This invention relates to improved compositions which are effective corrosion inhibitors and which are non-corrosive to silver, silver alloys and similar metal. More particularly, it pertains to oil-soluble compositions of the type of lubricants and hydrocarbon motor fuels, which are non-corrosive to silver and similar metal which inhibit the corrosion thereof by sulfur and/or corrosive sulfur-containing organic compounds.

To meet the increased demands upon engine lubricants, many types of lubricant additives have been developed to obtain certain desired characteristics thereof. Among the more effective additive agents which have been developed for compounding with lubricants are many sulfur-containing organic compounds, such as by way of example, sulfonized terpenes, sulfonized hydrocarbon oils, vegetable oils or animal oils, xanthate esters, organic polysulfides, particularly polyalkyl polysulfides, etc., which contain active-sulfur or sulfur compounds which are corrosive to silver, copper, etc.

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, copper and similar metals. A still further object of the invention is to provide a composition which will inhibit the corrosion of silver, copper and similar metals by sulfur and/or organo 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 agent which will inhibit the corrosion of silver, copper and similar metal by sulfur and/or organo sulfur-containing compounds. A further object of the invention is to provide a method of inhibiting the corrosion of silver, copper and similar metal. Another object of the invention is to provide a non-corrosive increased metal and similar metal parts and inhibiting the corrosion of such metals by lubricants which contain sulfur and/or organo sulfur-containing compounds.

In accordance with the present invention the foregoing objects can be attained by employing in oleaginous material corrosion inhibiting amounts, viz., from about 0.0001% to about 5%, and preferably from about 0.0005% to about 2.5% of an hydrocarbon polysulfide derivative of 2,5-dimercapto-1,3,4-thiadiazole (1,3,4-thiadiazole polysulfide) having the general formula:

\[
\text{R}-(\text{s})_{x}\text{C}-(\text{s})_{y}\text{R}'
\]

wherein R and R' are the same or different hydrocarbon radicals, x and y are numbers 0 to about 8, the sum of x and y is at least 1, and preferably 2 to about 16. The radicals R and R' can be aliphatic or aromatic, including alkyl, aralkyl, aryl and alkaryl radicals. The acyclic radicals can contain from 2 to about 30 carbon atoms, and preferably from about 4 to about 16 carbon atoms. Examples of suitable hydrocarbon radicals are ethyl, propyl, butyl, hexyl, octyl, nonyl, decyl, dodecyl, tridecyl, hexadecyl, octadecyl, cyclohexyl, phenyl, tolyl, benzyl, styryl, naphthyl, etc.

The herein-described polysulfide derivatives of 2,5-dimercapto-1,3,4-thiadiazole can be suitably prepared by several methods. For example, they can be prepared by reacting 2,5-dimercapto-1,3,4-thiadiazole with a suitable sulfenyl chloride, or by reacting the mercaptan with chlorine and reacting the resultant disulfenyl chloride with a primary or tertiary mercaptan. Bis-trisulfide derivatives are obtained by reacting the dimercapto with a mercaptan and a sulfur chloride in molar ratios of from 1:2:2 to 1:2:4 at a temperature of from about 50-100° C. Higher polysulfides can be prepared by reacting the thiaazole di- or trisulfides with sulfur at temperatures of about 200-400° F. Another method of preparing the polysulfides of the present invention involves reacting 2,5-dimercapto-1,3,4-thiadiazole with a mercaptan and sulfur in the molar ratio of from 1:1:1 to 1:4:16 at temperatures of from about 75° C. to about 150° C.

The preparation of the polysulfide derivatives of 2,5-dimercapto-1,3,4-thiadiazole is illustrated by the following examples:

**EXAMPLE I**

A solution of 284 grams (1.4 mole) of n-dodecyl mercaptan in 600 cubic centimeters of carbon tetrachloride was chlorinated at 5° C. to 0° C. over a two hour period with 1.47 moles of chlorine. The sulfenyl chloride so formed was stripped with nitrogen to remove HCl, and was added to a carbon tetrachloride slurry of 86 grams of 2,5-dimercapto-1,3,4-thiadiazole, and the mixture heated to 30° C. for one and one-half hours. The resultant di-sulfide

\[
\text{R}-(\text{s})_{x}\text{C}-(\text{s})_{y}\text{R'}
\]

was recovered by washing with water and sodium bicarbonate and stripping in vacuum to remove the carbon tetrachloride.

**EXAMPLE II**

A solution of 75 parts 2,5-dimercapto-1,3,4-thiadiazole in 2000 cubic centimeters ethyl acetate was stirred at room temperature (about 75° F.) while passing 72 parts of chlorine into the solution; about 2 hours were required for the addition of the chlorine. To the chlorinated mercaptan were added 204 parts of tertiary dodecyl mercaptan and the mixture stirred at room temperature (about 75° F.) for twelve hours. The ethyl acetate and unreacted
mercaptan were removed in vacuo and the stripped product filtered, through Celite. The product

\[ \text{CpH}_{2}-\text{S} \quad \text{N} \quad \text{N} \quad \text{H}_{2}\text{Cu} \]

was an oil-soluble clear yellow viscous oily material.

**EXAMPLE III**

The method of Example II was followed, using tertiary octyl mercaptao. The product was a clear green viscous oil-soluble material.

**EXAMPLE IV**

2,5-bis-lauryldithiobenzo-1,3,4-thiazidazole was sulfurized at 270°C. Further, for one and one-half hours with 2, 4, 6, 8, 10, 12, and 14 equivalents of sulfur to obtain the corresponding polysulfide derivatives.

**EXAMPLE V**

To a mixture of 75 grams (0.5 mole) 2,5-dimercapto-1,3,4-thiazidazole and 20.2 grams (0.1 mole) n-dodecyl mercaptao in 100 cubic centimeters of benzene, a solution of 10.3 grams (0.1 mole) sulfur dichloride, in 20 cc. of benzene was added, dropwise, at a temperature of 20°C. to 30°C. After addition of the sulfur dichloride, the mixture was heated to a temperature of 70°C. to 80°C. and the reaction mixture then washed with dilute sodium hydroxide. The washed product was then steamed at 150°C. for one hour and extracted with naphtha. The naphtha extract was dried over calcium chloride and the dried naphtha solution concentrated by vacuum distillation. An amber colored viscous oil was recovered having a sulfur content of 35.6%; calculated for 1,3,4-thiazidazole 2,5-bis-n-dodecyl trisulfide, sulfur 36.5%.

**EXAMPLE VI**

A solution of 10.3 grams of sulfur dichloride in dioxane was added, dropwise, to a solution of 7.5 grams of 2,5-dimercapto-1,3,4-thiazidazole and 14.6 grams tertiary octyl mercaptao in 10 cc. dioxane, at 25°C. and the reaction mixture then heated for three hours at 50°C. The reaction mixture was then poured into water and the oily product taken up in hexane. The hexane solution was then washed with dilute sodium hydroxide, then with water, and the washed product filtered through silica gel. Upon removal of the hexane from the filtrate, a reddish oily product was recovered having a sulfur content of 41.1%.

**EXAMPLE VII**

Equimolar amounts of 2-mercapto-5-alpha-methylstylene sulfide-1,3,4-thiazidazole and n-dodecyl mercaptao were dissolved in benzene and the solution reacted with an equivalent molar amount of sulfur dichloride at 50°C. for three hours and the reaction product

\[ \text{C}_{14} \text{H}_{22} \text{O} \quad \text{N} \quad \text{N} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{C}_{12} \text{H}_{25} \quad \text{Sulfur-27%} \quad \text{Nitrogen-39%} \]

recovered as in Example VI.

**EXAMPLE VIII**

A mixture of 90 grams (0.6 mole) 2,5-dimercapto-1,3,4-thiazidazole, 300 cc. Cellosolve, 87.6 grams (0.6 mole) tertiary octyl mercaptao and 20 grams (0.62 mole) of sulfur was heated at 110°C. for four hours. The Cellosolve and unreacted mercaptao were then stripped in vacuo from the reaction mixture and the product filtered hot through Celite. A light yellow solid was recovered having a sulfur content of 43% and a nitrogen content of 12.7%.

**EXAMPLE IX**

A mixture of 30 grams (0.2 mole) 2,5-dimercapto-1,3,4-thiazidazole and 58.4 grams (0.4 mole) tertiary dodecyl mercaptao in 100 cc. dioxane was heated with 25.6 grams (0.8 mole) sulfur at 75°C. and the mixture was then stripped in vacuo and filtered, and a light, yellow viscous oily product recovered having a sulfur content of 19% and 45.1% and a nitrogen content of 4.5%.

**EXAMPLE X**

A solution of 30 grams (0.2 mole) 2,5-dimercapto-1,3,4-thiazidazole and 80.8 grams (0.4 mole) tertiary dodecyl mercaptao in 100 cc. dioxane was heated with 25.6 grams (0.8 mole) sulfur at 75°C. and the mixture was then stripped in vacuo and filtered, and a light, yellow viscous oily product recovered having a sulfur content of 44% and 38.4% and a nitrogen content of 4.4%.

**EXAMPLE XI**

A solution of 68.2 grams (0.254 mole) of 2-mercapto-5-alpha-methylstylene sulfide-1,3,4-thiazidazole in carbon tetrachloride was treated at 0°C. with 0.282 mole of lauryl sulfonyl chloride, prepared as in Example I. The reaction mixture was warmed to 50°C. and stirred for three hours. It was washed with ethyl alcohol, hydroxide and with water, and then stripped with nitrogen at 110°C. to remove the carbon tetrachloride. The recovered product contained 22% sulfur and 7.11% nitrogen. Calculated for

\[ \text{C}_{14} \text{H}_{22} \text{N} \quad \text{N} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{S} \quad \text{C}_{12} \text{H}_{25} \quad \text{Sulfur-27%} \quad \text{Nitrogen-39%} \]

The above-described reaction product can be used in amounts of from about 0.0001% to about 5%, and preferably from about 0.005% to about 2.5% in oil-soluble compositions containing elemental sulfur and/or organic sulfur-containing compounds normally corrosive to silver, copper and similar metals. Such oil-soluble compositions can be lubricant compositions, motor fuels, etc. The lubricant compositions can contain as base oils hydrocarbon oils, synthetic hydrocarbons, such as those obtained by the polymerization of hydrocarbons, such as olein polymers, for example, polybutenes, polypropylene and mixtures thereof, etc.; 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 poly-carboxylic acid ester-type oils, such as the esters of adipic acid, sebacic acid, maleic acid, azelaic acid, etc.

Under certain conditions, it is desirable to use in combination with lubricant base oils from about 0.05% to about 10% elemental sulfur or an organic sulfur-containing compound, such as sulfurized terpenes, sulfurized hydrocarbon oils, sulfurized vegetable oils, sulfurized animal oils, sulfurized marine oils, xanthate esters, organic polysulfides, etc., which contain active sulfur. Effective sulfur-containing organic compounds are sulfurized terpenes, including mononuclear, bicyclic, acyclic terpenes, as well as polyterpenes. Examples of such terpenes are pine oil, turpentine, camphene, alpha-pineene, beta-pineene, allo-camene, fenchene, bornylenes, menthadienes, limonene, dipentene, terpine, diterpene and polyterpenes, mixtures of such terpenes can also be sulfurized. Sulfurization of the terpenes can be accomplished by the usual manner of adding sulfur to the terpene and heating to the sulfurization temperature or they can be prepared by the methods of U.S. 2,445,983 issued to R. W. Watson July 27, 1948.

Frequently, such sulfur-containing organic compounds
are used in lubricant compositions in conjunction with from about 0.05% to about 5%, other additives for example, neutralized sulfur- and phosphorus-containing reaction products of a phosphorus sulfide and a hydrocarbon, for example, polyolefins, such as polybutenes, polypropylene, etc. Suitable phosphorus sulfide-hydrocarbon reaction products are those described in U. S. 2,316,080 and U. S. 2,316,082 issued to C. M. Louis et al. April 6, 1943. The combination of such phosphorus and sulfide-hydrocarbon reaction products and sulfur-containing organic compounds of the type above described in lubricant compositions is described in U. S. Reissue 22,464 issued to Kelso et al. April 4, 1944 and U. S. 2,422,585 issued to Rogers et al. June 17, 1947.

While the sulfur-containing organic compounds impart highly desired properties to lubricants, they are corrosive to silver and similar metals, particularly when they contain active sulfur, as evidenced by the darkening of a copper strip submerged in a 0.5% solution of the compound in a hydrocarbon oil maintained at a temperature of about 210° F.

In accordance with the present invention, the incorporation in such lubricant compositions of from about 0.05% to about 5%, and preferably from about 0.1% to about 2.5% of a 1,3,4-thiadiazole polysulfide of the type herein described effectively inhibits the corrosion of copper, silver and similar metals.

The silver corrosion-inhibiting properties of these polysulfides is determined by the following test: this test is frequently referred to as a 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. glass beaker, and the oil heated to a temperature of 300° F. ±2° F.) and the silver test 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 stirring arm at 300 R. P. M. At the end of twenty-four hours, the silver 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 compositions were subjected to the above test and the data obtained are tabulated in Table I:

<table>
<thead>
<tr>
<th>Sample A.</th>
<th>Silver Corrosion (Wt. Losses Mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>110</td>
</tr>
<tr>
<td>B</td>
<td>0/1</td>
</tr>
<tr>
<td>C</td>
<td>0/1</td>
</tr>
<tr>
<td>D</td>
<td>8/2</td>
</tr>
<tr>
<td>E</td>
<td>16/2</td>
</tr>
<tr>
<td>F</td>
<td>19/3</td>
</tr>
<tr>
<td>G</td>
<td>4</td>
</tr>
<tr>
<td>H</td>
<td>7</td>
</tr>
</tbody>
</table>

For comparison purposes, lubricant compositions containing 3.3% neutralized reaction products of PSS and a polybutene will give a weight loss of 10 milligrams in the silver corrosion test in the absence of 1,3,4-thiadiazole polysulfide and usually a weight loss of zero milligrams in the presence of a polysulfide of the type herein described.

As indicated by the above data, the 1,3,4-thiadiazole polysulfides effectively inhibit the corrosion tendencies of active sulfur-containing organic compounds towards silver. While the 1,3,4-thiadiazole polysulfides inhibit the silver corrosion tendency of the active sulfur-containing compound, e. g., sulfurized terpenes, they do not deleteriously affect the corrosion inhibiting properties of the latter with respect to copper and/or lead. This is demonstrated by subjecting lubricant compositions containing such additives 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. (±2° F.) while the contents are stirred by means of a stirrer rotating at 750 R. P. M. The contents of the beaker are maintained at this temperature for 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 the 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 gram 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 Sand Stirring Corrosion Test, is referred to hereinafter as "S. S. C. T."

The following compositions were subjected to the above test, and the data obtained are tabulated in Table II:

| Sample A'. | Control (Solvent-extracted Oil+3.3% barium-containing neutralized reaction product of PSS and a polybutene of about 1000 molecular weight+0.75% sulfurized dipentene) |
| Sample B'. | A'+0.2% product of Example I. |
| Sample C'. | A'+0.2% product of Example II. |
| Sample D'. | A'+0.2% product of Example IV using 2 equivalents of sulfur. |
| Sample E'. | A'+0.2% product of Example IV using 4 equivalents of sulfur. |
| Sample F'. | A'+0.2% product of Example IV using 8 equivalents of sulfur. |
| Sample G'. | A'+0.15% product of Example IX. |
| Sample H'. | A'+0.15% product of Example X. |
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.

1. A composition comprising a major proportion of an oleaginous compound containing a compound selected from the group consisting of sulfur, an active sulfur-containing organic compound and mixtures thereof, normally corrosive to a silver-containing metal, and from about 0.0001% to about 5% of a 1,3,4-thiadiazole polysulfide having the general formula:

\[
\text{R} -(S)_{x} = \text{O} - (S)_{y} - \text{R}'
\]

in which R and R' are hydrocarbon radicals, x and y are numbers 0 to about 8, and the sum of x and y is at least 1.

2. A composition as described in claim 1 in which R and R' are hydrocarbon radicals, at least one of which is an aliphatic radical of from 2 to about 30 carbon atoms.

3. A composition as described in claim 1 in which R and R' are hydrocarbon radicals at least one of which is an aromatic radical.

4. A composition as described in claim 1 in which R and R' are aliphatic radicals of from 2 to about 30 carbon atoms and x and y are numbers of 1 to 8.

5. A composition as described in claim 1 in which the oleaginous compound is a normally liquid hydrocarbon.

6. A composition comprising a major proportion of a hydrocarbon oil containing a compound selected from the group consisting of sulfur, an active sulfur-containing organic compound and mixtures thereof, normally corrosive to silver, and from about 0.0001% to about 5% of a 1,3,4-thiadiazole polysulfide having the general formula:

\[
\text{R} -(S)_{x} = \text{O} - (S)_{y} - \text{R}'
\]

in which R and R' are hydrocarbon radicals, x and y are numbers 0 to about 8, and the sum of x and y is at least 1.

7. A composition as described in claim 6 in which the polysulfide is 1,3,4-thiadiazole-2,5-bis(alkyl disulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

8. A composition as described in claim 6 in which the polysulfide is 1,3,4-thiadiazole-2,5-bis(octyl disulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

9. A composition as described in claim 6 in which the polysulfide is 1,3,4-thiadiazole-2,5-bis(alkyltrisulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

10. A composition as described in claim 6 in which the polysulfide is 1,3,4-thiadiazole-2,5-bis(alkyltetrasulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

11. A composition comprising a major proportion of a hydrocarbon lubricating oil, from about 0.05% to about 10% of a sulfurized terpene normally corrosive to silver, and from about 0.05% to about 5%, of a 1,3,4-thiadiazole polysulfide having the general formula:

\[
\text{R} -(S)_{x} = \text{O} - (S)_{y} - \text{R}'
\]

in which R and R' are hydrocarbon radicals, x and y are numbers 0 to about 8, and the sum of x and y is at least 1.
13. A lubricant composition as described in claim 12, in which the sulfurized terpene is sulfurized dipentene.

14. A lubricant composition as described in claim 12 in which the polysulfide is a 1,3,4-thiadiazole-2,5-bis(alkyl disulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

15. A lubricant composition as described in claim 12 in which the polysulfide is a 1,3,4-thiadiazole-2,5-bis(alkyl trisulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

16. A lubricant composition as described in claim 12 in which the polysulfide is a 1,3,4-thiadiazole-2,5-bis(alkyl tetrasulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

17. A lubricant composition as described in claim 12 containing a phosphorus- and sulfur-containing detergent-type additive.

18. An internal combustion engine motor fuel non-corrosive to silver comprising a hydrocarbon distillate in the gasoline distillation range containing a sulfur compound corrosive to silver and from about .0001% to about 0.2% of a 1,3,4-thiadiazole polysulfide having the general formula:

\[ \text{N-N} \]

\[ \text{R-\overline{(S)}_x-S-\overline{C}} \]

\[ \text{\overline{S}} \]

\[ \text{S-(\overline{S})_y-R'} \]

in which R and R' are hydrocarbon radicals, x and y are numbers 0 to about 8, and the sum of x and y is at least 1.

19. An internal combustion engine motor fuel as described in claim 18 in which the polysulfide is a 1,3,4-thiadiazole-2,5-bis(alkyl disulfide), said alkyl groups containing from 2 to about 30 carbon atoms.

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