formula



wherein R and R' are individually selected from the group consisting of hydrocarbyl and hydrocarbyloxy, R'' is selected from the group consisting of hydrogen and R or R', *n* is 0 or 1 and X is selected from the group consisting

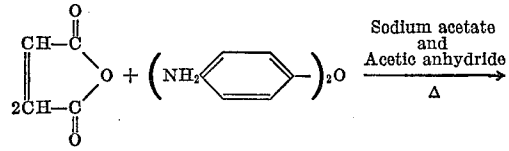
of oxygen and sulfur. It will be understood that R and R' can be the same or different, with respect both to the hydrocarbyl portion and to whether they are hydrocarbyl or hydrocarbyloxy, and that the two X's can also be the same or different.

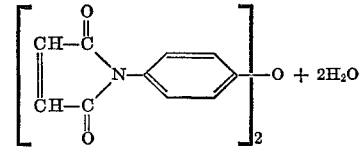
In the above, the hydrocarbyl portion preferably is selected from an alkyl of from 1 to about 20 carbon atoms, phenyl, substituted phenyl wherein the substituent is an alkyl group of from 1 to about 18 carbon atoms and an aralkyl group such as benzyl or phenethyl.

In addition, the invention is concerned with lubricant compositions containing a major proportion of a lubricant and an antiwear amount of the above compounds.

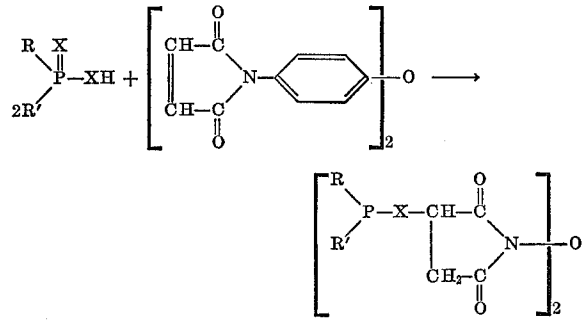
DESCRIPTION OF SPECIFIC EMBODIMENTS

The compounds of this invention where *n* in the above formula is 1 may be made by a three-step process, which steps are well known in the art, and from materials which are also known and readily available. The intermediate, 4,4'-dimaleimidobiphenyloxide, is common to all the inventive compounds made in accordance with the following reaction sequences:





This intermediate is then reacted with the appropriate phosphorus acid as follows to give the compound



It is possible, however, to prepare the compounds by first makng the phosphorus acid-maleic anhydride adduct, as will be demonstrated hereinbelow.

Compounds where *n* is 0 may be similarly prepared using benzidine, in place of the diaminobiphenyloxide. The benzidine is preferably substituted with alkoxy groups containing from 1 to about 6 carbon atoms.

As is apparent from the definition of the phosphorus acid given above, such acid may be a phosphoric acid, a phosphonic acid or a phosphinic acid. In addition the X portion of such acids may be oxygen, sulfur or combinations of these. In other words, the acid may be derivatives of phosphoric acid, phosphorothioic and -dithioic acids, phosphonic acid, phosphonothioic and -dithioic acids, phosphinic acid and phosphinothioic and -dithioic acids. Included among the useful phosphoric acids are dimethyl, diethyl, dibutyl, dioctyl, didodecyl, dieicosyl, diphenyl and dibenzyl phosphoric acids. Included also are those phosphoric acids wherein R and R' are different, as for example, the methyl ethyl, butyl octyl, octyl decyl and decyl

dodecyl esters of phosphoric acid. Some of the phosphorothioic and phosphorodithioic acids contemplated for use may be illustrated with the same ester and mixed ester groups as those just given.

The phosphonic acids and the thio derivatives include methyl methylphosphonic, -phosphonothioic and -phosphonodithioic acids, ethyl ethylphosphonic, -phosphonothioic and -phosphonodithioic acids, butyl butylphosphonic, -phosphonothioic and -phosphonodithioic acids, octyl octylphosphonic, -phosphonothioic and -phosphonodithioic acids, and so on up to those wherein R and R' are eicosyl, phenyl phenylphosphonic, -phosphonothioic and -phosphonodithioic acids and benzyl benzylphosphonic, -phosphonothioic and -phosphonodithioic acids. Some of these acids in which R and R' are different and which can be used in making the compounds of this invention are methyl ethylphosphonic, -phosphonothioic and -phosphonodithioic acid, butyl octylphosphonic, -phosphonothioic and -phosphonodithioic acids, decyl octadecylphosphonic, -phosphonothioic and -phosphonodithioic acids and ethyl phenylphosphonic, -phosphonothioic and -phosphonodithioic acids.

Similarly, diethylphosphinic, -phosphinothioic and -phosphinodithioic acids and those wherein R and R' are the same up to the dieicosyl member, and the dibenzyl or diphenyl derivatives may be used, as well as those wherein R and R' are different, as ethylbutylphosphinic, -phosphinothioic and -phosphinodithioic acids and phenylbenzylphosphinic, -phosphinothioic and -phosphinodithioic acids.

The lubricants which can be improved with respect to their antiwear properties include mineral oils such as naphthenic or paraffinic mineral oils, synthetic oils, including hydrocarbon base fluids, glycol ether fluids, poly(organo) siloxane fluids, acetals, polyphenyl ethers and the synthetic ester fluids produced from monohydric alcohols and polycarboxylic acids or from polyhydric alcohols, such as trimethylolpropane and pentaerythritol, and monocarboxylic acids having up to about 20 carbon atoms.

As an example of the hydrocarbon base fluid, there may be mentioned a polyolefinic fluid or a hydrogenated derivative thereof. One suitable fluid is similar to that disclosed and claimed in U.S. Pat. 3,149,178. In this patent, the olefinic fluids are polymeirzed normal alphamonoolefins which are distillated to yield a dimer fraction and a dimer-free fraction. The dimer-free fraction may be thereafter hydrogenated in the presence of a catalyst, such as boron trifluoride. Other useful olefinic fluids may be prepared in accordance with U.S. Pat. 3,382,291.

The poly(organo) siloxane fluids may be exemplified by those products obtained by reacting a polysiloxane containing the recurring unit



and having a molecular weight of from about 500 to about 10,000 with an unsaturated compound containing at least one double bond; which compound adds to the H of the above-shown structure. The unsaturated compound may be a mono-olefin, e.g., hexene-1, decene-1 and the like, a cycloolefin such as cyclohexene or cycloheptene, a polyolefin such as polybutadiene or polymeric materials containing ethylenic unsaturation such as polybutenes, and aromatic olefins such as styrene. Also included are unsaturates such as dioctyl maleate, dioctyl fumarate, methyl-10 -undecenoate, and glycerol monooleate. These poly(organo) siloxanes are described in detail in U.S. Application Serial No. 308,355, filed September 23, 1963.

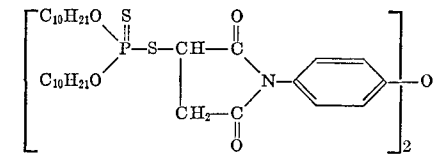
Also included among the useful organic fluids are the dehydrocondensed poly(organo) siloxanes, prepared simply by heating the above poly(organo) siloxane with a

hydrocarbyl hydroperoxide, a dihydrocarbyl peroxide, an acyl hydroperoxide or a diacyl peroxide. Of the peroxides, di-tertiary-butyl peroxide is preferred.

The compounds of this invention are effective antiwear agents when used in the above-mentioned lubricants to the extent of from about 0.01% to about 10% by weight thereof, preferably from about 0.03% to about 2% by weight.

The following will illustrate the compounds of this invention and their use as antiwear agents in lubricants. It will be understood that they are illustrative only and applicant does not intend that the invention shall be limited by them.

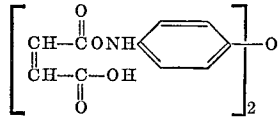
EXAMPLE 1



(a) Preparation of the intermediate, 4,4'-bimaleimidobiphenyloxide

About 196 g. (2 moles) of maleic anhydride and about 200 g. (1 mole) of 4,4'-diaminobiphenyloxide were placed in a reaction flask equipped with a reflux condenser, thermometer and stirrer. About 120 ml. of anhydrous diethyl ether was added and the mixture was stirred while maintaining the temperature at 35° C. by refluxing the ether, for a total of 17 hours. 400 ml. of ether was added and the mixture was cooled to about 5° C. The solid product was recovered by filtration on a vacuum filter.

At this point, the product is believed to be a mixed acid-amide of the formula



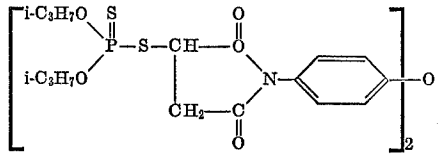
To close the ring, thus forming the imide, the product from the above step was placed in a reaction flask and a mixture of 66 g. of sodium acetate and 670 ml. of acetic anhydride was added. This mixture was stirred and heated to 80–90° C. The reaction was mildly exothermic upon reaching this temperature, and 80–90° C. was maintained, with only moderate heat input, for about 2.5 hours. The reaction mixture was slightly cooled and was poured into about 1500 ml. of ice water, using about 150 ml. of acetic anhydride to wash the solid product from the reaction flask. The product was recovered by filtration and was washed four times with water, filtering each time. It was then mixed with about 1500 ml. of water and a solution of 10 g. of Na_2CO_3 in 200 ml. of water. The product was recovered from this mixture, washed with water and finally with methanol and petroleum ether. After drying in a vacuum desiccator and vacuum oven, about 276 g. of product (about 77% yield) was obtained melting at 175–176.5° C.

(b) Preparation of the phosphorus derivative

About 41 g. (0.1 mole) of O,O-di-n-decyl phosphorodithioic acid was mixed with about 500 ml. of dry benzene in a reaction flask equipped with a stirrer, thermometer, refluxed condenser and addition funnel. The mixture was warmed to about 59° C. and 3 ml. of triethylamine and 0.1 g. of hydroquinone were added. About 18 g. (0.05 mole) of the product of (a) was dissolved in about 100 ml. of dry benzene and this was added to the stirred mixture over about 15 minutes. Heating and stirring was continued for about 2.5 hours. After cooling, the reaction mixture was filtered to remove traces of solid. The benzene solution was washed four times with water, and after evaporating the benzene, 48.7 g. of prod-

uct was obtained having the following analyses (percent): C, 61.8 (theory, 61.0); H, 8.30 (theory, 8.35); N, 2.35 (theory, 2.37); P, 4.73 (theory, 5.24); and S, 10.3 (theory, 10.9).

EXAMPLE 2



This compound was prepared in accordance with the procedure of Example 1 from 18 g. (about .05 mole) of part (a) of Example 1 and 21.4 g. (about 0.1 mole) of $(iC_3H_7O)_2P(S)SH$.

EXAMPLE 3

This example illustrates the preparation of the Example 2 compound by first making the acid-anhydride product.

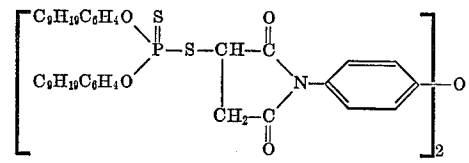
About 21.4 g. (0.1 mole) of O,O-diisopropylphosphorodithioic acid mixed with about 100 ml. of dry benzene was placed in a reaction flask equipped with a reflux condenser, thermometer, stirrer, and an addition funnel. About 0.1 g. of hydroquinone and about 2 ml. of trimethylamine was added to the mixture. The mixture was then stirred and warmed to 50–60° C. A solution of about 9.8 g. (0.1 mole) of maleic anhydride in about 100 ml. of benzene was slowly added to the reaction mixture through the addition funnel. The mixture was then stirred and warmed at about 55° C. for about 2½ hours. The cooled mixture was filtered and washed three times in a sepratory funnel with water containing a small amount of dissolved calcium chloride. The benzene solution was then dried over anhydrous sodium sulfate and filtered. The last traces of water were removed by azeotropic distillation with benzene. Final solvent removal was accomplished by distillation using a steam bath as heat source and reducing the pressure to ensure removal of all the solvent. 24.8 g. of the product were recovered.

About 22.4 g. of the above product was mixed with about 8.0 g. of 4,4' - biaminobiphenyloxide and about 150 ml. of dry benzene in a flask equipped with a stirrer, thermometer and water take off trap. The mixture was stirred and heated at reflux temperature (about 80° C.) for about three hours. About ½ cc. of water was collected.

The reaction mixture was cooled slightly to stop refluxing and 1.6 g. of anhydrous sodium acetate was added. Heating was then resumed and while the mixture was stirring and refluxing, about 0.16 mole (16.3 g.) of acetic anhydride was added. Heating and stirring at reflux temperature were continued for about one hour. The mixture was cooled to about 5° C. and about 500 ml. of wash water was added. Shaking resulted in a stable emulsion. The benzene (and a small amount of water) was removed by distillation and the remaining water decanted from the product (an apparently amorphous mass). This product was washed by stirring with water and decanting several times, then with sodium bicarbonate solution. Finally it was washed with water. The product was dissolved in benzene and filtered. The last of the water was removed by azeotropic distillation with the benzene. The product solution was filtered again. Final solvent removal was accomplished by distillation under vacuum. (Yield was not determined.)

Analysis.—Calcd. for $C_{32}H_{42}N_2O_9P_2S$ (percent): C, 48.7; H, 5.36; N, 3.55; P, 7.85; S, 16.3. Found (percent): C, 41.2; H, 5.47; N, 3.55; P, 5.42; S, 13.3.

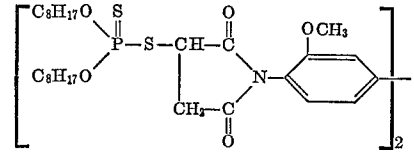
EXAMPLE 4



About 53.5 g. (0.1 mole) of O,O-dinonylphenylphosphorodithioic acid, about 18 g. (0.5 mole) of 4,4'-bimaleimidobiphenyloxide, about 200–250 ml. dry benzene, about 0.1 g. hydroquinone and about 3 ml. of triethylamine were mixed in a 500 ml. reaction flask equipped with a stirrer, thermometer, and reflux condenser. The mixture was stirred and warmed at 55–60° C. for about 1½ hours. The mixture was cooled and a small amount of solid was removed from the benzene solution by filtration.

The filtrate was washed once in a separatory funnel with about 100 ml. water containing a small amount of $CaCl_2$ to help reduce emulsifying problems and three times with water containing a small amount of ethanol. Separation of the layers was slow and the final benzene solution was cloudy; filtration three times through coarse filter paper yielded a clear solution. The solvent was evaporated in a rotary evaporator at reduced pressure. 68.9 g. of product was obtained.

EXAMPLE 5



(a) Into a reaction vessel were placed 196 g. (2 moles) of maleic anhydride and 244 g. (1 mole) of 3,3'-dimethoxybenzidine. To this was added about 1250 ml. of anhydrous ethyl ether and the reaction mixture was stirred for 2½ hours at the temperature of refluxing ether. 250 ml. of more ether was added and the mixture stood about 48 hours.

After stirring for another 3 hours, the reaction mixture was cooled to 5° C. and was filtered to remove the solid. This solid was returned to a reaction flask and 66 g. of sodium acetate and 1000 ml. of acetic anhydride and the reaction mixture was stirred for about 2 hours at 70–80° C. The solid was removed by filtration, placed in a beaker, mixed with 2 liters of water containing about 50 g. of sodium carbonate, stirred and filtered. This step was repeated, and then the solid was similarly washed three times with water. The final water pH was about 7.0. Finally, the solid was washed three times with between 1500 and 2000 ml. of methyl alcohol each wash, once with petroleum ether and then dried. Product yield was 346.9 g.

(b) A reaction flask was charged with 20.2 g. (0.05 mole) of the product made in (a), 35.4 g. (0.1 mole) of dioctyl phosphorodithioic acid, 0.1 g. of hydroquinone, 3 ml. of triethylamine and about 250 ml. of dry benzene. This mixture was stirred under reflux (about 80° C.) for about 18½ hours and was then cooled to 30–35° C. The mixture was filtered, yielding a dark but clear filtrate. This filtrate was washed once with 250 ml. of H_2O containing a small amount of ethyl alcohol and once with 250 ml. of water containing some dissolved calcium sulfate. This was followed by filtration, shaking with more calcium sulfate, another filtration and removal of solvent on a water bath at 95° C. There was a 45% yield of product.

EVALUATION OF PRODUCTS

Four-ball machine wear test

In this procedure, three ½-inch diameter balls of 52100 steel are held stationary by a ring in a steel cup con-

taining the test lubricant. A fourth ball, positioned on a rotatable vertical axis, is brought into contact with the three stationary balls and is rotated against them. The force with which the rotatable ball is held against the stationary balls can be varied according to the desired load. The sliding speed and the time of the test can also be varied as desired. At the end of the test the wear scars on the stationary balls are measured. The average size of the wear scars and the rate of wear per unit of sliding distance represent the effectiveness of the lubricant as an antiwear agent.

The above compounds were run in this test, using a mineral oil made up from about 80% 150" paraffinic Bright stock and 20% 200" paraffinic Neutral stock. Each test was run for 30 minutes. The following table summarizes the data obtained with 1% by weight of the compound.

TABLE I

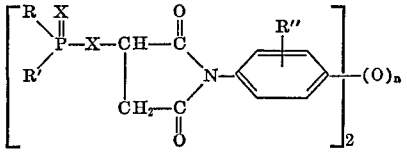
Additive	Load. kg.	Temperature. ° F.	Sliding speed. r.p.m	Coefficient of friction	Wear scar diameter. mm.	Wear rate. cc./cm.
None	40	300	600	0.08	0.60	4.2×10^{-11}
Do	40	400	600	0.10	0.75	11×10^{-11}
Do	40	550	600	0.16	0.99	23×10^{-11}
Do	100	300	600	0.08	1.1	47×10^{-11}
Do	40	300	3,000	0.04	2.4	$1,200\times10^{-11}$
Ex. 1	40	300	600	0.11	0.42	0.7×10^{-11}
Do	40	400	600	0.10	0.43	0.8×10^{-11}
Do	40	550	600	0.08	0.69	7.7×10^{-11}
Do	100	300	600	0.11	0.91	23.0×10^{-11}
Do	40	300	3,000	0.07	0.62	1.0×10^{-11}
Ex. 2	40	300	600	0.12	0.43	0.8×10^{-11}
Do	40	400	600	0.10	0.45	1.0×10^{-11}
Do	40	550	600	0.11	0.70	8.5×10^{-11}
Do	100	300	600	0.10	0.81	14×10^{-11}
Do	40	300	3,000	0.06	0.49	0.3×10^{-11}
Ex. 4	40	300	600	0.09	0.43	0.8×10^{-11}
Do	40	500	600	0.10	0.67	6.8×10^{-11}
Do	80	300	600	0.11	0.87	19×10^{-11}
Do	40	300	3,000	0.09	0.88	4.3×10^{-11}
Ex. 5	40	300	600	0.09	0.45	1.1×10^{-11}
Do	40	400	600	0.06	0.47	1.4×10^{-11}
Do	40	550	600	0.07	0.73	9.7×10^{-11}
Do	100	300	600	0.10	0.94	26×10^{-11}
Do	40	300	3,000	0.09	0.76	2.4×10^{-11}

The compounds of this invention may be utilized effectively with other additives commonly used in lubricants. These include antioxidants, detergents, metal suppressants and the like.

Although the present invention has been described with certain specific embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of this invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the appended claims.

I claim:

1. A lubricant composition comprising a major proportion of a lubricant and an antiwear amount of a compound of the formula



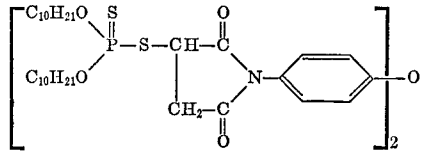
wherein R and R' are individually selected from the group consisting of hydrocarbyl and hydrocarbyloxy, R" is selected from the group consisting of hydrogen, R and R', n is 0 or 1 and X is oxygen or sulfur.

2. The composition of claim 1 wherein the hydrocarbyl portion is selected from the group consisting of alkyl of from 1 to about 20 carbon atoms, phenyl, alkyl-substituted phenyl, wherein the substituent is an alkyl of from 1 to about 18 carbon atoms and aralkyl.

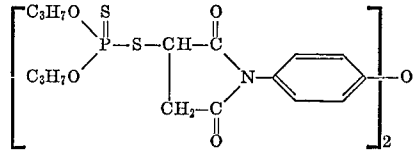
3. The composition of claim 1 wherein the compound is present to the extent of from about 0.01% to about 10% by weight.

4. The composition of claim 1 wherein the lubricant is a mineral oil.

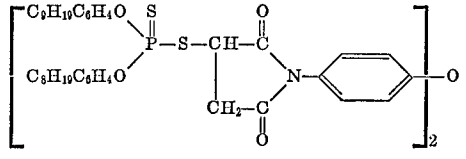
5. The composition of claim 1 wherein the compound is



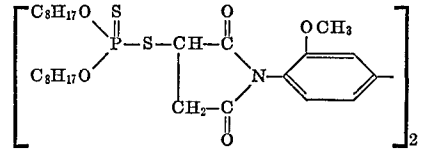
6. The composition of claim 1 wherein the compound is



7. The composition of claim 1 wherein the compound is



8. The composition of claim 1 wherein the compound is



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U.S. Cl. X.R.

252—49.9; 260—326.3