# THIOPHOSPHORIC ACID PRODUCTS FOR ANTIWEAR ADDITIVES

## TECHNICAL FIELD

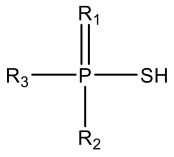
**[0001]** The present disclosure relates to thiophosphoric acid products suitable for preparing antiwear additives with improved copper corrosion.

## BACKGROUND

**[0002]** Lubricating compositions are designed to strike a balance between low wear and low friction and, at the same time, minimize other performance shortcomings. For instance, zinc dialkyl dithiophosphates, commonly known as ZDDP, are a widely used antiwear additive in lubricants such as engine oils, transmission fluids, and/or hydraulic oils. Ashless, i.e., metal-free, dithiophosphates are another common antiwear additive in use today. While both the metal and ashless dithiophosphates commonly have good antiwear and extreme pressure performance, these additives may have a tendency to corrode metal and, in particular, copper and bronze materials.

## SUMMARY

**[0002a]** In a first aspect of the present disclosure, there is provided a thiophosphoric acid product comprising at least a compound having the structure of Formula I




(Formula I)

wherein

$R_1$ is sulfur or oxygen;

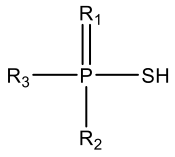
$R_2$ and $R_3$ are, independently, one of -$OR_4$ or -OH, and each $R_4$ if included is, independently, a C3 to C18 linear or branched alkyl group, a C5 to C6 cycloalkyl group, a phenyl group, or a C6 to C18 alkylphenol group; and

wherein the thiophosphoric acid product has 0.1 mmoles/gram or less of active sulfur as measured via titration with triphenyl phosphine.

**[0002b]** In another aspect of the present disclosure, there is provided an antiwear additive for lubricating compositions comprising the reaction product of the thiophosphoric acid product as disclosed herein and a reactant selected from (i) an unsaturated carboxylic acid, (ii) a basic or neutral metal compound including one or more of a metal oxide, a metal hydroxide, or a metal carbonate; or (iii) an unsaturated ester of a carboxylic acid.

**[0002c]** In a further aspect of the present disclosure, there is provided a lubricating composition including the antiwear additive as disclosed herein.

**[0003]** In one approach or example, an additive, a thiophosphoric acid product comprising at least a compound having the structure of Formula I




(Formula I)

wherein $R_1$ is sulfur or oxygen; $R_2$ and $R_3$ are, independently, one of $-OR_4$ or -OH, and each $R_4$ if included is, independently, a C3 to C18 linear or branched alkyl group, a C5 to C6 cycloalkyl group, a phenyl group, or a C6 to C18 alkylphenol group; and wherein the thiophosphoric acid product has about 0.1 mmoles/gram or less of active sulfur as measured via titration with triphenyl phosphine as described herein (in other approaches, about 0.08 mmoles/gram or less, about 0.05 mmoles/gram or less, or about 0.02 mmoles/gram or less).

**[0004]** The thiophosphoric acid product of the previous paragraph may include one or more optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein $R_1$ is sulfur, $R_2$ and $R_3$ are,

independently, the -$OR_4$ group with each $R_4$, independently, a C3 to C18 linear or branched alkyl group; and/or wherein the thiophosphoric acid product is substantially free of phosphorus polysulfide compounds; and/or wherein the thiophosphoric acid product includes phosphorus polysulfide compounds, but no more than about 1 weight percent of the phosphorus polysulfide compounds, no more than about 0.5 weight percent, no more than about 0.25 weight percent, no more than about 0.1 weight percent, or no amounts of the phosphorus polysulfide compounds; and/or wherein the compound of Formula I includes the reaction product of an organic hydroxy compound and phosphorus pentasulfide; and/or wherein the organic hydroxy compound is provided in a molar ratio relative to the phosphorus pentasulfide of about 4:1 to about 10:1; and/or wherein the organic hydroxy compound is one or more of methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, tert-butyl alcohol, sec-butyl alcohol, phenol, naphthol, an amyl alcohol, hexyl alcohol, iso-hexyl alcohol, octyl alcohol, decyl alcohol, dodecyl alcohol, octadecyl alcohol, 2-ethylhexyl alcohol, 4-methyl-2-pentyl alcohol, phenyl alcohol, butylphenyl alcohol, cyclohexyl alcohol, methylcyclopentyl alcohol, propenyl alcohol, butenyl alcohol, or combinations thereof; and/or wherein the thiophosphoric acid product is distilled and recovered as a condensate of the distillation; and/or wherein the distillation occurs at a temperature of at least about 80°C and/or a pressure of at least about 0.4 torr; and/or wherein the condensate is recovered at a temperature of about 10°C or less; and/or wherein the distillation occurs in a falling-film evaporator, a wiped-film evaporator, a thin-film evaporator, a short-path evaporator, or combinations thereof; and/or wherein the compound of Formula I is selected from a dipropyl dithiophosphoric acid, a diisopropyl dithiophosphoric acid, a dibutyl dithiophosphoric acid, a diisobutyl dithiophosphoric acid, a di-ethylhexyl dithiophosphoric acid, or combinations thereof.

**[0005]** In yet another approach or example, an antiwear additive for lubricating compositions comprising the reaction product of the thiophosphoric acid product of any above-described example and a reactant selected from (i) an unsaturated carboxylic acid, (ii) a basic or neutral metal compound including one or more of a metal oxide, a metal hydroxide, or a metal carbonate; or (iii) an unsaturated ester of a carboxylic acid.

**[0006]** In yet other approaches, the antiwear additive of the previous paragraph may include further optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein the reactant is (i) the

unsaturated ester of a carboxylic acid and wherein the unsaturated ester of a carboxylic acid is an C1 to C20 alkyl (meth)acrylate; and/or wherein the unsaturated ester of a carboxylic acid is methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, or combinations thereof; and/or wherein the reactant is (ii) the basic or neutral metal compound and includes a metal oxide, a metal hydroxide, or a metal carbonate of aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, zirconium, zinc, or combinations thereof; and/or wherein the basic or neutral metal compound is a molar excess of zinc oxide; and/or wherein the reactant is (iii) the unsaturated carboxylic acid and wherein the unsaturated carboxylic acid is a C3 to C20 unsaturated fatty acid; and/or wherein the unsaturated carboxylic acid is acrylic acid, methacrylic acid, 2-ethyl acrylic acid, or combinations thereof.

**[0007]** In yet another approach, a lubricating composition including the antiwear additive of any example herein is further described by this disclosure.

**[0008]** In yet another approach, the use of any example of the thiophosphoric acid product herein for preparing an antiwear additives is also described herein by this disclsoure.

**[0009]** Other examples of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the disclosure disclosed herein. The following definitions of terms are provided in order to clarify the meanings of certain terms as used herein.

**[00010]** The terms “gear oil,” “gear fluid,” “gear lubricant,” “base gear lubricant,” “lubricating oil,” “lubricant composition,” “lubricating composition,” “lubricant” and “lubricating fluid” refer to a finished lubrication product comprising a major amount of a base oil plus a minor amount of an additive composition as discussed herein. In one approach, such fluids are for use in extreme pressure situations such as for transmissions and gear drive components having metal-on-metal contact situations, for instance, in a transmission and/or a limited-slip differential. In other approaches, such fluids are suitable for lubricating a crankcase of an engine.

**[00011]** As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly hydrocarbon character. Each hydrocarbyl group is independently selected from hydrocarbon substituents, and substituted hydrocarbon substituents containing one or more of

halo groups, hydroxyl groups, alkoxy groups, mercapto groups, nitro groups, nitroso groups, amino groups, pyridyl groups, furyl groups, imidazolyl groups, oxygen and nitrogen, and wherein no more than two non-hydrocarbon substituents are present for every ten carbon atoms in the hydrocarbyl group.

**[00012]** As used herein, the term "percent by weight" or “wt%”, unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition. All percent numbers herein, unless specified otherwise, is weight percent.

**[00013]** The terms "soluble," "oil-soluble," or "dispersible" used herein may, but does not necessarily, indicate that the compounds or additives are soluble, dissolvable, miscible, or capable of being suspended in the oil in all proportions. The foregoing terms do mean, however, that they are, for instance, soluble, suspendable, dissolvable, or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

**[00014]** The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties from about 1 to about 200 carbon atoms. The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties from about 3 to about 30 carbon atoms. The term “aryl” as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, and oxygen.

**[00015]** As used herein, the molecular weight is determined by gel permeation chromatography (GPC) using commercially available polystyrene standards (with a Mn of about 180 to about 18,000 as the calibration reference). The molecular weight (Mn) for any example herein may be determined with a gel permeation chromatography (GPC) instrument obtained from Waters or the like instrument and the data processed with Waters Empower Software or the like software. The GPC instrument may be equipped with a Waters Separations Module and Waters Refractive Index detector (or the like optional equipment). The GPC operating conditions may include a guard column, 4 Agilent PLgel columns (length of 300×7.5 mm; particle size of 5 µ, and pore size ranging from 100-10000 Å) with the column temperature at about 40 °C. Un-stabilized HPLC grade tetrahydrofuran (THF) may be used as solvent, at a

flow rate of 1.0 mL/min. The GPC instrument may be calibrated with commercially available polystyrene (PS) standards having a narrow molecular weight distribution ranging from 500 – 380,000 g/mol. The calibration curve can be extrapolated for samples having a mass less than 500 g/mol. Samples and PS standards can be in dissolved in THF and prepared at concentration of 0.1-0.5 weight percent and used without filtration. GPC measurements are also described in US 5,266,223, which is incorporated herein by reference. The GPC method additionally provides molecular weight distribution information; *see, for example,* W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979, also incorporated herein by reference.

**[00016]** As used herein, active sulfur of any example of the thiophosphoric acid products herein is determined as follows: triphenyl phosphine (about 65 mg or about 0.25 mmol) is dissolved in about 4 ml of $d^6$-benzene in a suitable reaction flask equipped with a magnetic stirring bar. To this solution is added the thiophosphoric acid product (about 157 mg) and the reaction left to stir for about 24 hours at ambient temperature or approximately 20°C. A proton decoupled $^{31}$P-NMR spectrum is then acquired on a reaction sample taken at 24 hours using a Bruker Avance-3 HD 500MHz instrument or equivalent equipped with a 5mm BBO Prodigy probe operating at a frequency of 202.47 MHz with D1 = 10 seconds. Peaks corresponding to triphenyl phosphine (TPP, δ -5 ppm), triphenyl phosphine oxide (TPPO, δ 29 ppm) and triphenyl phosphine sulfide (TPPS, δ 43 ppm) were integrated and then active sulfur calculated as

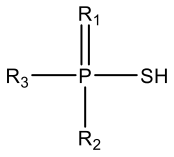
$$Active\ Sulfur = \frac{Integral\ TPPS}{Sum\ of\ Integrals\ for\ TPPS, TPPO\ and\ TPP} \times \frac{TPP\ \{in\ mmoles\}}{sample\ mass\ \{in\ grams\}}$$

**[00017]** It is to be understood that throughout the present disclosure, the terms "comprises," "includes," "contains," etc. are considered open-ended and include any element, step, or ingredient not explicitly listed. The phrase "consists essentially of" is meant to include any expressly listed element, step, or ingredient and any additional elements, steps, or ingredients that do not materially affect the basic and novel examples of the disclosure. The present disclosure also contemplates that any composition described using the terms, "comprises," "includes," "contains," is also to be interpreted as including a disclosure of the same composition "consisting essentially of" or "consisting of" the specifically listed components thereof.

## CLAIMS

WHAT IS CLAIMED IS

1. A thiophosphoric acid product comprising at least a compound having the structure of Formula I



(Formula I)

wherein

$R_1$ is sulfur or oxygen;

$R_2$ and $R_3$ are, independently, one of -$OR_4$ or -OH, and each $R_4$ if included is, independently, a C3 to C18 linear or branched alkyl group, a C5 to C6 cycloalkyl group, a phenyl group, or a C6 to C18 alkylphenol group; and

wherein the thiophosphoric acid product has 0.1 mmoles/gram or less of active sulfur as measured via titration with triphenyl phosphine.

2. The thiophosphoric acid product of claim 1, wherein $R_1$ is sulfur, $R_2$ and $R_3$ are, independently, the -$OR_4$ group with each $R_4$, independently, a C3 to C18 linear or branched alkyl group.

3. The thiophosphoric acid product of claim 1, wherein the thiophosphoric acid product is substantially free of phosphorus polysulfide compounds.

4. The thiophosphoric acid product of claim 3, wherein the thiophosphoric acid product includes phosphorus polysulfide compounds, but no more than 1 weight percent of the phosphorus polysulfide compounds.

5. The thiophosphoric acid product of claim 1, wherein the compound of Formula I includes the reaction product of an organic hydroxy compound and phosphorus pentasulfide.

6. The thiophosphoric acid product of claim 5, wherein the organic hydroxy compound is provided in a molar ratio relative to the phosphorus pentasulfide of 4:1 to 10:1.

7. The thiophosphoric acid product of claim 5, wherein the organic hydroxy compound is one or more of methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, tert-butyl alcohol, sec-butyl alcohol, phenol, naphthol, an amyl alcohol, hexyl alcohol, iso-hexyl alcohol, octyl alcohol, decyl alcohol, dodecyl alcohol, octadecyl alcohol, 2-ethylhexyl alcohol, 4-methyl-2-pentyl alcohol, phenyl alcohol, butylphenyl alcohol, cyclohexyl alcohol, methylcyclopentyl alcohol, propenyl alcohol, butenyl alcohol, or combinations thereof.

8. The thiophosphoric acid product of claim 1, wherein the thiophosphoric acid product is distilled and recovered as a condensate of the distillation.

9. The thiophosphoric acid product of claim 8, wherein the distillation occurs at a temperature of at least 80° C. and/or a pressure of at least 0.4 torr.

10. The thiophosphoric acid product of claim 9, wherein the condensate is recovered at a temperature of 10° C. or less.

11. The thiophosphoric acid product of claim 8, wherein the distillation occurs in a falling-film evaporator, a wiped-film evaporator, a thin-film evaporator, a short-path evaporator, or combinations thereof.

12. The thiophosphoric acid product of claim 1, wherein the compound of Formula I is selected from a dipropyl dithiophosphoric acid, a diisopropyl dithiophosphoric acid, a dibutyl dithiophosphoric acid, a diisobutyl dithiophosphoric acid, a di-ethylhexyl dithiophosphoric acid, or combinations thereof.

13. An antiwear additive for lubricating compositions comprising the reaction product of the thiophosphoric acid product of claim 1 and a reactant selected from (i) an unsaturated

carboxylic acid, (ii) a basic or neutral metal compound including one or more of a metal oxide, a metal hydroxide, or a metal carbonate; or (iii) an unsaturated ester of a carboxylic acid.

14. The antiwear additive of claim 13, wherein the reactant is (i) the unsaturated ester of a carboxylic acid and wherein the unsaturated ester of a carboxylic acid is an C1 to C20 alkyl (meth)acrylate.

15. The antiwear additive of claim 14, wherein the unsaturated ester of a carboxylic acid is methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, or combinations thereof.

16. The antiwear additive of claim 13, wherein the reactant is (ii) the basic or neutral metal compound and includes a metal oxide, a metal hydroxide, or a metal carbonate of aluminum, lead, tin, molybdenum, manganese, nickel, copper, titanium, zirconium, zinc, or combinations thereof.

17. The antiwear additive of claim 16, wherein the basic or neutral metal compound is a molar excess of zinc oxide.

18. The antiwear additive of claim 13, wherein the reactant is (iii) the unsaturated carboxylic acid and wherein the unsaturated carboxylic acid is a C3 to C20 unsaturated fatty acid.

19. The antiwear additive of claim 18, wherein the unsaturated carboxylic acid is acrylic acid, methacrylic acid, 2-ethyl acrylic acid, or combinations thereof.

20. A lubricating composition including the antiwear additive of claim 13.