United States Patent [19]

Dickert, Jr. et al.

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[54] **LUBRICATING COMPOSITIONS CONTAINING METAL PHOSPHONATES**

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[22] Filed: **Oct. 1, 1973**

[21] Appl. No.: **402,238**

Related U.S. Application Data

[60] Division of Ser. No. 280,604, Aug. 14, 1972, Pat. No. 3,798,162, which is a continuation-in-part of Ser. No. 70,901, Sept. 9, 1970, abandoned.

[52] **U.S. Cl.** ..... **427/401;** 260/430; 252/32.5; 117/70 C; 427/445

[51] **Int. Cl.** **C23f 7/08**

[58] **Field of Search** ..... 117/71 M, 70 C, 89, 130 E, 117/131, 62, 130 R, 160 R, DIG. 1; 252/32.5

[56] **References Cited**

UNITED STATES PATENTS

3,798,162 3/1974 Dickert et al. 252/32.5

Primary Examiner—Ralph S. Kendall
Assistant Examiner—Charles R. Wolfe, Jr.
Attorney, Agent, or Firm—Charles A. Huggett; Raymond W. Barclay; Claude E. Setliff

[57] **ABSTRACT**

The extreme pressure properties of organic fluids are improved by adding thereto a small amount of a gold hydrocarbyl hydrocarbylphosphonate complexed with a basic nitrogen compound or another metal hydrocarbyl hydrocarbylphosphonate which may or may not be so complexed.

13 Claims, No Drawings

LUBRICATING COMPOSITIONS CONTAINING METAL PHOSPHONATES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of U.S. application Ser. No. 280,604, now U.S. Pat. No. 3,798,162, filed Aug. 14, 1972 which in turn is a continuation-in-part of U.S. application Ser. No. 70,901, filed Sept. 9, 1970, and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates in one of its aspects to novel lubricant compositions. More particularly, it relates to such compositions containing anti-wear amounts of metal phosphonates either uncomplexed or complexed with a basic nitrogen compound. In another of its aspects, the invention relates to a novel method of protecting rubbing metal surfaces and in still another aspect to new metal phosphonate complexes.

2. Description of the Prior Art

The metal surfaces of machinery or engines operating under heavy loads wherein metal slides against metal may undergo excessive wear or corrosion. Often the lubricants used to protect the metal surfaces deteriorate under such heavy loads and as a result, do not prevent wear at the points of metal to metal contact. Consequently, the performance of the machine or engine will suffer, and in aggravated cases the machine or engine may become completely inoperative.

There have been many attempts to devise additive systems which would provide satisfactory protection, but these have not always been successful. The metal phosphonate additives of the present invention are believed capable of overcoming some of the deficiencies of prior art additives and to provide lubricating oil compositions with enhanced anti-wear characteristics.

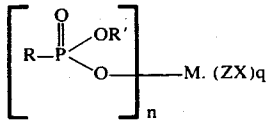
U.S. Pat. No. 2,758,971 describes a class of metal phosphonates which are disclosed as having properties which prevent breakdown of oils at high temperatures. These additives may be described as diorgano hydroxyorganophosphonates or certain metal salts thereof.

In another U.S. Pat. No. 2,792,374 are disclosed the alkali metal salts of certain alkyl alkylphosphonic acids as defoamants in aqueous systems.

U.S. Pat. No. 2,982,727 discloses lubricating oil compositions containing certain salts of oxygen-containing esters of phosphorus. The esters are phosphonates similar to those described in U.S. Pat. No. 2,758,971.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided a compound of the formula:



wherein R is hydrocarbyl containing from 14 to about 30 carbon atoms, R' is hydrocarbyl containing from 1 to about 6 carbon atoms, X is a basic nitrogen-containing compound, Z is from 1 to 4, q is 0 or 1, M is a metal selected from the group consisting of Groups IB, IIB, and IVA of the Periodic Table and n is the valence of M, q being 1 and n being 3 when M is gold and a method of depositing a metal on a lubricated surface by contacting the surface with a lubricant containing the copper, gold or silver compound or the complexes thereof.

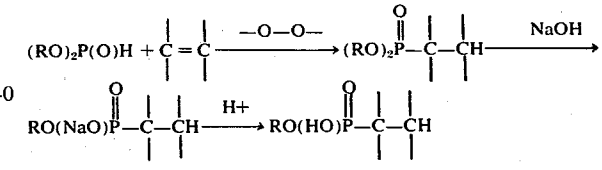
When used for anti-wear action, these compounds may be present in the lubricant in a concentration of from about 0.001 to about 10%, preferably from about 0.1 to about 5% by weight thereof.

DESCRIPTION OF SPECIFIC EMBODIMENTS

As has already been stated, R' of the above formula contains from 1 to about 6 carbon atoms. Preferably, R' will contain from 1 to 3 carbon atoms and more preferably R' will be the methyl group. Thus, among those compounds contemplated will be the following:

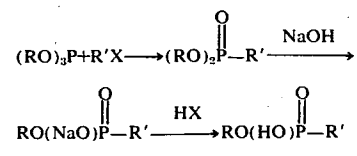
R'	R	M
methyl	tetradecyl	Cu, Au, Ag, Pb, Zn or Hg
methyl	eicosyl	do.
methyl	triacontyl	do.
ethyl	hexadecyl	do.
propyl	octadecyl	do.
butyl	docosyl	do.
pentyl	tricosyl	do.
hexyl	tetracosyl	do.

The above and other compounds may be prepared by known means. One such means involves as a first step, the preparation of the appropriate phosphonic acid by reacting a hydrogen phosphonate [$(RO)_2P(O)H$] and an olefin under the influence of a free-radical catalyst, hydrolysing one of the methyl groups in a basic medium and acidifying, essentially as follows:



The metal salts used in this invention may then be formed for example, by making the NH_4^+ salts of the phosphonic acid in solution and then displacing the NH_4^+ ion with the appropriate metal ion. The metal complex can be formed, in one way, by running the reaction in an excess of the basic compound.

As an alternative to the above scheme for making the phosphonic acid, the following is well known and may be used:



Several useful methods exist for producing the salts of this invention from the acid. Initially, ammonia or ammonium hydroxide may be reacted with the acid to form the intermediate ammonium phosphonate. This in turn is reacted with, for example, a gold or copper compound, preferably in the form of its halide (e.g., auric chloride), to yield the final salt or the metal complex when excess base is present.

More specifically the reaction between the ammonium phosphonate and the metal halide to form the salt is carried out, usually, at room temperature, or with moderate heating, using equimolar amounts of reactants. The reaction, which usually is run in water, produces a solid product which may be isolated from the reaction medium by any conventional means of separation.

For the most part, the metal phosphonates of this invention, as well as the complexes thereof, appear to function as most conventional additives do. That is, it is believed that they undergo chemical decomposition during use and that such decomposition products actually react with the metal of the surfaces being lubricated and form a film which reduces mechanical wear.

Several of the phosphonates of the present invention, however, do not depend for their effectiveness of forming a film by chemical reaction with the metal. It has been observed that the gold complexes and the silver and copper salts or their complexes, actually have their metal ions reduced to the free metal, which in turn forms a very thin film of such free metal on the surface being lubricated. The film thus deposited is a fixed, virtually permanent solid lubricant. In other words, the solid films formed permit the surfaces of the lubricated parts to move against each other with minimal wear, or no wear at all. Even if the solid film does wear, no substrate metal is lost (assuming some film is always present) because it is not chemically involved in the formation of the copper or gold film.

With respect to the gold, silver, and copper compounds, it is theorized that, since they deposit a coating of a solid that is softer than the metal substrate, this may provide improved lubrication by providing a softer, more yielding surface. However, no evidence has been found that this phenomenon of deposition is operative with the use of the other phosphonates disclosed herein.

The gold, silver and copper compounds of this invention are initially soluble in the oil phase. Breakdown during lubrication begins the deposition of the metallic solid upon the substrate metal of the mechanism being lubricated. Thus, the gold, silver and copper compounds can actually function two ways in keeping the sliding metal surfaces from wearing.

The phosphonates of this invention are preferably used in lubricating oil compositions. These include mineral oils, both paraffinic and naphthenic, and synthetic oils. These synthetic oils include synthetic ester lubricating oils such as esters of 2,2-disubstituted,1,3-propanediol, trimethylolpropane, or pentaerythritol with monocarboxylic acids having from 4 to about 25 carbon atoms. The synthetic oils also include polyolefin fluids, polysiloxane fluids, polyglycol ether fluids and polyphenyl ether and polyphenyl thioether fluids. Suitable thickners may be added to the liquid compositions to produce greases or other thickened forms of lubricants. Other additives, such as antioxidants and detergents, may also be present, collectively or alternatively.

The basic nitrogen-containing compound useful in forming the complexes of this invention may be selected from a wide range of materials. They include ammonia as well as primary, secondary, and tertiary alkyl amines, wherein the alkyl group contains from 1 to about 30 carbon atoms, primary, secondary and tertiary aryl amines, the aryl group containing from 6 to about 30 carbon atoms, the polyalkylene polyamines such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, nonaethylene decamine, and the like. Also included are heterocyclic amines, both cycloaliphatic and aromatic.

Illustrative of the alkylamines that may be used are the mono-, di-, and trimethylamines, the mono-, di-, and trihexylamines and the like. The mono-, di-, and triphenylamines illustrate aryl amines that one can employ. Pyridine is a useful heterocyclic aromatic amine.

The following specific embodiments will serve to illustrate the practice of this invention. It will be understood that no limitation on the scope of the invention is intended by such illustrations.

EXAMPLE 1

About 45g (0.2 mole) of 1-hexadecene and about 55g (0.5 mole) of dimethyl phosphite were placed in a reaction flask equipped with a stirrer, thermometer, reflux condenser, addition funnel, and a nitrogen inlet tube. The system was flushed well with nitrogen and the reaction mixture was stirred and warmed to about 150°C.

About 2.0g of di-t-butylperoxide was added slowly to the reaction mixture over about ¾ hour. The heating and stirring were continued during the addition and for 1½ hours thereafter. The excess dimethyl phosphite was removed under heat and vacuum distillation. 69.5g (0.2 mole) of dimethyl n-hexadecylphosphonate was recovered.

About 67g (0.2 mole) of the above dimethyl n-hexadecylphosphonate was mixed with a solution of about 10g (0.25 mole) of sodium hydroxide in about 150 ml of methanol. The mixture was stirred and warmed at the temperature of reflux for about 3 hours. The mixture was allowed to cool to room temperature and about 0.25 mole of HCl as concentrated hydrochloric acid solution was slowly added to the stirred mixture. This was followed by the addition of 500 ml of water. The product was recovered on a suction filter and washed twice, each time by stirring in a beaker with 500 ml of water, then recovering by suction filtration. The crude product was recrystallized from a hexane-petroleum ether mixture to give the pure methyl n-hexadecylphosphonate.

About 9.6g (0.03 mole) of the above methyl n-hexadecylphosphonate was mixed with a solution of 5 ml ammonium hydroxide (28–30% sp. g. 0.9). About 3.9g (0.1 mole) $HAuCl_4\ 3H_2O$ was dissolved in 20 ml of water and added to the phosphonate solution. An excess of ammonium hydroxide was added and the mixture was extracted twice with diethyl ether. The solvent was removed from the ether extract by distillation and the solid product was washed twice by stirring with water and decanting. The last of the water was removed from the product by azeotropic distillation with benzene and finally removing the benzene. A phosphonate was formed in which the gold was Au^{+3} and which was complexed with four parts of ammonia per part of gold phosphonate.

EXAMPLE 2

About 232g (0.75 mole) of 1-docosene and about 247g (2.25 moles) of dimethyl phosphite were placed in a reaction flask equipped with a stirrer, thermometer, reflux condenser (with a drying tube attached to the outlet), and an addition funnel. The flask was purged with nitrogen before adding the reagents. The

mixture was stirred and warmed to about 150°C. While maintaining the temperature, about 3g of di-t-butylperoxide was added in small increments over about one hour. The temperature of the stirred mixture was maintained at about 150°C for another hour after the peroxide addition was completed.

The mixture was allowed to cool and the apparatus was adapted for vacuum distillation. The excess dimethyl phosphite was removed by distillation up to a pot temperature of about 100°C and an estimated pressure of 10–20 mm Hg. 311g of dimethyl n-docosylphosphonate was recovered.

About 300g (0.72 mole) of the above dimethyl n-docosylphosphonate was mixed with a solution of about 40g (1 mole) of sodium hydroxide in about 450 ml of methanol. The mixture was stirred and warmed at reflux temperature (about 68°C) for about 3½ hours and was then allowed to cool. While the temperature was kept between 45°–50°C (to keep the product liquid) 83 ml of aqueous 37% hydrochloric acid solution and 400 ml water were added to the mixture. This produced an unfilterable emulsion at this stage. About two volumes of acetone were added and the product was isolated on a suction filter. The product was recrystallized from a solution of benzene and petroleum ether. After drying, 299g of methyl n-docosylphosphonate was obtained.

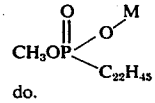
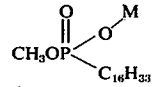
A small amount (e.g., 0.2 mole, about 8.1g) of the above methyl n-docosylphosphonate was dissolved in about 50 ml of warm 95% ethanol. An equivalent amount of a water soluble salt of the desired metal [e.g., 0.01 mole $Pb(NO_3)_2$, 0.02 mole $AgNO_3$, 0.01 mole $CuCl_2$, etc.] was mixed with the warm ethanol solution of the phosphonate and warmed on a steam bath for 10–15 minutes. After cooling, the solid product was isolated by filtration and purified by washing and recrystallization.

Alternately, the methyl n-docosylphosphonate was dissolved in an equivalent amount of ammonium hydroxide solution, then reacted with the metal ion.

EVALUATION OF PRODUCTS

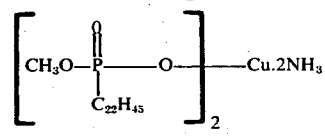
The test used to obtain the data in the following table was the well-known Shell Four-Ball Test. In this test, three steel balls of 52100 steel are held in a ball cup. A fourth ball positioned on a rotatable vertical shaft is brought into contact with the three balls and is rotated against them at a predetermined load. The test lubricant is added to the ball cup, and at the end of the test, the steel balls are examined for wear scar. The size of the scar and rate of wear per unit of sliding distance allow one to determine the effectiveness of the lubricant as an anti-wear agent.

The data in the table below was obtained by placing a metal methyl alkylphosphonate in n-hexadecane (except where noted) and running the above noted test under the conditions shown.

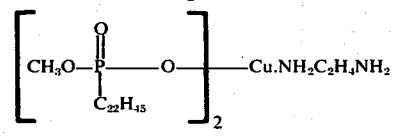
Metal, M	Metal Phosphonate	% Phosphonate	Temp, °F	Load, Kg	RPM	Time, Min.	Wear Scar, mm	Wear Rate, cc/cm
None	None	None	200	20	600	30	0.775	12.9×10^{-11}
Cu^{+2}		1.31	200	20	600	30	.349	$.38 \times 10^{-11}$
Hg^{+2}	do.	1.51	200	20	600	30	.302	$.16 \times 10^{-11}$
Ag^{+1}	do.	1.53	200	20	600	30	.370	$.51 \times 10^{-11}$
Pb^{+2}	do.	1.52	200	20	600	30	.483	1.77×10^{-11}
Au^{+3}		0.475	200	20	600	30	.368	$.50 \times 10^{-11}$
Au^{+3}	do.	0.475	300	20	600	30	.351	$.39 \times 10^{-11}$

Copper phosphonates were prepared in a manner similar to the procedure of Example 2. These, however, were complexed with nitrogen-containing compounds, and analyses for carbon, hydrogen, phosphorus, nitrogen and metal content indicated the following structures:

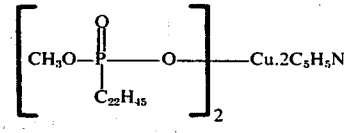
Example 3



Example 4

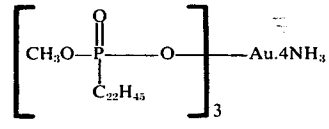


Example 5

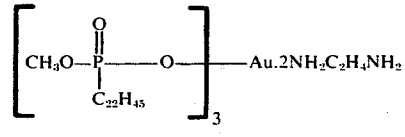


Similarly, additional complexes of gold phosphonates were prepared generally according to Example 1. Analyses indicated the following structures:

EXAMPLE 6



EXAMPLE 7

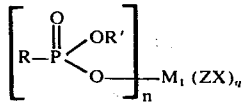


The compounds of Examples 3 to 7 were also tested in the Four-Ball Test described above. The phosphonate to be tested was placed in a base grease prepared by adding a modified clay thickener to polydecene fluid. The test was run for 30 minutes at 200°F under a 20 Kg load at 600 RPM. Following are illustrative results:

Example	% By Wt. Phosphonate	Wear Scar mm	Wear Rate cc/cm
—	none	0.401	0.76×10^{-11}
3	7.5	.338	$.31\times10^{-11}$
6	7.5	.354	$.40\times10^{-11}$
7	7.5	.356	$.42\times10^{-11}$

What is claimed is:

1. A method of depositing a free metal upon a lubricated metal surface comprising contacting said metal surface with a lubricant composition comprising a lubricant and from about 0.001 to about 10% of a compound of the formula



wherein R is a hydrocarbyl containing from 14 to about 30 carbon atoms, R′ is a hydrocarbyl containing from 1 to about 6 carbon atoms, X is a basic nitrogen-containing compound, Z is 1 to 4, q is 0 or 1, M is a metal selected from the group consisting of copper, silver and gold and n is the valence of M, q being 1 and n being 3 when M is gold wherein reduced metal is obtained, which metal is deposited on the lubricated surface.

2. The method of claim **1** wherein the reduced metal is gold.

3. The method of claim **1** wherein the reduced metal is copper.

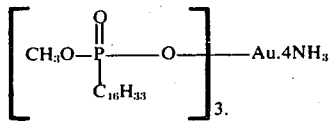
4. The method of claim **1** wherein the reduced metal is silver.

5. The method of claim **1** in which R is hexadecyl and R′ is methyl.

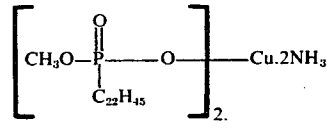
6. The method of claim **1** in which R is docosyl and R′ is methyl.

7. The method of claim **1** in which the lubricant is a polydecene fluid.

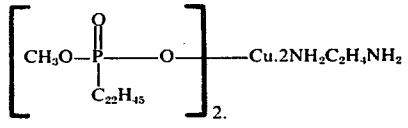
8. The method of claim **1** in which the compound is



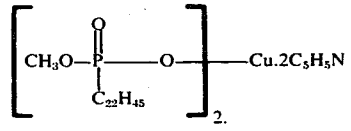
9. The method of claim **1** in which the compound is



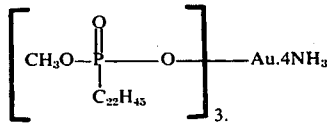
10. The method of claim **1** in which the compound is



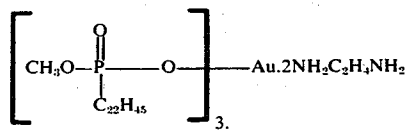
11. The method of claim **1** in which the compound is



12. The method of claim **1** in which the compound is



13. The method of claim **1** in which the compound is



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