United States Patent Office 2,963,432
Patented Dec. 6, 1960

2,963,432

NON-CORROSIVE LUBRICANT COMPOSITION

Randel Q. Little, Jr., Munster, and Roger W. Watson, Highland, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Filed Dec. 2, 1957, Ser. No. 699,884

14 Claims. (Cl. 252—32.7)

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

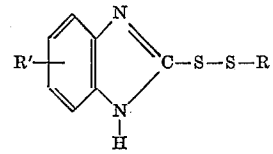
Advances in the design and construction of internal combustion engines to produce improved and more efficient and economical engines have presented many problems in the lubrication of the modern internal combustion engine. To meet the increased severe demands upon engine lubricants, many types of lubricant additives have been developed to obtain certain desired characteristics thereof. Among the more effective addition agents which have been developed for compounding with lubricants are many sulfur-containing organic compounds, such as by way of example, 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.

Increased use of silver and copper and similar metal 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 and copper 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 of matter. 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 addition 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. Still another object of the invention is to provide a method of lubricating internal combustion engines containing silver, copper, 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 incorporating in lubricant compositions small amounts sufficient to inhibit the corrosion of silver, copper and similar metals by sulfur and sulfur-containing compounds, of an oil-soluble 2-

(alkyldithio)benzimidazole having the general formula



in which R is an allkyl radical having from about 1 to about 30 carbon atoms, and R' is hydrogen and/or an alkyl radical of 1 to about 30 carbon atoms. The total number of carbon atoms in R and R' being sufficient to impart oil solubility to the compound.

Examples of 2(alkyldithio)benzimidazoles are

2(amyldithio)benzimidazole
2(octyldithio)benzimidazole
2(nonyldithio)benzimidazole
2(dodecyldithio)benzimidazole
2(octadecyldithio)benzimidazole
2(docosyldithio)benzimidazole
2(triacontyldithio)benzimidazole
2(amyldithio)dodecylbenzimidazole
2(dodecyldithio)propylbenzimidazole
2(nonyldithio)hexylbenzimidazole

It is not intended to imply that all 2(alkyldithio)benzimidazoles serve with identical efficiency. While they are all effective corrosion inhibitors, they may exhibit some variation depending upon the nature and severity of the service, the nature and condition of the metal to be protected, etc.

The amount of the inhibitor employed to inhibit the corrosion of silver and/or copper is largely governed by the amount of corrosive sulfur in the composition. It has been determined that corrosion of silver is inhibited at mole inhibitor-to-sulfur ratios of at least about 0.25 and corrosion of copper is inhibited at mole inhibitor-to-sulfur ratios of at least about 0.1. In general, corrosion inhibited lubricant compositions comprise a major amount of a normally liquid lubricating oil and from about 0.05% to about 5.0%, preferably from about 0.1% to about 2.0% of the above inhibitor.

The 2(alkyldithio)benzimidazole can be prepared by reacting molar ratios of an alkanesulfenyl chloride and 2-mercaptobenzimidazole at a temperature of from about 0° F. to about 80° F. for a period of from about 2 hours to about 6 hours, the resultant product diluted with a mixture of water and benzene and the organic layer separated from the water layer. The organic layer is then washed successively with water, hydrochloric acid, sodium carbonate and again with water. The washed product is then dried, distilled and the residue recovered. If desired, the product can be recrystallized from a solvent such as hexane.

The preparation of the herein described additive is illustrated by the preparation of 2(dodecyldithio)benzimidazole carried out as follows:

A solution of dodecanesulfenyl chloride in carbon tetrachloride was prepared by reacting 67 g. (0.33 M) dodecyl mercaptan with 25 g. (0.35 M) chlorine at less than 50° F. This solution was blown for 30 minutes and then 10 ml. pyridine was added to remove excess hydrogen chloride. The dodecane-sulfenyl chloride solution was added to a suspension of the sodium salt of 2-mercaptobenzimidazole, 58 g. (0.33 M), at such a rate to maintain the temperature below 50° F. The solution was allowed to gradually warm to room temperature, over a 2 to 3 hour period. The reaction mixture was diluted with about 500 ml. of water and about 200 ml. benzene. A small amount of insoluble yellow solid was filtered off and the organic layer was separated from the water layer. The organic layer, which contained the reaction

product, was washed successively with water, aqueous 5% hydrochloric acid, water, aqueous 5% sodium carbonate and two times with water. The reaction mixture was dried over anhydrous sodium sulfate and the solvent was removed by distillation under reduced pressure. The orange solid residue was recrystallized from hexane, after treatment with activated charcoal, to give 33 g. of a cream colored product. M.P.: 90–92° C. Analysis for 2(dodecyldithio)benzimidazole:

	Percent S	Percent N
Theory	18.3	8.0
Found	18.3, 18.5	7.24, 7.70

The above-described products are effective corrosion inhibitors, particularly with respect to silver, copper, and similar metals when used 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, 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 polycarboxylic acid ester type oils, such as the esters of adipic acid, sebacic acid, maleic acid, azelaic acid, etc.

The effectiveness of the herein described 2(alkyldithio) benzimidazole in inhibiting the corrosion of silver and/or copper by sulfur or sulfur compounds, is demonstrated by the data in Table I. These data were obtained by immersing freshly polished copper strips (½" x 3" x 1/32") and silver strips (½" x 3" x 1/16") in 15 cc. of the test sample for three hours at 212° F. At the end of the test period, the strips are removed, washed with hexane, dried by air evaporation and rated visually. In this rating system, strips having the appearance of a freshly polished strip is rated "0," while a scaly black strip is rated "5"; intermediate stages of corrosion are rated "1," "2," "3," and "4." The test is essentially the same as A.S.T.M. Test D–130–54T. In the test the vehicles used were decalin containing 0.047% (0.013 M) sulfur or 0.69% (0.013 M) di-dodecyl tetrasulfide, an SAE–10 base mineral containing 0.047% (0.013 M) sulfur, and a heater oil. Decalin was used in order to insure the absence of extraneous sulfur compounds. The following samples were subjected to the foregoing test and the results obtained tabulated in Table I.

Sample A [1]—Decalin (no inhibitor)
Sample B [1]—A+0.52% (.013) M 2(dodecyldithio-benzimidazole
Sample C—SAE–10 base mineral lubricating oil (no inhibitor)
Sample D—C+0.52% (.013 M) 2(dodecyldithio)benzimidazole
Sample E—Heater oil (no inhibitor)
Sample F—E+0.001% 2(dodecyldithio)benzimidazole
Sample G—E+0.005% 2(dodecyldithio)benzimidazole
Sample H—E+0.01% 2(dodecyldithio)benzimidazole

[1] One hour test.

Table I

Sample	Copper Rating Added Sulfur			Silver Strip Rating Added Sulfur—Elemental Sulfur
	None	Elemental Sulfur	Di-dodecyl tetrasulfide	
A	0	5	5	5
B	0	0	0	0
C	------	4C	------	------
D	------	1A	------	------
E	4A	------	------	------
F	3A	------	------	------
G	1A	------	------	------
H	1A	------	------	------

The corrosion inhibiting property of the herein described additives is further demonstrated by the data obtained in a modification of the so-called EMD test, a corrosion test developed by General Motors, Electromotive Diesel Division. In this test weighed freshly polished ¾" x 2" x 1/16" silver strips and 1" x 2" x 1/16" copper strips are immersed in 300 grams of the test sample, stirred at 300 r.p.m., at 285° F. for 72 hours. At the end of the test period, the strips are removed, and cleaned electrolytically in 5% KOH to remove deposits, and weighed. The degree of corrosion is measured by determining the milligram weight loss of the test strips.

The test oil used in this test was a heavy duty SAE–30 grade oil containing 4.0% of a barium-containing neutralized reaction product of P_2S_5 and a polybutene of about 800–1000 molecular weight, and 0.75% (0.08 M sulfur) sulfurized dipentene.

Table II

Inhibitor	Corrosion—mg. wt. loss	
	Silver	Copper
None	145	163
1.05% (0.03 M) 2(dodecyldithio)-benzimidazole	3.7	8.7

The effect of the inhibitor-to-corrosive sulfur ratio is shown by the data in Table III. The data in this table were obtained by subjecting oil blends containing varying amounts of the inhibitor to the above described modified EMD test. The oil employed was a solvent extracted SAE–30 mineral oil containing 0.032% elemental sulfur.

Table III

Mole Ratio of Inhibitor-to-Sulfur	Percent 2(dodecyldithio)-benzimidazole	Mg. Wt. Loss	
		Silver	Copper
	0.0	113	239
1:15 (0.067)	0.023	205	91
1:12 (0.083)	0.030	234	61
1:10 (0.10)	0.035	222	5
1:6 (0.17)	0.058	135	3
1:5 (0.20)	0.070	37	2
1:4 (0.25)	0.088	6	4
1:3 (0.33)	0.116	4	2
1:2 (0.50)	0.175	5	3
1:1 (1.0)	0.350	2	3

Since, in the EMD test a weight loss of not more than 20 milligrams is considered passing, the above data demonstrate that for silver, corrosion is adequately inhibited with a mole ratio of inhibitor to sulfur of at least about 0.25, and that for copper, corrosion is inhibited with a mole ratio of inhibitor to sulfur of at least about 0.1.

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 monocyclic, bicyclic, acyclic terpenes, as well as polyterpenes. Examples of such terpenes are pine oil, turpentine, cymene, alphapinene, beta-pinene, allo-ocimene, fenchenes, bornylenes, menthadienes, limonene, dipentene, terpinene, diterpene, Δ-carene, and polyter-

penes, 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 15%, detergent-type 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. Loane 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, copper and similar metals, particularly when they contain active sulfur, as evidenced by the darkening of a copper strip submerged in an 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%, of a heterocyclic compound of the type herein described effectively inhibits the corrosion of copper, silver and similar metals.

Concentrates of a suitable oil base containing more than 5%, for example, up to 50% or more, of the herein described heterocyclic compounds, 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 0.05% to about 5.0% of the herein described heterocyclic compounds.

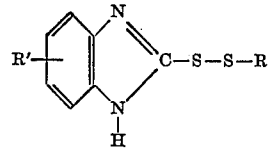
While this invention has been described in connection with the use of the herein described additives and lubricant compositions, their use is not limited thereto but the same can be used in products other than lubricating oils, such as for example, fuel oils, insulating oils, greases, non-drying animal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

Unless otherwise stated, percentages given herein and in the appended claims are weight percentages.

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.

We claim:

1. An oil composition non-corrosive to silver and copper comprising a major proportion of an oil containing a sulfur compound normally corrosive to silver and copper, and an oil-soluble 2(alkyldithio)benzimidazole having the general formula



in which R is an alkyl radical of from about 1 to about 30 carbon atoms, and R' is a substituent selected from the group consisting of hydrogen and an alkyl radical having from 1 to about 30 carbon atoms, said 2(alkyldithio)benzimidazole being present in said composition in a small but sufficient amount to inhibit the corrosion of silver and copper.

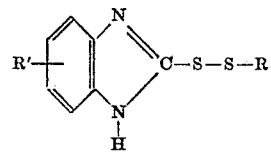
2. An oil composition as described in claim 1 in which R is an alkyl radical of 8 carbon atoms.

3. An oil composition as described in claim 1 in which R is an alkyl radical of 12 carbon atoms.

4. An oil composition as described in claim 1 in which R is an alkyl radical of 18 carbon atoms.

5. An oil composition as described in claim 1 in which the oil is a hydrocarbon oil.

6. A lubricant composition comprising a major proportion of a hydrocarbon oil containing a sulfur compound normally corrosive to silver and copper and from about 0.05% to about 5% of an oil-soluble 2(alkyldithio)benzimidazole having the general formula

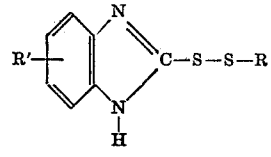


in which R is an alkyl radical of from about 1 to about 30 carbon atoms, and R' is a substituent selected from the group consisting of hydrogen and an alkyl radical having from 1 to about 30 carbon atoms, said 2(alkyldithio)benzimidazole being present in said composition in a small but sufficient amount to inhibit the corrosion of silver and copper.

7. A lubricant composition as described in claim 6 in which the 2(alkyldithio)benzimidazole is 2(dodecyldithio)benzimidazole.

8. A lubricant composition as described in claim 6 in which the sulfur compound is sulfurized terpene.

9. A lubricant composition comprising a major proportion of a viscous hydrocarbon, from about 0.05% to about 10% of a phosphorus- and sulfur-containing detergent additive, from about 0.05% to about 10% of a sulfurized terpene normally corrosive to silver and copper and from about 0.05% to about 5.0% of an oil-soluble 2(alkyldithio)benzimidazole having the general formula



in which R is an alkyl radical having from about 1 to about 30 carbon atoms, and R' is a substituent selected from the group consisting of hydrogen and an alkyl radical having from 1 to about 30 carbon atoms, said 2(alkyldithio)benzimidazole being present in said composition in a small but sufficient amount to inhibit the corrosion of silver and copper.

10. A lubricant composition as described in claim 9 in which the detergent additive is a neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

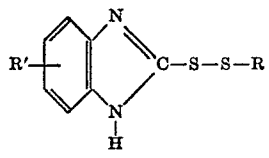
11. A lubricant composition as described in claim 9 in which the detergent additive is an alkaline earth-containing neutralized reaction product of a phosphorus sulfide and an olefin polymer.

12. A lubricant composition as described in claim 11 in which the alkaline earth is barium.

13. A lubricant composition as described in claim 11 in which the olefin polymer is a polybutene.

14. A concentrate addition agent for lubricant compositions comprising a lubricating oil containing more

than 5% of an oil-soluble 2(alkyldithio)benzimidazole having the general formula



in which R is an alkyl radical of from about 1 to about

30 carbon atoms, and R' is a substituent selected from the group consisting of hydrogen and an alkyl radical having from 1 to about 30 carbon atoms, said concentrate being capable of dilution with a lubricating oil to form a homogeneous mixture containing from about 0.05% to about 5% of said 2(alkyldithio)benzimidazole.

References Cited in the file of this patent

UNITED STATES PATENTS

2,642,396	Roddy	June 16, 1953
2,719,125	Roberts	Sept. 27, 1955
2,719,126	Fields et al.	Sept. 27, 1955