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PHOSPHORODITHIOATE SALTS AS ANTIWEAR AGENTS

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ABSTRACT OF THE DISCLOSURE

The dihydrocarbyl phosphorodithioate salts of gold, in industrial fluids used to lubricate moving or sliding metal surfaces provide a unique phenomenon of depositing a layer of metal over the metal surfaces. This deposit aids in lubricating the moving metal by forming new contact surfaces and prevents wear of the metal substrate. This discovery represents also a novel method of depositing a metal coating upon a metal substrate and of improving the lubricating of metal surfaces under high torque or high shear movement.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to novel lubricating oil compositions containing gold phosphorodithioates, and to a novel means of protecting rubbing metal surfaces requiring antiwear protection.

Description of the prior art

U.S. Pat. Nos. 2,552,570, 3,102,096 and 3,210,275 describe metal phosphorodithioates useful for antioxidants and other functions in lubricating compositions. These additives function conventionally, in that they undergo chemical deterioration during use. It is believed that the products thereof react with the metal of the surfaces being lubricated and form a film consisting of this metal reaction product which reduces mechanical wear. However, this interaction causes chemical corrosion of the metal surfaces to some extent. Moreover, the shearing forces can also "wipe" away these films, thus, in effect, removing metal. Hence, these additives cannot always maintain a fixed film barrier between the metal surfaces.

SUMMARY OF THE INVENTION

It has now been discovered that by adding to a lubricating oil a dihydrocarbyl phosphorodithioate salt of gold, improved long-lasting antiwear protection is provided. The novel mechanism involves the chemical deposition and adhesion to the sliding metal surfaces being lubricated of a coating of the reduced gold.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Surprisingly, the gold dihydrocarbylphosphorodithioate salts of this invention avoid the disadvantages of the prior art by a novel mechanism. These salts deposit close, strongly bonded metallic coatings of gold metal directly onto the metal surfaces being lubricated as a fixed, almost permanent solid lubricant. In other words, solid films are formed thereby permitting the surfaces to move against each other with minimal or almost no wear at all to the metal substrate. Even if the solid film does wear, no substrate metal is lost because the substrate metal is not chemically involved in the formation of the metal film.

It is theorized that since the salts employed in this invention deposit a coating of a solid that is softer than the metal substrate, this may provide the improved lubrication obtained from the deposition. Steel, the usual metal of construction, is a harder metal than gold, the

novel effect of this invention may be obtained because the softer and therefore more yielding nature of the gold has unique lubricating properties. However, it has been found that the phenomenon of deposition accompanying the use of the salts of this invention is not observed with the use of other salts having metals softer than steel, i.e., zinc, copper, and the like. Such metal phosphorodithioates leave no apparent metallic deposit.

The salts of this invention are initially completely soluble in the oil phase. Breakdown during lubrication commences the chemical deposition of the metallic solid upon the metal of the engine, or motor, or bearings or whatever mechanism is being lubricated. As evidence of this increasing deposition, it has been unexpectedly found that the average wear rate of the metal substrate actually decreases with time.

The dihydrocarbyl salts of this invention are prepared by known means. They are salts of the phosphorodithioic acid



wherein R is a hydrocarbyl group, including alkyl, cycloalkyl, alkenyl, aralkyl, aryl, and alkaryl having from 3 to 30 carbon atoms.

These acids may be produced by known means by reacting an alcohol or phenol or naphthol with phosphorus pentasulfide. Propanol, butanol, pentanol, hexanol, decanol, hexadecanol, hexadecenol, phenol, benzylalcohol, naphthol, and the branched isomers and other alkyl derivatives thereof, are included. Alkyl-substituted aromatic hydroxy compounds may have from 3 to about 24 carbon atoms in the alkyl groups. Preferred are the dialkylphosphorodithioates containing 3 to 12 carbon atoms.

Many methods of producing the salts of this invention from the acid are well known. To illustrate one satisfactory method, the ammonium salt is first formed. Ammonia or ammonium hydroxide reacts with the acid to form the intermediate ammonium dihydrocarbylphosphorodithioate. The ammonium salt is then reacted with a gold compound to yield the final salt. The reacting compound is preferably a halide, such as auric chloride.

More specifically, the reaction between the ammonium phosphorodithioate and the gold halide is carried out usually at room temperature or with moderate heating using equimolar amounts of reactants. The reaction takes place in water. The phosphorodithioate salt precipitates out and may be isolated from the reaction mixture by the usual means of separation. As stated previously, this reaction is not a limitation of the present invention; alternative reactions may be employed.

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

The following more specific embodiments serve to illustrate the preferred mode of carrying out the invention. All parts of and percentages are on a weight basis.

EXAMPLE 1

Preparation of the ammonium diisopropylphosphorodithioate

Into a four-necked, three-liter flask equipped with a stirrer, thermometer, addition funnel, and a water take-

off-trap was added one liter of benzene. The benzene was heated to reflux until water (frequently present in trace amounts in benzene) ceased to enter the trap. The benzene was cooled to room temperature and the trap was replaced by a reflux condenser. About 222 grams (1 mole) of phosphorus pentasulfide was added. The mixture was stirred and heated to reflux using an inert nitrogen blanket. To this mixture was added slowly a solution of about 240 grams (4 moles) of isopropyl alcohol in benzene. An exothermic reaction accompanied this addition maintaining the temperature of the mixture at reflux. Heat was applied after the addition was completed until almost all of the solid phosphorus pentasulfide was reacted. The mixture was thereafter cooled and filtered to remove traces of the solid. The benzene was removed by distillation.

The acid remaining after the distillation was dissolved in a paraffinic hydrocarbon (30° to 60° petroleum ether) and the solution was cooled with ice water to about 15° C. The cooled solution was stirred and ammonia gas was added until precipitation of the ammonium salt was complete. The temperature was maintained at between 15° to 25° C. The precipitated ammonium salt was filtered off and dried. The yield was about 75% of theoretical.

EXAMPLE 2

Preparation of the gold diisopropyl phosphorodithioate

In a suitable reactor, about 0.3 mole of the ammonium O,O-diisopropylphosphorodithioate of Example 1 was dissolved in about 25 to 50 ml. of water and filtered. In another vessel, about 0.1 mole of $HAuCl_4 \cdot 3H_2O$ was dissolved in about 25 to 50 ml. of water. The gold solution was filtered and mixed with the filtered phosphorodithioate solution. A precipitate formed which was separated from the reaction mixture by filtration. The precipitate was recrystallized from methanol and 95% ethanol; the resulting product had a melting point of 109° to 110.5° C.

Analysis.—Calc'd for $C_6H_{14}O_2PS_2Au$ (percent): C, 17.57; H, 3.44; Au, 48.01; P, 7.55; S, 15.63. Found (percent): C, 17.45; H, 3.48; Au, 48.1; P, 7.11; S, 15.71.

EXAMPLE 3

Preparation of the gold dineopentyl phosphorodithioate

The steps of Examples 1 and 2 were repeated except that the alcohol was neopentyl alcohol. The recrystallization solvent was a 95% ethanol-acetone mixture. The product had a melting point of 189° to 190.5° C.

Analysis.—Calc'd for $C_{10}H_{22}O_2PS_2Au$ (percent): C, 25.76; H, 4.75; P, 6.64; S, 13.75; Au, 42.24. Found (percent): C, 25.51; H, 4.48; P, 6.01; S, 13.44; Au, 42.6.

EVALUATION OF THE PRODUCTS

The products of this invention were tested in the presence of hexadecane(cetane) for antiwear properties. The following test was used:

A stationary pin having a hemispherical tip is held upright against an axially-mounted rotatable disk 7.6 cm. in diameter. The disk can be rotated at a constant velocity. The pin describes a circle on the surface of the disk concentric with the axis thereof. Both pin and disk are submerged in a vessel holding the test lubricant so that the point of contact between the pin and the rotating disk in lubricated at all times. The force of the disk against the pin may be changed by varying a load outside of the lubricant vessel. Both the pin and the disk are AISI 1020 steel.

A series of lubricant test samples were tested in the pin-on-disk machine under a load of 8 kg. and a sliding velocity of 10 centimeters per second. The salt was aurous diisopropylphosphorodithioate dissolved in cetane at a concentration sufficient to provide 1.5×10^{-3} gram atoms of phosphorus per 100 grams of total composition.

The evaluation is the wear rate in units of cc./cm.: volume of metal worn away from the pin per distance traveled by the pin. Both wear volume and the coefficient of friction are also reported for each test. Comparison is made between lubricants containing aurous O,O-diisopropylphosphorodithioate and the corresponding zinc salt, at 93° C. and 149° C., and one lubricant containing no salt at all.

The results are tabulated below:

Metal	Temp., °C.	Time, min.	Wear rate, cc./cm.×10⁻⁹	Wear volume, cc.×10⁻⁵	Coefficient of friction
No salt	93		2,500		
Zinc	93	300	1.8	32.90	0.43
Zinc	149	290	0.29	5.13	0.23
Gold	93	300	0.050	0.89	0.08
Gold	149	301	0.0035	0.063	0.11

The same test was conducted using aurous O,O-dienopentylphosphorodithioate. The antiwear performance was as low as that of the isopropyl derivative. The following results were obtained:

Temperature, °C.	Test time, min.	Wear rate, cc./cm.×10⁻⁹	Wear volume, cc.×10⁻⁵	Coefficient of friction
93	308	0.0042	0.078	0.07
149	300	0.0060	0.11	0.06
93	301	*0.0053	0.096	0.12

*Concentration of salt at 4.5×10^{-4} gram atoms of phosphorus per 100 grams.

As described previously, it was noted unexpectedly that the effect of the gold salts of this invention is novel in that a solid layer of the metal is deposited upon the surfaces of the machine being lubricated. This effect is evidenced by increasing anti-wear protection with the passage of time. The following results were obtained using the same equipment and conditions as in the previous tests, except that the temperature was 93° C. throughout. The salt used was aurous O,O-dineopentyl-phosphorodithioate.

Duration of test, min.	Average wear rate, cc./cm.×10⁻⁹	Wear volume, cc.×10⁻⁵	Average coefficient of friction
15	0.043	0.039	0.19
30.5	0.030	0.056	0.04
60	0.015	0.056	0.06
105	0.0060	0.044	0.09
308	0.0042	0.078	0.07
1,000	0.0015	0.087	0.05

It may thus be seen that the wear rate decreases; the average wear rate of a 17-hour run is about 1/30 of the average rate of a 15-minute run. Inspection of the metal surfaces at the completion of the test showed that gold had been deposited thereon during the test. Improvement in the coefficient of friction shows that this solid deposit facilitates the passage of metal on metal.

Having described our invention we claim:

1. A fluid lubricant composition comprising a major proportion of an organic base fluid and a minor proportion sufficient to provide antiwear properties thereto of a gold dihydrocarbylphosphorodithioate salt.

2. The composition of claim 1 wherein the hydrocarbyl groups each contain 3 to about 30 carbon atoms.

3. The composition of claim 1 wherein the hydrocarbyl groups are selected from the groups consisting of alkyl, cycloalkyl, alkenyl, aralkyl, aryl and alkaryl.

4. The composition of claim 1 wherein the salt is an aurous salt.

5. The composition of claim 4 wherein the aurous salt is an aurous O,O-dialkylphosphorodithioate salt containing from 3 to 12 carbon atoms.

6. The composition of claim 5 wheren the hydrocarbyl group is isopropyl.

7. The composition of claim 5 wherein the hydrocarbyl group is neopentyl.

8. A method of depositing a metal upon a metal surface by contacting said metal surface with the composition of claim 1 under conditions which cause chemical deterioration of the said dihydrocarbyl salt.

9. A method of preventing undue wear of rubbing metal surfaces by lubricating said surfaces with the composition of claim 1.

10. The method of claim 9 wherein during the passage of said movement in the presence of the lubricant composition a layer of gold is deposited upon said rubbing metal surfaces.

11. The method of claim 10 wherein the lubricant composition contains an aurous dihydrocarbylphosphorodithioate salt and the deposited layer is gold.

12. The method of claim 9 wherein the rubbing metal surfaces are steel surfaces.

References Cited

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,554,908 Dated January 12, 1971

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 66, "in" should be -- is --. Column 4, footnote, "concentratlon" should be -- concentration --. Column 4, third table, first line under "Average Coefficie of Friction", "0.19" should be -- 0.10 --. Column 4, Claim 6, "wheren" should be -- wherein --.

Signed and sealed this 11th day of May 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
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WILLIAM E. SCHUYLER, JR.
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