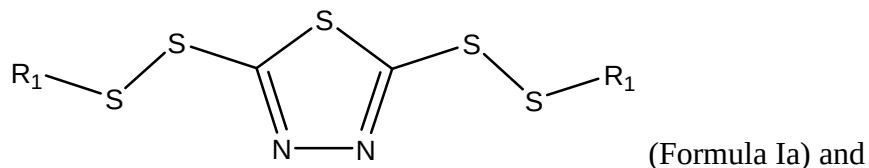


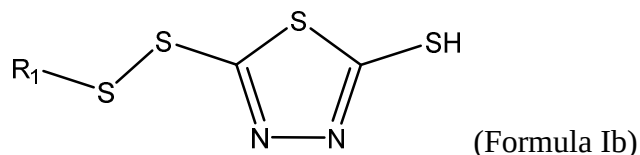
SUMMARY

[0004] In one approach or example, a corrosion inhibitor is described herein made by a process comprising (a) reacting a 1,3,4-dimercapto thiadiazole or alkali metal salt thereof with an alkyl mercaptan in the presence of an acid to form a first reaction intermediate; (b) reacting the first reaction intermediate with hydrogen peroxide to form the corrosion inhibitor; and (c) wherein the 1,3,4-dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : greater than 2.0.

[0005] In other approaches or examples, the corrosion inhibitor of the previous paragraph may be combined with optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein the acid is a strong acid provided in molar excess to the 1,3,4-dimercapto thiadiazole; and/or wherein the corrosion inhibitor is about 95 weight percent or more of a 2,5-dialkyl-dithiothiadiazole compound and about 5 weight percent or less of a monoalkyl-dithiothiadiazole compound; and/or wherein the corrosion inhibitor has a total acid number of 10 or less; and/or wherein the process further includes heating the corrosion inhibitor to a temperature effective to separate any aqueous layer and optionally subjecting the heated corrosion inhibitor to a vacuum strip; and/or wherein the 2,5-dialkyl-dithiothiadiazole compound has the structure of Formula Ia:



wherein the monoalkyl-dithiothiadiazole compound has the structure of Formula Ib:



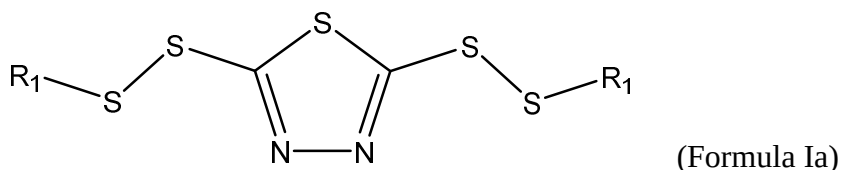
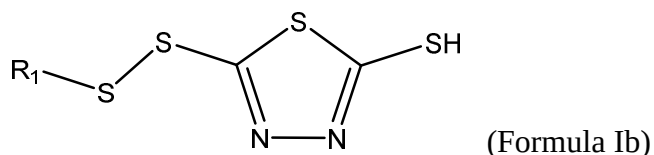
wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbyl group; and/or wherein the alkyl moiety of the alkyl mercaptan is an aliphatic or aromatic hydrocarbyl group; and/or wherein the alkyl moiety of the alkyl mercaptan is a linear or branched C₁ to C₃₀ hydrocarbyl group; and/or wherein the dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 - 2.4.

[0005a] In one aspect, the present disclosure refers to a corrosion inhibitor made by a process comprising:

(a) reacting a 1,3,4-dimercapto thiadiazole or alkali metal salt thereof with an alkyl mercaptan in the presence of an acid to form a first reaction intermediate;

(b) reacting the first reaction intermediate with hydrogen peroxide to form the corrosion inhibitor; and

(c) wherein the 1,3,4-dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 - 2.4; the corrosion inhibitor is a blend of about 95 mol percent or more of a 2,5-dialkyl-dithiothiadiazole compound of Formula Ia and about 5 mol percent or less of a monoalkyl-dithiothiadiazole compound of Formula Ib:

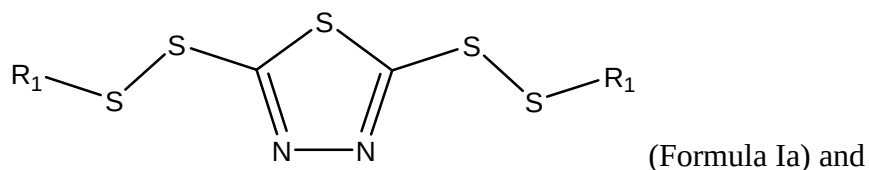


wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbyl group.

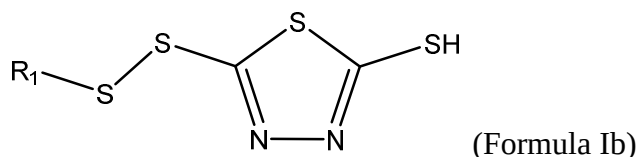
[0006] In another approach or example, a lubricant is described herein comprising: (a) a

majority of base oil; and (b) a corrosion inhibitor made by a process comprising: (i) reacting a 1,3,4-dimercapto thiadiazole or alkali metal salt thereof with an alkyl mercaptan in the presence of an acid to form a first reaction intermediate; (ii) reacting the first reaction intermediate with hydrogen peroxide to form the corrosion inhibitor; and (iii) wherein the 1,3,4-dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : greater than 2.0.

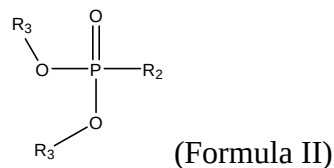
[0007] In other approaches or examples, the lubricant of the previous paragraph may be combined with optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein the acid is a strong acid provided in molar excess to the 1,3,4-dimercapto thiadiazole; and/or further comprising one or more phosphonate ester compounds including, based on the total weight percent of phosphonate ester compounds, about 90 weight percent or more of a phosphonate diester and no more than about 10 weight percent of a phosphonate monoester; and/or wherein the corrosion inhibitor is about 95 weight percent or more of a 2,5-dialkyl-dithiothiadiazole compound and about 5 weight percent or less of a monoalkyl-dithiothiadiazole compound; and/or wherein the 2,5-dialkyl-dithiothiadiazole compound has the structure of Formula Ia:



wherein the monoalkyl-dithiothiadiazole compound has the structure of Formula Ib:

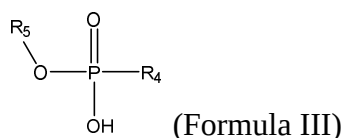


wherein each R₁ of Formula Ia and/or Formula Ib is, independently, a linear or branched C₄ to C₂₀ hydrocarbyl group; and/or wherein the phosphonate diester has a structure of Formula II



wherein R₂ is a C₁ to C₅₀ hydrocarbyl group and each R₃ is, independently, a C₁ to C₂₀ alkyl group; and/or wherein the phosphonate diester is dimethyl octadecyl phosphonate (DMOP);

and/or wherein the phosphonate monoester has a structure of Formula III

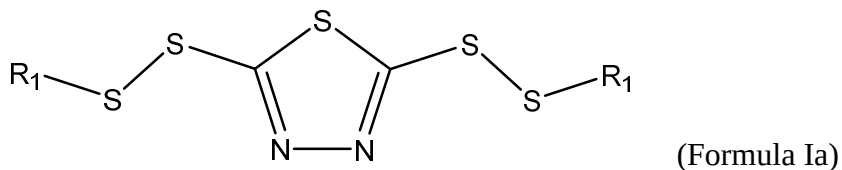
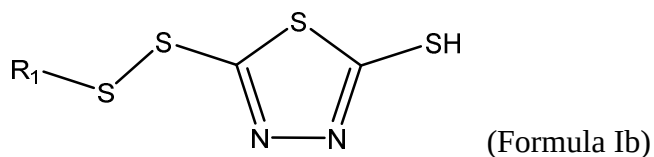


wherein R₄ is a C1 to C50 hydrocarbyl group and R₅ is a C1 to C20 alkyl group; and/or wherein the phosphonate monoester is methyl octadecyl phosphonate (MOP); and/or wherein the process further includes heating the corrosion inhibitor to a temperature effective to separate any aqueous layer and optionally subjecting the heated corrosion inhibitor to a vacuum strip; and/or wherein the lubricant exhibits a FAG FE8 roller bearing weight loss of about 12 mg or less pursuant to DIN 51819-3 after 80 hours of runtime at 80°C, 7.5 rpm, and 100 kN.

[0007a] In one aspect, the present disclosure refers to a lubricant comprising:

- (a) a majority of base oil; and
- (b) a corrosion inhibitor made by a process comprising:
 - (i) reacting a 1,3,4-dimercapto thiadiazole or alkali metal salt thereof with an alkyl mercaptan in the presence of an acid to form a first reaction intermediate;
 - (ii) reacting the first reaction intermediate with hydrogen peroxide to form the corrosion inhibitor; and
 - (iii) wherein the 1,3,4-dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 – 2.4;

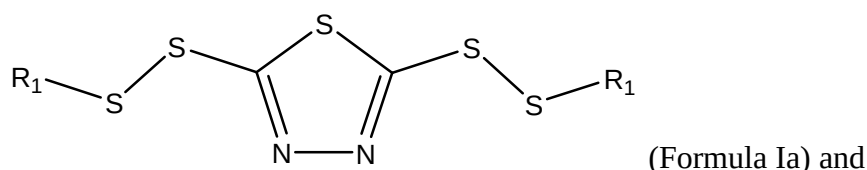
wherein the corrosion inhibitor is a blend of about 95 mol percent or more of a 2,5-dialkyl-dithiothiadiazole compound of Formula Ia and about 5 mol percent or less of a monoalkyl-dithiothiadiazole compound of Formula Ib:



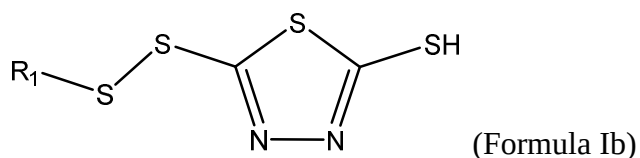
wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C4 to C20 hydrocarbyl group.

[0008] In yet further approaches or examples, a corrosion inhibitor additive is described herein comprising: (a) about 95 weight percent or more of a 2,5-dialkyl-dithiothiadiazole compound; (b) a monoalkyl-dithiothiadiazole compound, but no more than about 5 weight percent of the monoalkyl-dithiothiadiazole compound; and (c) wherein the total acid number of the corrosion inhibitor additive is about 10 or less.

[0009] In other approaches or examples, the corrosion inhibitor additive of the previous paragraph may be combined with optional features or examples in any combination. These optional features or examples may include one or more of the following: wherein the 2,5-dialkyl-dithiothiadiazole compound has the structure of Formula Ia:



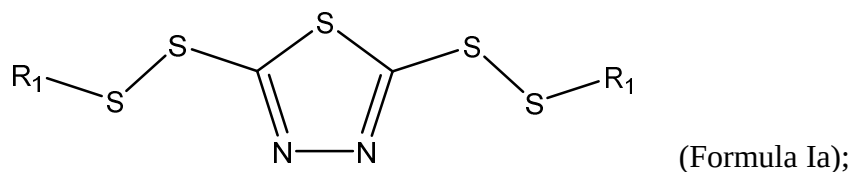
wherein the monoalkyl-dithiothiadiazole compound has the structure of Formula Ib:



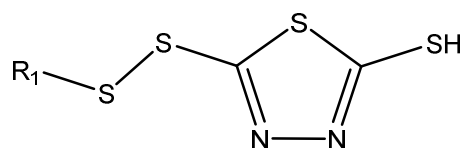
wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbyl group; and/or wherein the corrosion inhibitor is obtained from a dimercapto thiadiazole or alkali metal salt thereof, an alkyl mercaptan, and a hydrogen peroxide provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 - 2.4.

[0009a] In one aspect, the present disclosure refers to a corrosion inhibitor additive comprising:

(a) about 95 mol percent or more of a 2,5-dialkyl-dithiothiadiazole compound of Formula Ia:



(b) a monoalkyl-dithiothiadiazole compound, but no more than about 5 mol percent of the monoalkyl-dithiothiadiazole compound of Formula Ib:



(Formula Ib); and

(c) wherein the total acid number of the corrosion inhibitor additive is about 10 or less;
and

wherein the corrosion inhibitor is obtained from a dimercapto thiadiazole or alkali metal salt thereof, an alkyl mercaptan, and a hydrogen peroxide provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 - 2.4;

wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbyl group.

[00010] In yet further approaches or examples, the use of any example of the

corrosion inhibitor or lubricant of this Summary is described for achieving a passing FAG FE8 roller bearing weight loss of about 12 mg or less pursuant to DIN 51819-3 after 80 hours of runtime at 80°C, 7.5 rpm, and 100 kN

[00011] 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.

[00012] 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. Such gear 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 (manual or automatic) and/or a gear differential.

[00013] 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.

[00014] As used herein, the term “percent by weight” or “wt%” or “weight percent”, 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.

[00015] 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.

[00016] 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.

[00017] 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. Unstabilized 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 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.

[00018] 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 DRAWING FIGURES

[00019] FIG. 1 is a graph of weight percent MOP in a comparative and inventive industrial lubricant subjected to aging at about 40°C; and

[00020] FIG. 2 is a graph of weight percent MOP in a comparative and inventive industrial lubricant aged at about 55°C.

DETAILED DESCRIPTION

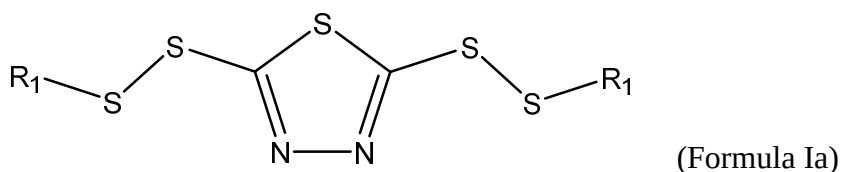
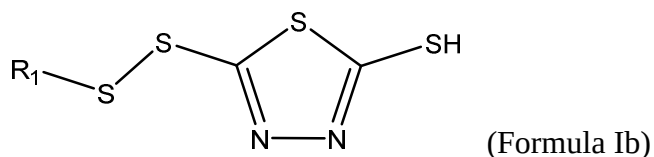
[00021] In one approach or embodiment, disclosed herein are corrosion inhibitors suitable for heavy-duty and/or industrial lubricants and industrial lubricating compositions including such corrosion inhibitors. In some embodiments, the industrial lubricating compositions herein include unique corrosion inhibitors combined with one or more phosphonate diesters to provide good copper corrosion and roller bearing protection at the same time. The corrosion inhibitors and lubricants including such corrosion inhibitors are suitable for use as industrial gear oils for transmission fluids (i.e., manual, automatic, or dual-clutch transmissions), gear fluids, axle fluids, differential fluids, and/or lubricating fluids for other gear-type applications configured for heavy-duty use such as turbines, wind turbines, and the like.

[00022] In one aspect of the present disclosure, a corrosion inhibitor is made by a unique process with select molar ratios of a dimercapto thiadiazole or alkali metal salt thereof, an alkyl mercaptan, and a hydrogen peroxide to form a corrosion inhibitor maximizing a dialkyl-dithiothiadiazole content. In other approaches or embodiments, the corrosion inhibitor has a maximized amount of the dialkyl thiadiazole compound with about 95 weight percent or more of a 2,5-dialkyl-dithiothiadiazole compound and about 5 weight percent or less of a monoalkyl-dithiothiadiazole compound.

CLAIMS

WHAT IS CLAIMED IS

1. A corrosion inhibitor made by a process comprising:
 - (a) reacting a 1,3,4-dimercapto thiadiazole or alkali metal salt thereof with an alkyl mercaptan in the presence of an acid to form a first reaction intermediate;
 - (b) reacting the first reaction intermediate with hydrogen peroxide to form the corrosion inhibitor; and
 - (c) wherein the 1,3,4-dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 - 2.4; the corrosion inhibitor is a blend of about 95 mol percent or more of a 2,5-dialkyl-dithiothiadiazole compound of Formula Ia and about 5 mol percent or less of a monoalkyl-dithiothiadiazole compound of Formula Ib:

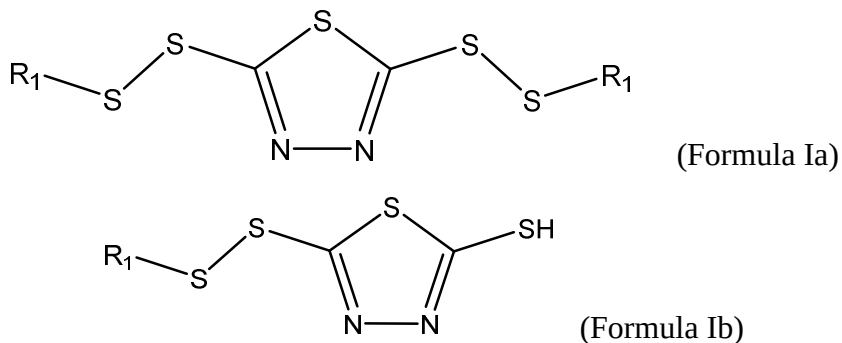


wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbonyl group.

2. The corrosion inhibitor of claim 1, wherein the acid is a strong acid provided in molar excess to the 1,3,4-dimercapto thiadiazole.
3. The corrosion inhibitor of claim 1, wherein the corrosion inhibitor has a total acid number of 10 or less.
4. The corrosion inhibitor of claim 1, wherein the process further includes heating the corrosion inhibitor to a temperature effective to separate any aqueous layer and optionally subjecting the heated corrosion inhibitor to a vacuum strip.

5. A lubricant comprising:
- (a) a majority of base oil; and
 - (b) a corrosion inhibitor made by a process comprising:
 - (i) reacting a 1,3,4-dimercapto thiadiazole or alkali metal salt thereof with an alkyl mercaptan in the presence of an acid to form a first reaction intermediate;
 - (ii) reacting the first reaction intermediate with hydrogen peroxide to form the corrosion inhibitor; and
 - (iii) wherein the 1,3,4-dimercapto thiadiazole or alkali metal salt thereof, the alkyl mercaptan, and the hydrogen peroxide are provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 – 2.4;

wherein the corrosion inhibitor is a blend of about 95 mol percent or more of a 2,5-dialkyl-dithiothiadiazole compound of Formula Ia and about 5 mol percent or less of a monoalkyl-dithiothiadiazole compound of Formula Ib:

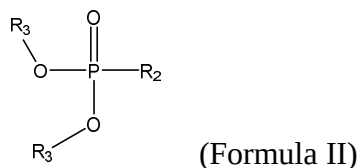


wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbyl group.

6. The lubricant of claim 5, wherein the acid is a strong acid provided in molar excess to the 1,3,4-dimercapto thiadiazole.

7. The lubricant of claim 5, further comprising one or more phosphonate ester compounds including, based on the total weight percent of phosphonate ester compounds, about 90 weight percent or more of a phosphonate diester and no more than about 10 weight percent of a phosphonate monoester.

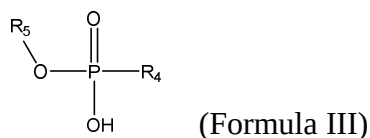
8. The lubricant of claim 7, wherein the phosphonate diester has a structure of Formula II



wherein R₂ is a C₁ to C₅₀ hydrocarbyl group and each R₃ is, independently, a C₁ to C₂₀ alkyl group.

9. The lubricant of claim 8, wherein the phosphonate diester is dimethyl octadecyl phosphonate.

10. The lubricant of claim 7, wherein the phosphonate monoester has a structure of Formula III



wherein R₄ is a C₁ to C₅₀ hydrocarbyl group and R₅ is a C₁ to C₂₀ alkyl group.

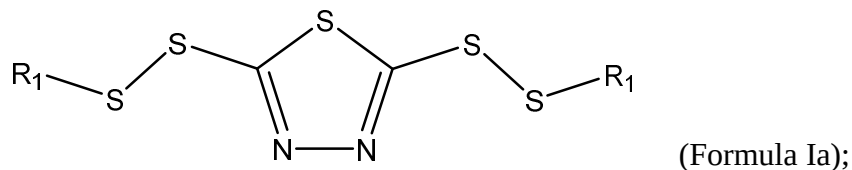
11. The lubricant of claim 10, wherein the phosphonate monoester is methyl octadecyl phosphonate.

12. The lubricant of claim 5, wherein the process further includes heating the corrosion inhibitor to a temperature effective to separate any aqueous layer and optionally subjecting the heated corrosion inhibitor to a vacuum strip.

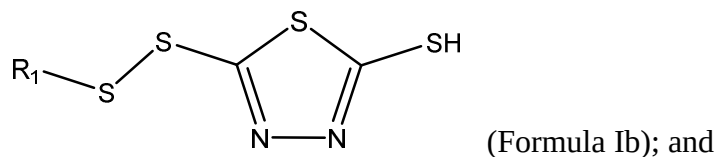
13. The lubricant of claim 5, wherein the lubricant exhibits a FAG FE8 roller bearing weight loss of about 12 mg or less pursuant to DIN 51819-3 after 80 hours of runtime at 80°C, 7.5 rpm, and 100 kN.

14. A corrosion inhibitor additive comprising:

(a) about 95 mol percent or more of a 2,5-dialkyl-dithiothiadiazole compound of Formula Ia:



(b) a monoalkyl-dithiothiadiazole compound, but no more than about 5 mol percent of the monoalkyl-dithiothiadiazole compound of Formula Ib:



(c) wherein the total acid number of the corrosion inhibitor additive is about 10 or less;
and

wherein the corrosion inhibitor is obtained from a dimercapto thiadiazole or alkali metal salt thereof, an alkyl mercaptan, and a hydrogen peroxide provided at a molar ratio of 1 : 1.95 - 2.15 : 2.1 - 2.4;

wherein each R₁ of Formula Ia and/or Formula Ib is independently a linear or branched C₄ to C₂₀ hydrocarbyl group.