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2,799,652

CORROSION RESISTANT COMPOSITION

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This invention relates to improved compositions which are effective corrosion inhibitors and which are non-corrosive to silver, silver alloys and similar metals. More particularly, the invention pertains to lubricant compositions which are non-corrosive to such metals and inhibit the corrosion thereof by sulfur and/or corrosive sulfur-containing compounds.

Advances in the design and construction of internal combustion engines aimed at increased efficiency and economy have led to lubrication problems. To meet the increased severe demands upon engines, many types of lubricant additives have been developed to obtain certain desired characteristics. Among the more effective addition agents which have been developed for compounding with lubricants are many sulfur-containing organic compounds, such as sulfurized terpenes, sulfurized hydrocarbon oils, vegetable oils or animal oils, xanthate esters, organic polysulfides, particularly polyalkyl polysulfides, metal salts of organo-substituted thioacids of phosphorus, metal salts of the reaction product of a phosphorus sulfide and a hydrocarbon, such as for example, polybutenes and other polyolefins, and combinations of the foregoing.

Recent increased use of silver and similar metals in the construction of improved internal combustion engines has created new problems in the use of sulfur-containing additives in lubricants for such engines; the primary problem created being the corrosion of such silver parts of the engine by the sulfur-containing additives. While such corrosion can be eliminated by avoiding the use of sulfur-containing additives in lubricants for such engines, this solution of the problem is accompanied by the loss of the highly desired beneficial effects of the additives of this type.

It is an object of the present invention to provide a non-corrosive composition. Another object of the invention is to provide a composition non-corrosive to silver and similar metals. A still further object of the invention is to provide a composition which will inhibit the corrosion of silver and similar metals by sulfur and/or organic sulfur-containing compounds. A still further object of the invention is to provide a lubricant composition which is non-corrosive. Still another object of the invention is to provide a lubricant composition containing an addition agent which will inhibit the corrosion of silver and similar metals by sulfur and/or organic sulfur-containing compounds. A further object of the invention is to provide a method of inhibiting the corrosion of silver and similar metals. Still another object of the invention is to provide a method of lubricating internal combustion engines containing silver and similar metal parts, and inhibiting the corrosion of such metals by lubricants which contain sulfur and/or organic sulfur-containing compounds.

In accordance with the present invention, the foregoing objects can be attained by employing in oleaginous materials from about 0.02% to about 10%, and preferably from about 0.25% to about 5%, of the oil-soluble product obtained by reacting 2,5-dimercapto-1,3,4-thiadiazole with

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an unsaturated ketone in the molar ratio of from 1:2 to 4:1. The reaction is carried out by heating the mixture of the thiadiazole and unsaturated ketone at a temperature of from about 40° C. to about 140° C. for a period of 0.5 hour to about 16 hours. To facilitate the reaction a solvent such as dioxane, Cellosolve, ethylene glycol, ethyl ether, etc., can be used.

The ketone can be an aliphatic, aromatic or heterocyclic unsaturated ketone containing from about 4 to about 40 carbons and from 1 to 6 double bonds. Mixtures of such unsaturated ketones can also be used. Examples of such ketones are mesityl oxide, phorone, isophorone, benzal acetophenone, furfural acetone, difurfural acetone, butylidene methyl ethyl ketones, etc.

The following examples are illustrative of the preparation of the above referred to reaction products:

EXAMPLE I

A solution of 41.0 grams (0.2 mole) benzal acetophenone and 15 grams (0.1 mole) 2,5-dimercapto-1,3,4-thiadiazole in 50 cc. dioxane was refluxed for 5 hours and the mixture then cooled. The cooled mixture was poured into water, the lower layer taken up in benzene, washed with water and dried. The dried solution was filtered and the filtrate freed of benzene by evaporation. A dark viscous product having a sulfur content of 15.3%, a nitrogen content of 4.38%, a carbon content of 69.5% and a hydrogen content of 4.89% was recovered.

EXAMPLE II

A mixture of 30 grams (.2 mole) 2,5-dimercapto-1,3,4-thiadiazole and 55 cc. (.44 mole) mesityl oxide was heated at 85–90° C. for 6 hours and the resultant clear dark solution stripped in vacuo. The recovered product had a sulfur content of 37.6% and a nitrogen content of 10.8%.

The above-described reaction products can be used in amounts of from about 0.02% to about 10%, and preferably from about 0.25% to about 5%, in combination with lubricant base oils, such as hydrocarbon oils, synthetic hydrocarbon oils, such as those obtained by the polymerization of hydrocarbons, such as olefin polymers; synthetic lubricating oils of the alkylene-oxide type, for example, the "Ucon oils," marketed by Carbide and Carbon Corporation, as well as other synthetic oils, such as the polycarboxylic acid ester-type oils, such as the esters of adipic acid, sebacic acid, maleic acid, azelaic acid, etc.

While the above-described reaction products can be suitably employed alone in combination with a base oil, they are usually used in combination with other lubricant addition agents which impart various desired characteristics to the base oil. Usually, these reaction products are used in conjunction with detergent-type additives, particularly those which contain sulfur and/or phosphorus and sulfur. Additives of this type are usually used in amounts of from about 0.002% to about 10%, and preferably from about 0.01% to about 5%. Among the phosphorus- and sulfur-containing addition agents are the neutralized reaction products of a phosphorus sulfide and a hydrocarbon, an alcohol and a ketone, an amine or an ester. Of the phosphorus sulfide reaction product additives, the neutralized reaction products of a phosphorus sulfide, such as a phosphorus pentasulfide, and a hydrocarbon of the type described in U. S. 2,316,082, issued to C. M. Loane et al. April 6, 1943, are preferred. As taught in this patent, the preferred hydrocarbon constituent of the reaction is a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefin hydrocarbons, such as propylene, butenes, amylenes or copolymers thereof. Such polymers may be obtained by the polymerization of mono-olefins of less than 6 carbon atoms in the presence of a

catalyst, such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and iso-mono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably from about 500 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid phase of a hydrocarbon mixture containing mono- and isomono-olefins, such as butylene and iso-butylene at a temperature of from about -80°F. to about 100°F. in the presence of a metal halide catalyst of the Friedel-Crafts type, such as for example, boron fluoride, aluminum chloride, and the like. In the preparation of these polymers a hydrocarbon mixture containing iso-butylene, butylenes and butanes recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline can be used.

Another suitable polymer is that obtained by polymerizing, in the liquid phase, a hydrocarbon mixture comprising substantially C_3 hydrocarbons in the presence of an aluminum chloride-complex catalyst. The catalyst is preferably prepared by heating aluminum chloride with isooctane. The hydrocarbon mixture is introduced into the bottom of the reactor and passed upwardly through the catalyst layer, while a temperature of from about 50°F. to about 110°F. is maintained in the reactor. The propane and other saturated gases pass through the catalyst while the propylene is polymerized under these conditions. The propylene polymer can be fractionated to any desired molecular weight, preferably from about 500 to about 1000, or higher.

Other suitable polymers are those obtained by polymerizing a hydrocarbon mixture containing about 10% to about 25% isobutylene at a temperature of from about 0°F. to about 100°F. , and preferably 0°F. to about 32°F. in the presence of boron fluoride. After the polymerization of the isobutylene, together with a relatively minor amount of the normal olefins present, the reaction mass is neutralized, washed free of acidic substances, and the unreacted hydrocarbons subsequently separated from the polymers by distillation. The polymer mixture so obtained, depending upon the temperature of reaction, varies in consistency from a light liquid to viscous oily material and contains polymers having molecular weights ranging from about 100 to about 2000, or higher. The polymers so obtained may be used as such or the polymers may be fractionated under reduced pressure into fractions of increasing molecular weights and suitable fractions obtained reacted with the phosphorus sulfide to obtain the desired reaction products. The bottoms resulting from the fractionation of the polymer which have Saybolt Universal viscosities at 210°F. ranging from about 50 seconds to about 10,000 seconds are well suited for this purpose.

Essentially paraffinic hydrocarbons, such as bright stock residuums, lubricating oil distillates, petrolatums, or paraffin waxes, may be used. There can also be employed the condensation products of any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbons and reacting with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride, and the like.

Examples of other high molecular weight olefinic hydrocarbons which can be employed are cetene (C_{16}), cerotene (C_{26}), melene (C_{30}) and mixed high molecular weight alkenes obtained by cracking petroleum oils.

Other preferred olefins suitable for the preparation of the phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 13 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained by the dehydrogena-

tion of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes.

As a starting material there can be used the polymer or synthetic lubricating oil obtained by polymerizing unsaturated hydrocarbons resulting from the vapor phase cracking of paraffin waxes in the presence of aluminum chloride which is fully described in U. S. Patents 1,955,260; 1,970,402 and 2,091,398. Still another type of olefin polymer which may be employed is the polymer resulting from the treatment of vapor phase cracked gasoline and/or gasoline fractions with sulfuric acid or solid adsorbents, such as fuller's earth, whereby unsaturated polymerized hydrocarbons are removed. The reaction products of the phosphorus sulfide and the polymers resulting from the volatilization of hydrocarbons as described, for example, in U. S. Patents 2,197,768 and 2,191,787 are also suitable.

Other hydrocarbons that can be reacted with a phosphorus sulfide are aromatic hydrocarbons, such as for example, benzene, naphthalene, toluene, xylene, diphenyl and the like, or an alkylated aromatic hydrocarbon, such as for example, benzene having an alkyl substituent having at least 4 carbon atoms, and preferably at least 8 carbon atoms, such as a long chain paraffin wax.

The phosphorus sulfide-hydrocarbon reaction product can be readily obtained by reacting a phosphorus sulfide, for example, P_2S_5 with the hydrocarbon at a temperature of from about 200°F. to about 500°F. , and preferably from about 200°F. to about 400°F. , using from about 1% to about 50%, and preferably from about 5% to about 25% of the phosphorus sulfide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere, such as for example, an atmosphere of nitrogen above the reaction mixture. Usually, it is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess amount of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a hydrocarbon solvent, such as hexane, filtering and subsequently removing the solvent by suitable means, such as by distillation. If desired, the reaction product can be further treated with steam at an elevated temperature of from about 100°F. to about 600°F.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The phosphorus sulfide-hydrocarbon reaction product when neutralized with a basic reagent containing a metal constituent is characterized by the presence or retention of the metal constituent of the basic reagent.

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the acidic reaction product with a suitable basic compound, such as hydroxide, carbonate, oxide or sulfide of an alkaline earth metal or an alkali metal, such as for example, potassium hydroxide, sodium hydroxide, sodium sulfide, calcium oxide, lime, barium hydroxide, barium oxide, etc. Other basic reagents can be used, such as for example, ammonia or an alkyl- or aryl-substituted ammonia, such as amines. The neutralization of the phosphorus sulfide-hydrocarbon reaction product is carried out preferably in a non-oxidizing atmosphere by contacting the acidic reaction product either as such or dissolved in a suitable solvent, such as naphtha, with a solution of the basic agent. As an alternative method the reaction product can be treated with solid alkaline compounds, such as KOH , NaOH , Na_2CO_3 , K_2CO_3 , CaO , BaO , $\text{Ba}(\text{OH})_2$, Na_2S , and the like, at an elevated temperature of from about 100°F. to about 600°F. Neutralized reaction products containing a heavy metal constituent, such as for example, tin, titanium, aluminum, chromium, cobalt, zinc, iron, and the like, can be obtained by reacting a salt of the desired heavy metal with the phosphorus sulfide-hydrocar-

bon reaction product which has been treated with a basic reagent such as above-described.

Other phosphorus sulfide reaction products which can be used are the reaction products of a phosphorus sulfide and a fatty acid ester of the type described in U. S. 2,399,243; the phosphorus sulfide-degras reaction products of U. S. 2,413,322; the reaction product of an alkylated phenol with the condensation product of P_2S_5 and turpentine of U. S. 2,409,877 and U. S. 2,409,878; the reaction product of a phosphorus sulfide and stearonitrile of U. S. 2,416,807, etc.

The silver corrosion inhibiting property of the above-described thiadiazole reaction products is demonstrated by the data in Table I, which were obtained by subjecting mixtures of a hydrocarbon oil, a neutralized reaction product of P_2S_5 and a polybutene, and the above-described 2,5-dimercapto-1,3,4-thiadiazole reaction products to the following test, hereinafter referred to as the modified EMD test:

A silver strip 2 cm. x 5.5 cm. with a small hole at one end for suspension is lightly abraded with No. 0 steel wool, wiped free of any adhering steel wool, washed with carbon tetrachloride, air-dried and then weighed to 0.1 milligram. 300 cc. of the oil to be tested is placed in a 500 cc. lipless glass beaker and the oil heated to a temperature of 300° F. ($\pm 2^\circ$ F.) and the silver strip suspended in the oil so that the strip is 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 twenty-four hours the silver test strip is removed and while still hot rinsed thoroughly with carbon tetrachloride and air-dried. The appearance of the strip is then visually noted and given ratings according to the following scale:

- 1—Bright
- 2—Stained
- 3—Grey-Black
- 4—Black, Smooth
- 5—Black, Flake

After the visual inspection the silver strip is immersed in a 10% potassium cyanide solution at room temperature until the silver surface assumes its original bright or silver appearance. The silver strip is then washed successively with distilled water and acetone, air-dried and weighed.

The following lubricant compositions were subjected to the above test and the results obtained tabulated in Table I.

Sample A.—Control (solvent-extracted SAE-30 oil+3.3% barium-containing neutralized reaction product of P_2S_5 and a polybutene of about 1000 molecular weight).

Sample B.—A+0.75% product of Example I.

Sample C.—A+0.75% product of Example II.

Table I

Sample	Silver Corrosion	
	Wt. Loss in mg.	Visual Rating
A	20	3
B	0	1
C	0	1

Since a weight loss of no more than 20 milligrams is desirable, the ability of the 2,5-dimercapto-1,3,4-thiadiazole-ketone reaction product of this invention to inhibit silver corrosion is demonstrated by the above data.

The effectiveness of the herein-described thiadiazole reaction products in inhibiting corrosion toward copper and/or lead-containing metals, such as for example, copper-lead alloys, is demonstrated by the data in Table II, obtained by subjecting the above samples to the following test:

A copper-lead 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 tri-sodium phosphate solution, rinsed with water, acetone and dried, and 250 grams of the oil to be tested, together with 0.625 gram 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. ($\pm 2^\circ$ 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 twenty-four 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 added to the test oil. At the end of an additional twenty-four hours of test operation the test specimen is again removed, rinsed and dried as before, and weighed. The test specimen is again placed in the beaker, together with an additional 0.250 grams of lead oxide, and the test continued for another twenty-four hours (seventy-two hours total). At the conclusion of this time the test specimen is removed from the beaker, rinsed in naphtha, dried and weighed.

The loss in weight of the test specimen is recorded after each weighing.

This test, known as the Stirring Sand Corrosion Test, is referred to hereinafter as "S. S. C. T."

Table II

Sample	S. S. C. T. (mg. Weight Loss)		
	24 hrs.	48 hrs.	72 hrs.
A	305	580	850
B	38	79	103
C	1	13	34

Since weight losses of no more than 200 milligrams in 48 hours and 500 milligrams in 72 hours are desirable, the copper-lead corrosive inhibiting property of the herein-described 2,5-dimercapto-1,3,4-thiadiazole derivatives is clearly demonstrated by the above data.

Under certain conditions it is desirable to use in lubricant compositions elemental sulfur or an organic sulfur-containing compound of the type hereinabove described either alone or in combination with other additives. Effective lubricant compositions are obtained by the combination of the neutralized reaction products of a phosphorus sulfide and a hydrocarbon, as above described, with elemental sulfur, or an organic sulfur-containing compound, such as sulfurized mineral oils, sulfurized non-drying animal and vegetable oils, sulfurized olefins and olefin polymers, sulfurized sperm oil, etc., as described and claimed in U. S. Reissue 22,464, issued to C. D. Kelso et al., April 4, 1944, or with sulfurized terpenes, for example, dipentene, as described and claimed in U. S. 2,422,585, issued to T. H. Rogers et al., June 17, 1947.

While these compounds impart highly desired characteristics to lubricants and effectively inhibit the corrosion of copper and/or lead, they are under certain conditions corrosive to silver and similar metals, and for this reason, lubricants containing such addition agents at times fail to pass the above-described EMD test. In accordance with the present invention, however, the incorporation in such lubricant compositions of small amounts, namely, from about 0.1% to about 10%, and preferably from about 0.25% to about 5% of the herein-described 2,5-dimercapto-1,3,4-thiadiazole reaction products effectively inhibits the corrosiveness of the silver corrosive compounds without impairing their other desired properties.

The ability of the herein-described 2,5-dimercapto-1,3,4-thiadiazole derivatives to inhibit the silver corrosion tendency of active sulfur-containing organic compounds

is demonstrated by the following EMD data in Table III, obtained with the following compositions:

Sample A¹.—Control (solvent-extracted SAE-30 mineral oil +3.3% barium-containing neutralized reaction product of P₂S₅ and a polybutene of about 1000 molecular weight +0.75% sulfurized dipentene).

Sample B¹.—A¹+0.15% product of Example I.

Table III

Sample	Silver Corrosion (Weight loss in mg.)
A ¹	100
B ¹	3

As noted with respect to the data in Table I, *supra*, a weight loss of less than 20 is desirable.

Although the invention has been described in connection with the use of the herein-described 2,5-dimercapto-1,3,4-thiadiazole derivatives in combination with the one or more secondary additives in lubricant compositions, the invention is not restricted to such use, since these derivatives find utility when used alone in various lubricant compositions or hydrocarbon oil compositions to impart improved and desired characteristics thereto. Thus, for example, these derivatives may be used alone in hydrocarbon oils of high sulfur crudes to inhibit the corrosion of such oils to silver or copper and/or lead-containing metals, and to effectively inhibit the oxidation of hydrocarbon oils.

While this invention has been described in connection with the use of the herein-described additives and lubricant compositions, their use is not limited thereto; but the same can be used in products other than lubricating oils, such as for example, fuel oils, insulating oils, greases, non-drying animal and vegetable oils, waxes, asphalts, and any fuels for internal combustion engines, particularly where sulfur corrosion must be combatted.

Concentrates of a suitable oil base containing more than 10%, for example, up to 50% or more of the herein-described thiadiazole derivatives, alone or in combination with more than 10% of other additives, such as detergent-type additives, can be used for blending with hydrocarbon oils or other oils in the proportions desired for the particular conditions of use to give a finished product containing from about 0.02% to about 10% of the 2,5-dimercapto-1,3,4 - thiadiazole-unsaturated ketone reaction product.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as come within the spirit of the appended claims.

I claim:

1. A lubricant composition comprising a major proportion of an oleaginous material containing a compound normally corrosive to silver selected from the group consisting of elemental sulfur, a sulfur-containing organic compound and mixtures thereof and from about 0.02% to about 10% of an oil-soluble reaction product of 2,5-dimercapto-1,3,4-thiadiazole, and an unsaturated ketone having at least one olefinic double bond, and from about 4 to about 40 carbon atoms selected from the class consisting of an unsaturated aliphatic ketone and an unsaturated aromatic ketone, said reaction product being obtained by reacting said thiadiazole and said ketone in the molar ratio of from 1:2 to 4:1, respectively, at a temperature of from about 40° C. to about 140° C.

2. A composition as described in claim 1 in which the unsaturated ketone is an aliphatic unsaturated ketone.

3. A composition as described in claim 1 in which the unsaturated ketone is an aromatic unsaturated ketone.

4. A composition as described in claim 2 in which the ketone is mesityl oxide.

5. A composition as described in claim 3 in which the ketone is benzal acetophenone.

6. A lubricant composition comprising a major proportion of an oleaginous material, from about 0.001% to about 10% of a compound normally corrosive to silver selected from the group consisting of elemental sulfur, a sulfur-containing organic compound and mixtures thereof, and from about 0.02% to about 10% of an oil-soluble reaction product of 2,5-dimercapto-1,3,4-thiadiazole and an unsaturated ketone having at least one olefinic double bond, and from about 4 to about 40 carbon atoms selected from the class consisting of an unsaturated aliphatic ketone and an unsaturated aromatic ketone, said reaction product being obtained by reacting said thiadiazole and said ketone in the molar ratio of from 1:2 to 4:1, respectively, at a temperature of from about 40° C. to about 140° C.

7. A lubricant composition comprising a major proportion of a lubricating oil, from about 0.001% to about 10% of a phosphorus- and sulfur-containing detergent-type additive, and from about 0.02% to about 10% of an oil-soluble reaction product of 2,5-dimercapto-1,3,4-thiadiazole and an unsaturated ketone having at least one olefinic double bond, and from about 4 to about 40 carbon atoms selected from the class consisting of an unsaturated aliphatic ketone and an unsaturated aromatic ketone, said reaction product being obtained by reacting said thiadiazole and said ketone in the molar ratio of from 1:2 to 4:1, respectively, at a temperature of from about 40° C. to about 140° C.

8. A lubricant composition as described in claim 7 in which the unsaturated ketone is an aliphatic unsaturated ketone.

9. A lubricant composition as described in claim 7 in which the unsaturated ketone is an aromatic unsaturated ketone.

10. A lubricant composition as described in claim 7 in which the detergent-type additive is a neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

11. A lubricant composition as described in claim 7 in which the detergent-type additive is an alkaline earth metal-containing reaction product of a phosphorus sulfide and a hydrocarbon.

12. A lubricant composition as described in claim 7 in which the detergent-type additive is a barium-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer.

13. A lubricant composition as described in claim 7 in which the detergent-type additive is an alkali metal-containing reaction product of a phosphorus sulfide and a hydrocarbon.

14. A lubricant composition as described in claim 8 in which the ketone is mesityl oxide.

15. A lubricant composition as described in claim 9 in which the ketone is benzal acetophenone.

16. An addition agent for lubricant compositions containing a compound normally corrosive to silver selected from the group consisting of elemental sulfur, a sulfur-containing organic compound and mixtures thereof, comprising a concentrated solution of a hydrocarbon oil containing more than 10% of an oil-soluble reaction product obtained by reacting 2,5-dimercapto-1,3,4-thiadiazole and an unsaturated ketone having at least one olefinic double bond selected from the class consisting of an unsaturated aliphatic ketone and an unsaturated aromatic ketone in the molar ratio of from 1:2 to 4:1 respectively, at a temperature of from about 40° C. to about 140° C., said solution being capable of dilution with a hydrocarbon oil containing a compound normally corrosive to silver selected from the group consisting of elemental sulfur, a

sulfur-containing organic compound and mixtures thereof to form a homogeneous mixture containing from about 0.02% to about 10% of said oil-soluble reaction product.

17. A method of inhibiting the corrosion of silver by an oleaginous material containing from about 0.001% to about 10% of an active sulfur-containing organic compound normally corrosive to silver comprising incorporating in said oleaginous material a small amount, sufficient to inhibit said corrosion, of an oil-soluble reaction product of 2,5-dimercapto-1,3,4-thiadiazole and an unsaturated 10

ketone having at least one olefinic double bond, and from about 4 to about 40 carbon atoms selected from the class consisting of an unsaturated aliphatic ketone and an unsaturated aromatic ketone, said reaction product being obtained by reacting said thiadiazole and said ketone in the molar ratio of from 1:2 to 4:1, respectively, at a temperature of from about 40° C. to about 140° C.

No references cited.