ANTIWEAR SYSTEM FOR IMPROVED COPPER CORROSION

TECHNICAL FIELD

[0001] The present disclosure relates to oil-soluble phosphorus antiwear additives and to lubricating composition including the oil-soluble phosphorus 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. However, the zinc provided by such additives can be less desired in some applications leading to an increased use of so-called ashless or metal-free antiwear additives. Ashless (i.e., metal-free) dithiophosphates are one such alternative, but while ashless dithiophosphates have good antiwear and extreme pressure performance, these additives may have a tendency to corrode metal and, in particular, copper and bronze metals.

SUMMARY

[0003] In one approach or example, the present disclosure describes a lubricating composition comprising a majority of one or more base oils of lubricating viscosity; and an oil-soluble phosphorus antiwear additive made by a process comprising the steps of (a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) distilling the reaction product and recovering a condensate; and (c) reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive.

[0003a] In one aspect, the present disclosure refers to a lubricating composition comprising:

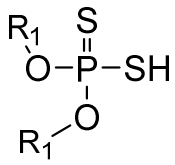
a majority of one or more base oils of lubricating viscosity; and

an oil-soluble phosphorus antiwear additive made by a process comprising the steps of

(a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) distilling the reaction product and recovering a condensate; and (c) reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive; wherein

the reaction product comprises diesters of dithiophosphoric acids having the structure of Formula 1 below; and

the condensate includes the diesters of dithiophosphoric acids having the structure of Formula 1 below and having a content of phosphorus polysulfides derived from the reaction product of less than 1 wt%



Formula 1

wherein R_1 is a residue derived from an organic hydroxy compound.

[0004] In another approach or example, the lubricating composition described in the previous paragraph may include optional features and/or examples in any combination. These optional features or examples may include one or more of the following: wherein the distillation occurs at one or more of a temperature of at least about 50°C, a pressure of at least about 0.1 torr, or combinations thereof; 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 condensate includes a dialkyl dithiophosphoric acid; and/or wherein the dialkyl dithiophosphoric acid is dipropyl dithiophosphoric acid, diisopropyl dithiophosphoric acid, dibutyl dithiophosphoric acid, diisobutyl dithiophosphoric acid, or combinations thereof; and/or wherein the unsaturated carboxylic acid is an C1 to C20 fatty acid; and/or wherein the unsaturated fatty acid is acrylic acid, methacrylic acid, 2-ethyl acrylic acid, or combinations thereof; and/or wherein the organic hydroxy compound is a C1 to C6 linear or branched alcohol, a hydroxyl aryl compound, or mixtures thereof; and/or wherein the organic hydroxy compound is 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 organic hydroxy compound is isobutyl alcohol, the reaction product comprises diisobutyl dithiophosphoric acid and one or more phosphorus polysulfides, the condensate includes the diisobutyl dithiophosphoric acid and is substantially free of the one or more phosphorus polysulfides, and the condensate is further reacted with methacrylic acid to form the oil-soluble phosphorus antiwear additive; and/or wherein the lubricating composition includes about 0.1 to about 5 weight percent of the oil-soluble phosphorus antiwear additive; 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 unsaturated carboxylic acid is provided in a molar ratio relative to the organic hydroxy compound of about 0.01:1 to about 0.5:1.

[0005] In yet another approach or example, a method of preparing an oil-soluble phosphorus antiwear additive is provided by this disclosure where the method comprises reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; distilling the reaction product and recovering a condensate therefrom; and reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive.

[0005a] In one aspect, the present disclosure refers to a method of preparing an oil-soluble phosphorus antiwear additive, the method comprising:

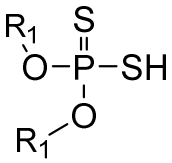
reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product;

distilling the reaction product and recovering a condensate therefrom; and

reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive; wherein

the reaction product comprises diesters of dithiophosphoric acids having the structure of Formula 1 below; and

the condensate includes the diesters of dithiophosphoric acids having the structure of Formula 1 below and having a content of phosphorus polysulfides derived from the reaction product of less than 1 wt%



Formula 1

wherein R_1 is a residue derived from an organic hydroxy compound.

[0006] In other approaches or examples, the method of the previous paragraph may include optional features, steps, or examples in any combination. These optional features,

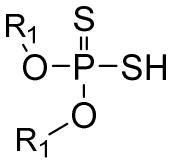
step, or examples may include one or more of the following: wherein the distillation occurs at a temperature of at least about 50°C; and/or wherein the distillation occurs at a pressure of at least about 0.1 torr; and/or wherein the condensate is recovered at a temperature of about 10°C or less; and/or 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 condensate includes a dialkyl dithiophosphorus acid; and/or wherein the dialkyl dithiophosphoric acid is dipropyl dithiophosphoric acid, diisopropyl dithiophosphoric acid, dibutyl dithiophosphoric acid, diisobutyl dithiophosphoric acid, or combinations thereof; and/or wherein the unsaturated carboxylic acid is an C1 to C20 fatty acid; and/or wherein the fatty acid is acrylic acid, methacrylic acid, 2-ethyl acrylic acid, or combinations thereof; and/or wherein the organic hydroxy compound is a C1 to C6 linear or branched alcohol, a hydroxy aryl compound, or mixtures thereof; and/or wherein the organic hydroxy compound is 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 organic hydroxy compound is isobutyl alcohol, the reaction product comprises diisobutyl dithiophosphoric acid and one or more phosphorus polysulfides, the condensate includes the diisobutyl dithiophosphoric acid and is substantially free of the one or more phosphorus polysulfides, and the condensate is further reacted with methacrylic acid to form the oil-soluble phosphorus antiwear additive; 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 unsaturated carboxylic acid is provided in a molar ratio relative to the organic hydroxy compound of about 0.01:1 to about 0.5:1.

[0007] In yet a further approach or example, an oil-soluble phosphorus antiwear additive is described herein wherein the additive is made by a process comprising the steps of (a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) distilling the reaction product and recovering a condensate therefrom; and (c) reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive. In yet other examples, the oil-soluble phosphorus antiwear additive may include

any of the optional features or examples as described by any example of the lubricant or method herein. In one aspect, the present disclosure refers to an oil-soluble phosphorus antiwear additive made by a process comprising the steps of (a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) distilling the reaction product and recovering a condensate therefrom; and (c) reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive; wherein

the reaction product comprises diesters of dithiophosphoric acids having the structure of Formula 1 below; and

the condensate includes the diesters of dithiophosphoric acids having the structure of Formula 1 below, having the content of phosphorus polysulfides derived from the reaction product of less than 1 wt%



Formula 1

wherein R_1 is a residue derived from an organic hydroxy compound.

[0008] In yet further approaches or examples, the use of evaporation or distillation to recover a condensate from the reaction product of an organic hydroxy compound reacted with phosphorus pentasulfide is described herein and wherein the condensate is further reacted with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive. The use herein may include any further example as described in this Summary

[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 for use in lubricating 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] 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 aspects 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.

BRIEF DESCRIPTION OF DRAWINGS

[00017] FIG. 1 is a ^{31}P NMR spectra of Comparative and Inventive hydraulic fluids including alkylated diisobutyl dithiophosphate antiwear additives of the present disclosure;

[00018] FIGS. 2 and 3 are plots of copper corrosion for two different treat rates of alkylated diisobutyl dithiophosphate antiwear additives in Comparative and Inventive hydraulic fluids;

[00019] FIG 4 is an image representing the comparative reaction product between an organic hydroxy compound and phosphorus pentasulfide; and

[00020] FIG. 5 is an image representing a condensate obtained from the distillation of reaction products between the organic hydroxy compound and the phosphorus pentasulfide.

DETAILED DESCRIPTION

[00021] Disclosed herein are improved ashless antiwear additives and lubricating compositions including such improved ashless antiwear additives providing good antiwear performance with improved copper corrosion at the same time. In one approach or embodiment, the ashless antiwear additives are oil-soluble phosphorus antiwear additives. In one aspect, the lubricating compositions herein include at least one or more base oils of lubricating viscosity and a novel ashless dithiophosphate ester antiwear additive. In another aspect, the oil-soluble phosphorus antiwear additives herein are prepared by (a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) evaporating and/or distilling the reaction product and recovering a condensate therefrom to provide a distilled reaction product including a diester of a dithiophosphoric acid; and (c) reacting the condensate with an organic

CLAIMS

WHAT IS CLAIMED IS

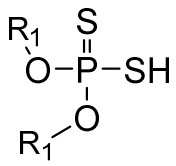
1. A lubricating composition comprising:

a majority of one or more base oils of lubricating viscosity; and

an oil-soluble phosphorus antiwear additive made by a process comprising the steps of (a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) distilling the reaction product and recovering a condensate; and (c) reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive; wherein

the reaction product comprises diesters of dithiophosphoric acids having the structure of Formula 1 below; and

the condensate includes the diesters of dithiophosphoric acids having the structure of Formula 1 below and having a content of phosphorus polysulfides derived from the reaction product of less than 1 wt%



Formula 1

wherein R_1 is a residue derived from an organic hydroxy compound.

2. The lubricating composition of claim 1, wherein the distillation occurs at one or more of a temperature of at least 50° C., a pressure of at least 0.1 torr, or combinations thereof; and/or wherein the condensate is recovered at a temperature of 10° C. or less.

3. The lubricating composition of claim 1, wherein the distillation occurs in a falling-film evaporator, a wiped-film evaporator, a thin-film evaporator, a short-path evaporator, or combinations thereof.

4. The lubricating composition of claim 1, wherein the condensate includes a dialkyl dithiophosphoric acid.

5. The lubricating composition of claim 4, wherein the dialkyl dithiophosphoric acid is dipropyl dithiophosphoric acid, diisopropyl dithiophosphoric acid, dibutyl dithiophosphoric acid, diisobutyl dithiophosphoric acid, or combinations thereof.

6. The lubricating composition of claim 1, wherein the unsaturated carboxylic acid is an C1 to C20 fatty acid.

7. The lubricating composition of claim 6, wherein the unsaturated fatty acid is acrylic acid, methacrylic acid, 2-ethyl acrylic acid, or combinations thereof.

8. The lubricating composition of claim 1, wherein the organic hydroxy compound is a C1 to C6 linear or branched alcohol, a hydroxyl aryl compound, or mixtures thereof.

9. The lubricating composition of claim 8, wherein the organic hydroxy compound is 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.

10. The lubricating composition of claim 1, wherein the organic hydroxy compound is isobutyl alcohol, the reaction product comprises diisobutyl dithiophosphoric acid and one or more phosphorus polysulfides, the condensate includes the diisobutyl dithiophosphoric acid and is substantially free of the one or more phosphorus polysulfides, and the condensate is further reacted with methacrylic acid to form the oil-soluble phosphorus antiwear additive.

11. The lubricating composition of claim 1, wherein the lubricating composition includes 0.1 to 5 weight percent of the oil-soluble phosphorus antiwear additive.

12. The lubricating composition of claim 1, wherein the organic hydroxy compound is provided in a molar ratio relative to the phosphorus pentasulfide of 4:1 to 10:1.

13. The lubricating composition of claim 12, wherein the unsaturated carboxylic acid is provided in a molar ratio relative to the organic hydroxy compound of 0.01:1 to 0.5:1.

14. A method of preparing an oil-soluble phosphorus antiwear additive, the method comprising:

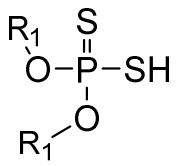
reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product;

distilling the reaction product and recovering a condensate therefrom; and

reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive; wherein

the reaction product comprises diesters of dithiophosphoric acids having the structure of Formula 1 below; and

the condensate includes the diesters of dithiophosphoric acids having the structure of Formula 1 below and having a content of phosphorus polysulfides derived from the reaction product of less than 1 wt%



Formula 1

wherein R_1 is a residue derived from an organic hydroxy compound.

15. The method of claim 14, wherein the distillation occurs at a temperature of at least 50°C.

16. The method of claim 15, wherein the distillation occurs at a pressure of at least 0.1 torr.

17. The method of claim 14, wherein the condensate is recovered at a temperature of 10° C. or less.

18. The method of claim 14, wherein the distillation occurs in a falling-film evaporator, a wiped-film evaporator, a thin-film evaporator, a short-path evaporator, or combinations thereof.

19. The method of claim 14, wherein the condensate includes a dialkyl dithiophosphorus acid.

20. The method of claim 19, wherein the dialkyl dithiophosphoric acid is dipropyl dithiophosphoric acid, diisopropyl dithiophosphoric acid, dibutyl dithiophosphoric acid, diisobutyl dithiophosphoric acid, or combinations thereof.

21. The method of claim 19, wherein the unsaturated carboxylic acid is an C1 to C20 fatty acid.

22. The method of claim 21, wherein the fatty acid is acrylic acid, methacrylic acid, 2-ethyl acrylic acid, or combinations thereof.

23. The method of claim 14, wherein the organic hydroxy compound is a C1 to C6 linear or branched alcohol, a hydroxy aryl compound, or mixtures thereof.

24. The method of claim 23, wherein the organic hydroxy compound is 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.

25. The method of claim 14, wherein the organic hydroxy compound is isobutyl alcohol, the reaction product comprises diisobutyl dithiophosphoric acid and one or more phosphorus polysulfides, the condensate includes the diisobutyl dithiophosphoric acid and is substantially free of the one or more phosphorus polysulfides, and the condensate is further reacted with methacrylic acid to form the oil-soluble phosphorus antiwear additive.

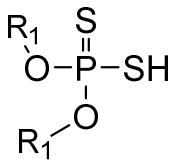
26. The method of claim 14, wherein the organic hydroxy compound is provided in a molar ratio relative to the phosphorus pentasulfide of 4:1 to 10:1.

27. The method of claim 26, wherein the unsaturated carboxylic acid is provided in a molar ratio relative to the organic hydroxy compound of 0.01:1 to 0.5:1.

28. An oil-soluble phosphorus antiwear additive made by a process comprising the steps of (a) reacting an organic hydroxy compound with phosphorus pentasulfide to form a reaction product; (b) distilling the reaction product and recovering a condensate therefrom; and (c) reacting the condensate with an unsaturated carboxylic acid to form the oil-soluble phosphorus antiwear additive; wherein

the reaction product comprises diesters of dithiophosphoric acids having the structure of Formula 1 below; and

the condensate includes the diesters of dithiophosphoric acids having the structure of Formula 1 below, having the content of phosphorus polysulfides derived from the reaction product of less than 1 wt%



Formula 1

wherein R_1 is a residue derived from an organic hydroxy compound.