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ZINC SALTS OF GLYCEROL MONOESTER DITHIOPHOSPHATES

George R. Tichelaar, Carmichael, Calif., and Roger W. Watson, Highland, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

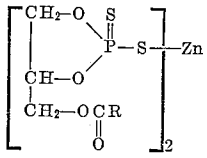
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This invention relates to new and useful zinc salts of substituted dithiophosphoric acids, and further relates to improvements in lubricant compositions by the inclusion of such salts therein.

It is known to use zinc dialkyl dithiophosphates in lubricating oil compositions to impart to such compositions certain desired properties, such as corrosion inhibiting properties. Lubricating oils containing such dialkyl dithiophosphates find particularly advantageous use as internal combustion engine lubricating oils. However, the zinc dialkyl dithiophosphates are often unstable at the higher internal combustion engine operating temperatures and tend to lose their desired properties.

It is an object of the present invention to provide new and useful zinc salts of substituted dithiophosphoric acids. It is another object of this invention to provide a zinc salt of a substituted dithiophosphoric acid which, when used as a lubricating oil addition agent for use in an internal combustion engine, is stable at higher internal combustion engine operating temperatures. It is a further object to provide lubricating oil compositions containing such zinc salts having desirable properties imparted thereto even at the higher operating temperatures. Other objects and advantages of the present invention will become apparent from the following description thereof.

In accordance with the present invention, the foregoing objects are attained by providing a zinc salt having the structural formula:



wherein R is an acyclic (open-chain) aliphatic hydrocarbon group having from 9 to about 65 carbon atoms, and preferably 9 to about 21 carbon atoms. R is the remainder of an acid.

The compounds of this invention are zinc salts of glycerol monoester dithiophosphates. They may be prepared by reacting 2 moles of a glycerol monoester with one mole of P_2S_5, e.g., at a temperature in the range of 125 to 150° F., and neutralizing the resulting glycerol monoester dithiophosphoric acid with 0.5 mole of a basic zinc compound, e.g., zinc oxide, per mole of the glycerol monoester dithiophosphoric acid, e.g., at a temperature in the range of 100–200° F.

The glycerol monoester may be prepared by reacting equimolar amounts of glycerin and a C_{10} or higher aliphatic carboxylic acid at about 200° C. until the acidity of the reaction mixture is less than 5 mg. KOH/g. This reaction usually gives off 110% of theoretical water.

The zinc salt of this invention may advantageously be used in a mineral lubricating oil in small amounts, e.g., from about 0.001 to about 10 weight percent, or more or less, and preferably from about one to about 5 weight percent. Additionally, concentrates of the zinc salt may be prepared in a suitable solvent in amounts of from about 10 weight percent to about 75 weight percent. Suitable solvents include lubricating oils, petroleum fractions in addition to petroleum lubricating oils, alcohols, such as hexanol, and the like.

The zinc salts are zinc salts of O,O-(glyceryl monoester) dithiophosphoric acid. The monoesters are monoesters of glycerol and open-chain aliphatic saturated or unsaturated carboxylic acids. Examples of suitable zinc salts are: zinc O,O-(glyceryl monolaurate) dithiophosphate, zinc O,O-(glyceryl monodecanoate) dithiophosphate, zinc O,O-(glyceryl monooleate) dithiophosphate, zinc O,O-(glyceryl monohexadecanoate) dithiophosphate, zinc O,O-(glyceryl monomyristate) dithiophosphate, zinc O,O-(glyceryl monodocosanoate) dithiophosphate, zinc O,O-(glyceryl monostearate) dithiophosphate, zinc O,O-(glyceryl monolinoleate) dithiophosphate, zinc O,O-(glyceryl monolinolenate) dithiophosphate, zinc O,O-(glyceryl monotrilinolenate) dithiophosphate, zinc O,O-(glyceryl monodilinolenate) dithiophosphate, zinc O,O-(glyceryl monopolylinolenate) dithiophosphate, etc. It is to be understood that mixtures of one or more of the salts encompassed within this disclosure may also be used. The salts formed from glycerol polymerized acid monoesters, e.g., zinc O,O-(glyceryl monopolylinoleate) dithiophosphate, have their R groups derived from polymeric acids, such as the polymeric acids prepared as by-products in the preparation of sebacic acid. Such polymeric acids generally consist of mixtures of monomer, dimer, trimer, and polymer of linoleic acid and may predominate in either trimer or dimer. Such mixtures of acids are available commercially and are usable in formation of compounds of this invention. Also usable in the formation of products of this invention are the glycerol monoesters of crude acids, such as the crude oleic aid marketed as Century CD Acid containing from about 80 to about 90% oleic acid and containing impurities in the form of acids in the C_{12} to C_{16} range; the Century CD Acid has an average molecular weight of about 220–250. Other usable crude acids are crude or whole tall oil, distilled fractions thereof, tall oil fatty acids, etc. In addition, the glycerol monoesters of other polymers of C_4 to C_{22} unsaturated acids are also intended. Such unsaturated acids and polymeric products thereof are well known in the art.

The active concentrate and/or lubricant composition can, of course, if desired, contain other addition agents, for example, additional corrosion inhibitors, such as sulfurized dipentene, a polymerized high molecular weight fatty acid, pour point depressors, additional anti-wear agents, anti-oxidants, sulfonates, V.I. improvers, etc.

The zinc salts of this invention function in the lubricating oil medium as corrosion and wear inhibitors and are especially effective against copper, silver and lead corrosion and wear, e.g., corrosion and wear of copper-lead bearings or silver-copper bearings. Additionally, in comparison with the zinc dialkyl dithiophosphate, the zinc salts of this invention inhibit the formation of carbon and lacquer on engine parts, e.g., in the piston grooves.

As a more particular illustration of the preparation of the zinc salts of this invention, the following are examples of preparation of the zinc salts of this invention.

Example I

111 g. (0.5 mole) of P_2S_5 in 60 g. of SAE 5 mineral oil was heated to a temperature of 130° F. and maintained in the temperature range of 130–145° F. while slowly adding thereto 244 g. (1.0 mole) of glycerol monodecanoate. After all of the glycerol monodecanoate was added, another 120 g. of SAE 5 mineral oil was added and the mixture was heated to 200° F. and held for three hours. The excess P_2S_5 was filtered from the mixture. 400 g. of resulting O,O-(glyceryl monodecanoate) dithiophosphoric acid were added to 36 g. (0.44 mole) of zinc oxide in 60 g. of SAE 5 mineral oil. The addition of the acid to zinc oxide in mineral oil was at such a rate so as to maintain the temperature at about 120° F. After all of the glyceryl monodecanoate dithio-

phosphoric acid was added, the mixture was held at 120–140° F. for one hour and then heated to 200° F. and blown dry with nitrogen. The product was filtered through a filter cell and recovered as filtrate.

Example II

Zinc O,O-(glyceryl monooleate) dithiophosphate was prepared in the same manner as in Example I using the same molar ratios of corresponding reactants.

Example III

Zinc O,O-(glyceryl monooleate) dithiophosphate was prepared in the same manner as Example I using the same molar amounts of corresponding reactants. The oleic acid used was a crude oleic acid marketed under the name Century CD Acid.

For purposes of comparison with the zinc salts of the present invention, the following zinc salts were also prepared:

Sample A—A zinc dialkyl dithiophosphate made from a mixture of 70 M percent isopropyl alcohol and 30 M percent oxodecyl alcohol and having a zinc content of 6.41 percent by weight.

Sample B—A commercial zinc dialkyl dithiophosphate corrosion inhibitor.

The effectiveness of the zinc salt addition agents of the present invention in inhibiting corrosion toward copper and/or lead-containing metals, as for example, copper-lead alloys used in engine bearings, is demonstrated by results of the following Sand Stirring Corrosion Test:

A copper-lead bearing test specimen is lightly abraded with steel wool, washed with naphtha, dried and weighed to the nearest milligram. The cleaned copper-lead test specimen is suspended in a steel beaker, cleaned with a hot trisodium phosphate solution, rinsed with water, and acetone, and dried, and 250 grams of the oil to be tested together with (0.5 weight percent) lead oxide and 50 grams of a 30–35 mesh sand charged to the beaker. The beaker is then placed in a bath or heating block and heated to a temperature of 300° F. (±2° F.) while the contents are stirred by means of a stirrer rotating at 750 r.p.m. The contents of the beaker are maintained at this temperature for 48 hours, after which the copper-lead test specimen is removed, rinsed with naphtha, dried and weighed. The test specimen is then replaced in the beaker and an additional 0.375 gram of lead oxide is added to the test oil. At the end of an additional 24 hours of test operation, the test specimen is again removed, rinsed, and dried, as before, and weighed. The loss in weight of the test specimen after 48 and 72 hours is recorded; a weight loss of 300 milligrams at 48 hours is considered failing.

Each of the addition agents identified in Table I below was tested in a solvent extracted SAE-30 mineral lubricating oil in an amount providing the equivalent of 0.6 volume percent of Sample A on a phosphorus basis. The results of the test were as follows:

TABLE 1.—SAND STIRRING CORROSION TEST

Addition Agent Identity	Copper-Lead Bearing Loss, Mg.	
	48 Hours	72 Hours
Example I	14.3	26.0
Example II	17.5	30.8
Example III	15.5	26.5
Sample A	28.5	234.3
Sample B	34.4	264.9

With reference to the above data, the weight loss using the compositions of this invention was lower than when using the zinc dialkyl dithiophosphate. The advantage was particularly noticeable after 72 hours. The data demonstrate excellent copper and lead corrosion inhibition over extended periods at high engine operating temperatures. In addition to the above test, the composition of the present invention was also subjected to the Modified EMD Test, a test designed to determine corrosion inhibition properties and particularly ability to inhibit the corrosion of silver parts. In this test, the oil samples used were formulated by adding the addition agent identified in Table 2 in an amount sufficient to provide 1.28 volume percent of Sample A or an equivalent amount of Example I on a phosphorus basis. The base oil was a sulfur extracted SAE-30 mineral lubricating oil containing 3.2 volume percent of a mixture of anti-foam agent and alkaline detergent (barium neutralized hydrolyzed phosphorus sulfide butylene polymer reaction product, neutralized in the presence of methanol and water). The silver corrosion inhibiting properties of a zinc salt of this invention (Example I) and of a prior art corrosion inhibitor (Sample A) are demonstrated by the data obtained from the following test designated the Modified EMD Test:

A strip of silver 2 cm. by 5.5 cm. with a small hole at one end for purposes of suspension is lightly abraded with No. 0 steel wool, scraped free of any adhering steel wool, washed with carbon tetrachloride, air dried, and then weighed to 0.1 mg. A sample of 300 grams of oil to be tested is placed in a 500 cc. lipless glass beaker, and the oil sample is heated to a temperature of 325° F. (±2° F.). The silver strip is then suspended in the oil so that the strip becomes completely immersed therein. The oil in the beaker is stirred by means of a glass stirrer operating at 300 r.p.m. At the end of 72 hours, the silver strip is removed, and while still hot, rinsed thoroughly with carbon tetrachloride, and air dried. The strip is then immersed in a 10% potassium cyanide solution at room temperature till the surface of the test strip assumes the original bright appearance. The strip is then washed successively with distilled water, and acetone, air dried, and weighed. The loss in weight over the test period is then determined as the difference in weight of the strip before and after the test. The weight loss in mg. is reported in Table 2.

TABLE 2

Addition agent:	Silver weight loss, mg.
Example I	8
Sample A	79

The data of Table 2 demonstrate the ability of the present addition agents to inhibit the corrosion of silver.

In addition, the composition of the present invention was also subjected to the L–38 Oxidation Stability Test, CRC designation L–38–559. This test is designed to determine oxidative stability of a motor oil. In accordance with the test procedure, the samples tested are used in motor lubricating oils in a single cylinder CLR (Labeco) engine. The test duration is 40 hours during which time the engine's speed is 3150 r.p.m., the load is 5 b.h.p., the air:fuel ratio is 14:1, the oil temperature is 280° F. and the water temperature is 200° F. After the test, the connecting rod bearing, a copper-lead bearing, is checked for bearing weight loss. The base oil used in the L–38 test was a solvent extracted mineral lubricating oil containing 2.4 volume percent total anti-foam and barium neutralized hydrolyzed phosphorus sulfide-butylene polymer (about 800 molecular weight) reaction product.

TABLE 3.—L–38 OXIDATION STABILITY TEST

Addition Agent		Bearing Wt. Loss, Mg.	
Identity	Amount, Wt. Percent	Top	Bottom
Example III	0.06	0.02	0.004
Sample A	0.06	0.04	0.130

The results of both Example III and Sample A are considered passing; however, the composition of Example III

gave superior results in bearing weight loss, especially on the bottom of the bearing.

Also the composition of the present invention was tested in accordance with a high temperature super-charged diesel test designed to determine the carbon and lacquer forming or inhibiting properties of addition agents. In accordance with this test procedure, a high temperature super-charged diesel engine is broken in by running 5 minutes at 500 r.p.m. at high load and then 5 minutes at 700 r.p.m. at high load. With the air intake pipe removed, 10 cc. of cleansing powder abrasive is slowly dusted in during a 2–3 minute period. The engine is then run in accordance with the following schedule sequence:

	R.P.M.	Load
10 min.	1,800	22 lbs.
10 min.	1,800	38 lbs.
10 min.	1,800	51 lbs.
20 min.	1,800	70 lbs. (air pressure 18 in. mercury gauge).

The engine is then checked down, the oil is drained, and the engine is recharged with 6 quarts of sample oil. The engine is restarted and run for 120 hours at 1800 r.p.m. and 70 lbs. load under the following conditions:

Water to cylinder block temperature, ° F.	180±10
Water from cylinder head temperature, ° F.	190±5
Oil to bearings temperature, ° F.	205±5
Air to engine temperature, ° F.	155
Oil to bearings pressure, p.s.i.	30
Air to engine pressure, Hg gauge	18
Fuel to injection pump pressure, p.s.i.	15–25

The test was run under the above conditions for 400 hours with engine oil drained every 120 hours. At the end of 480 hours, the piston is examined for percent carbon in the top groove and percent lacquer in the second groove; 30% carbon in the top groove and 30% lacquer in the second groove are considered maximum amounts for a passing result. After a number of tests utilizing the addition agents of Example III (representing this invention) and Sample A (representing the zinc dialkyl dithiophosphates) in amounts providing 0.1% zinc in an SAE 30 mineral lubricating oil, it was determined that the addition agent of this invention was superior in inhibiting build-up of carbon and lacquer compared with the zinc dialkyl dithiophosphate. Every test conducted using Example III passed the high temperature super-charged diesel test, i.e. resulted in less than 30% carbon in the top groove and 30% lacquer in the second groove, and the results usually gave about 15% carbon in the top groove and 15% lacquer in the second groove, while the zinc dialkyl dithiophosphate never passed the test and usually gave from 60–70% carbon in the top groove and from 70–80% black to amber lacquer in the second groove.

The results of the above tests establish the utility of the compositions of the present invention and actually demonstrate superiority over the zinc dialkyl dithiophosphate, especially in stability characteristics, e.g. at high temperatures.

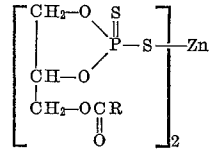
The herein described chemical compositions of the present invention can be used, as indicated above, in varying amounts in lubricating oils. Although the utility and preferred use of the compositions has been illustrated by the use of the chemical compositions as additives in mineral lubricating oils, it is not restricted thereto. Other lubricating oil bases can be used, such as hydrocarbon oils both natural and synthetic, for example, those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide type, and the mono- and poly-carboxylic acid ester type, such as the oil-soluble esters of pelargonic acid, adipic acid, sebacic acid, azaleic acid, etc. It is also contemplated, as indicated above, that various other well-known additives may be incorporated in lubricating oils containing the addition agents provided herein.

Unless otherwise stated, the percentages given herein and in the claims are percentages by weight.

It is evident from the foregoing that we have provided new and useful zinc salts of glycerol monoester dithiophosphates, and that we have also provided lubricating oil compositions containing same.

We claim:

1. As a composition of matter, a salt having the following structural formula:



wherein R is an acyclic aliphatic hydrocarbon having from 9 to about 21 carbon atoms.

2. The zinc salt of O,O-(glyceryl monodecanoate) dithiophosphoric acid.

3. The zinc salt of O,O-(glyceryl monooleate) dithiophosphoric acid.

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CHARLES B. PARKER, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

R. E. HUTZ, A. H. SUTTO, *Assistant Examiners.*