Patented June 7, 1949 2,472,318

UNITED STATES PATENT OFFICE

2,472,318

INHIBITOR

Philip Subkow, Los Angeles, Calif.

No Drawing. Application March 27, 1943, Serial No. 480,871

7 Claims. (Cl. 252—45)

1

This invention relates to lubricating oils and greases and particularly to lubricating oils and greases to which addition agents have been added for the purpose of improving the stability of the lubricating oil under the conditions of oxidation in use. It also relates to lubricating oils to which addition agents have been added for the purpose of reducing the corrosion of bearings occasioned by the use of lubricating oil, and also relates to the addition agents for lubricating oils in order to improve the color stability and to improve the lubricating properties of lubricating oils and greases.

Sulfur has a beneficial effect in inhibiting oxidation and in preventing corrosion of cadmium-silver and lead-copper bearing alloys when employing lubricating oil. Thus, sulfur in the form of thio-ether or sulfides, disulfide or polysulfide form is particularly efficacious.

Sulfur in the above forms, besides itself being efficacious as an inhibitor against oxidation and as a corrosion inhibitor in lubricating oils, has the beneficial property of imparting activity at relatively high temperature and imparting stability to the compound at such relatively high temperatures. This beneficial property is also extended to other inhibitor groups in a compound, e. g., compounds containing inhibitor groups such as hydroxy groups, amino groups or other sulfide, disulfide or polysulfide groups. The introduction of such additional sulfur grouping imparts activity and stability to the compound at the higher temperatures.

This property of relatively high temperature stability of the sulfur grouping is particularly important in Diesel engine lubrication where high temperatures are attained on the piston and on the cylinder linings. In lubrication of such engines, as well as in motor lubricating, this property is useful in inhibiting the corrosion of alloy bearings which are coming into wide use in both gasoline and Diesel engines.

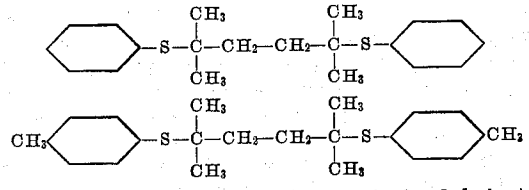
I propose, as an inhibitor for these and like purposes, compounds of the following formulations: RxR 'xR; RxR'xRD; or DRxR'xRD, in which R is an aryl or alkyl aryl, or a substituted aryl or alkyl aryl group, x is a sulfur, oxygen or tellurium, but preferably a sulfur group, R' is an alkyl or substituted alkyl group and D is an inhibitor group taken from the class of hydroxy, amino, sulfide, disulfide or polysulfide groups.

As an example of the type of compound which I wish to employ, I suggest:

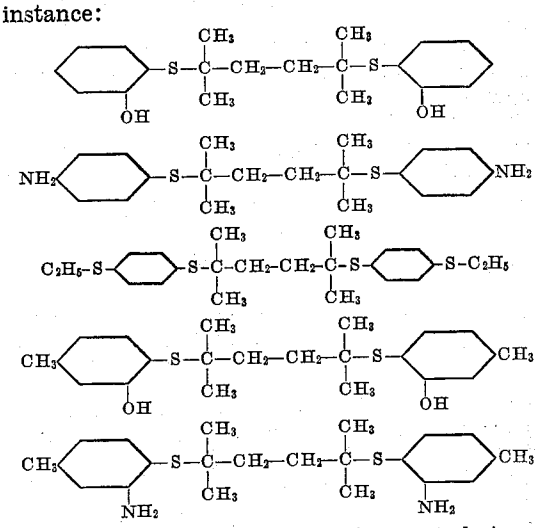
2,5 dimethyl hexane-2,5-bis (p-tolyl sulfide),

2

and also the corresponding thio-ether of the general formula:



I may also use as addition agents for lubricating oils and greases, instead of the above compounds, corresponding compounds wherein either one or both of the phenyl radicals or cresyl radicals in the compound carries as a substituent a hydroxy group or the NH_2 group, or the SH group, or a thio-ether group, wherein the sulfur is joined to an alkyl or aromatic and also to the carbon of the thio-phenol. We would have the corresponding substituent compounds, as for instance:



or corresponding compounds, but wherein but one of the aryl or alkyl aryl carries the substituent, OH, NH_2 or C_2H_5—S.

The action of sulfur in reinforcing the action of other inhibitor groups also manifests itself in inhibitor compounds in which the sulfur is directly joined to two ring carbons as in the case of phenyl thio-ethers or in the case of diphenyl disulfides or dibenzyl disulfide. In such compounds the beneficial action of the sulfur group may be imparted to diverse inhibitor groups which are joined to the phenyl radical. Thus, the presence of both the NH_2 and the OH group in a compound gives to the compound beneficial properties aris-

ing from the simultaneous presence of both groups, e. g., compounds of the general formula DRSRD or DR S—S—RD where R is an aryl, alkyl or arylalkyl group and D is an inhibitor group taken from the group such as the $OHNH_2$ or sulfide or polysulfide group.

In inhibitors having a phenol or cresol grouping the OH has acidic properties. Such groups have corrosive properties in themselves and while they inhibit the corrosion of the alloy bearings by inhibiting oxidation of the lubricating oil, they are themselves corrosive due to their acidity. The OH groupings also have, in some compounds, the property of limiting the oil solubility of the compound. The corrosivity may be retarded and oil solubility increased by neutralizing the OH with lime to form the corresponding calcium soap. However in use, some decomposition and some hydrolysis occurs liberating the acid group.

The presence of the NH_2 group will have the property of reducing this acidity while itself imparting inhibitor action to the compound. Compounds of the formulations D'RSRD and D'R—S—S—RD where R is an aryl, or aryl alkyl group and D' is an NH_2 group and D is an OH group joined to a ring carbon, having the above properties and examples of such compounds are given above.

These compounds may be dissolved in the lubricating oil and if they have acidic substituents, such as hydroxy group, may be converted into corresponding calcium soaps by saponification with calcium hydroxide or with other alkaline earth soaps, such as strontium and barium soaps. These compounds or their soaps may be employed by adding them to lubricating oil and/or grease in the order of from .05 to 1% by weight, more or less. They may be compounded along with other addition agents, as, for instance, with the calcium soap of chlorinated stearic or palmitic acid, such as calcium dichlorostearic acid to form a Diesel engine lubricating oil which, while noncorrosive, will prevent ring sticking, be stable against oxidation and degradation. Instead of the chlorinated fatty acid soap we may use the calcium soap of phenyl stearic acid. An oil carrier such as a purified naphthenic lubricating oil or a purified lubricating oil produced from a paraffinic oil is employed. Preferably I prefer to use naphthenic base oil. The calcium soap of the dichlor stearic acid, or the calcium soap of phenyl stearic acid or other soap used for the prevention of ring sticking, such as the soap of acids produced by the oxidation of petrolatum, is incorporated in lubricating oil in the order of from .1% to 2%, more or less, depending upon the character of the soap, the oil employed and the amount of ring sticking to which the oil may be subjected. To this may be added from .05% to 2% of the compounds herewith suggested. The addition agent may be added to motor lubricants which show a tendency to corrosion of cadmium-silver bearings and of copper-lead bearings, to prevent the corrosion of such bearings by such oil in use. The compounds may be used in the proportion depending upon the oil to which

they are being added and the degree of corrosion occasioned by such oil.

It may be desirable to add, in addition to such compounds, and in addition to the calcium soap or calcium stearic acid or of the dichlor stearic acid or the calcium soaps produced by oxidation of lubricating oil or petrolatum, a small amount of the calcium or other alkaline earth soap of a weak acid, as, for instance, oleic acid or stearic acid or palmitic acid. The purpose of this small amount of soap is to act as a solubilizing product to increase the compatibility of the oil with the addition agents employed and to increase the amount of calcium ions present in the mixture in order that as the oil is used and the acidity generated on use, either by the oxidation of the oil or liberation of the acids introduced as soaps, the reserve alkalinity introduced by means of the soap of the weak acid acts to combat this generated acidity. The amount of such soap to be added will vary with the oil and the addends and the formulations will be obvious to those skilled in the art, from what has been said before.

As a practical matter, it will be desirable to first make a concentrate of the inhibitor and soaps which are to be added to the lubricating oil, in a concentration in excess of the concentration to be finally used, for instance, in a concentration of 5 to 50 or more percentage. This concentrate may then be mixed in the required proportion with the lubricating oil to be compounded.

Particularly useful members of this group are the methylene bis and the ethylene bis aryl sulfides, such as ethylene bis phenyl sulfide, ethylene bis p-tolyl sulfide, the methylene bis phenyl sulfide, and the methylene bis p-tolyl sulfide. The effectivness of these materials as anti-oxidation inhibitors and anti-corrosion agents is evidenced by the following tests employing ethylene bis phenyl sulfide:

250 cc. of a Mid-Continent, 20W oil was heated in a 500 cc. beaker to a temperature of 320° to 330° F. in the presence of 5 square inches of copper and 10 square inches of iron. At intervals oil samples were taken and sludge, acid, and viscosity values determined. The following table gives the results:

Oil	Percent Added S	Vis. 100° F., Increase at Hrs., 48	Sludge, mg., 10 g. Oil at Hrs.		Acidity, mg. KOH/g. at Hrs.	
			24	48	24	48
M. C. 20W		1,880	250	1,000+	10.0	23.0
M. C. 20W	+.13, ½% ethylene bis phenyl sulfide	107	45	138	2.0	2.0

The same compound recorded as "Inhibitor" in the following table was also run in a Lauson engine of the type developed by the Lubri-Zol Corporation. This is a gasoline engine. It was run with an oil temperature of 280° F. and a jacket temperature of 295° F. The oil was a solvent extracted western oil No. 30 (S. A. E.) grade having a V. I. of 90. In the following experiments the sulphonate soap which was employed was the calcium salt of "Petronate," a mineral oil sulfonate obtained in the sulfuric acid refining for white oil production, as sold by the L. Sonneborn Sons, Inc. The Calcium Paranox employed was the calcium salt of the "Paranox" material sold by the Standard Oil Company of New Jersey, and it had an average constitution of 4 amyl phenol rings to 3 sulfur atoms. The formula of "Paranox" is:

$$(C_3H_7C_6H_3OH)_2S_x$$

The engine was run with copper lead bearings for the hours listed in the following table:

Lauson engine (Lubri-Zol engine)

	Bearing Loss
S. E. Oil #30	174 mg. in 20 hours.
S. E. Oil #30+½% Inhibitor	70 mg. in 20 hours. 133 mg. in 40 hours. 185 mg. in 60 hours.

[Compounded oil: Soap sulfonate type, calcium salt of Petronate (Sonneborn petroleum sulfonates)]

The inhibitors employed in the following test are of the same class, being the corresponding ethylene derivatives, i. e., bis ethylene bis phenyl sulfide, and also the ethylene bis p-tolyl sulfide. The oil employed in this test is S. A. E. 20, solvent extracted, high V. I. Western oil:

Thrust Bearing Corrosion machine (Cu-Pb Bearing), Preprint Pet.-Division A. C. S., Sept. 8–12, 1941, Delaware City, N. J. (see also National Pet. News, September 17, 1941, R–294).

	Anti Corrosion Agent	Bearing loss, mg./sq. cm.				
		120° C.	130° C.	140° C.	150° C.	160° C.
Oil	None	1.1	15.0			
Detergent oil	0.39% ethylene bis				.1	
S. A. E. 20	Phenyl sulfide, 0.43% ethylene bis p-tolyl sulfide		0.3	0.2	1.1	1.0

Conditions full 20 hrs., 2,400 R. P. M., 125 p. s. i.

The following oxidation were obtained on a Dornte type of apparatus (see Ind. and Eng. Chem. vol. 34, pages 183 and 927):

Oxidation stability

[Temp. 150° C.]

Oil	Additive	Catalyst	Ind. Period, Hrs.[3]	Oxidation[1] Time, Hrs.
White oil	None	None	0.4	1.6
	0.39% ethylene bis phenyl sulfide	do	72	73.5
S. A. E. 60 Solvent Ext. Mid-Continent	None	Cu (1 cm.²/gm.) of oil		9.4
	0.39% ethylene bis phenyl sulfide (1)	do		39.5
	0.43% ethylene bis p-tolyl sulfide (2)	do		45.8
S. A. E. 30 Solvent Ext.	None	do		6.7
	0.39% additive (1)	do		[2] 139

[1] Time to absorb 1800 ml. oxygen per 100 grams of oil.
[2] Oxidation curve is strongly "auto-retardant" in form. See Von Fuchs & Diamond, J. Ind. & Eng. Chem. 34, August 1942, p. 927.
[3] Induction period.

S. E. oil #30:	Bearing loss
+ soap (1.2%)	133 mg. at 20 hours
+ soap (1.2%), ¾% Ca Paranox	19 mg. at 20 hours 118 mg. at 40 hours 256 mg. at 60 hours
+ soap (1.2%), 1% of inhibitor	89 mg. at 20 hours 146 mg. at 40 hours 202 mg. at 60 hours

The following tests were also run with the Lauson engine under the same conditions with the following results:

1. S. E. oil #30 +sulfonate (1.2%) +.5% Ca Paranox +.5% inhibitor:

	Bearing loss, mg.
20 hours	55
40 hours	145
60 hours	228

2. Naphthenic oil (600[1] at 100° heavily acid treated about 10 V. I., +detergent, +1% inhibitor:

	Bearing loss, mg.
20 hours	63
40 hours	118
60 hours	160

3. Same oil +.7% detergent, +¾% Ca Paranox:

	Bearing loss, mg.
20 hours	42
40 hours	95
60 hours	146

[1] Seconds Saybolt.

The activity of the bis aryl sulfides of the form R*x*R′*x*R, the R is an aryl group such as phenyl group or a simple aryl alkyl group such as the tolyl group and R′ is a low molecular weight alkyl group such as an ethylene or a methylene group exhibits extraordinary activity as an oxidation inhibitor and as an anti-corrosion agent. The effectiveness of this low molecular alkyl linkage between the sulfide sulfurs is particularly notable in its effect upon the rate of the oxidation process. These compounds apparently act not merely as an inhibitor to impart a long induction period, such as is evidenced by its effect upon the white oil in the test previously cited, but also act as a negative catalyst to change the whole course of the oxidation process. Unlike most other anti-corrosion agents of the sulfur type in which the form of the curve of reaction with time is that of a typical auto-catalyzed oxidation process, being concaved downward. Such curves show a steeper and steeper slope as the oxidation process proceeds, increasing with time, indicating a constantly increasing rate of oxidation with time. The oils inhibited with the inhibitors of my invention, particularly those containing ethylene and methylene linkages, are concaved downward in form, i. e., auto-retardant in form, indicating that as the reaction proceeds, the reaction process gets slower and slower. In fact, in the example given showing 135-hour period to about 1800 cc. of oxygen, the slope of the curve was almost flat, indicating that the oxidation reaction had been substantially halted and that the oil would not further react with oxygen.

While the above compounds are useful in lubricating oils, they also may be used as inhibitors in greases. In formulating such greases the inhibitor is added to the lubricating oil which is to be compounded with the soaps for making the grease. The manner of formulating grease is well known and conventional in this art, the invention in this regard being the incorporation of the inhibitors of this invention in such grease. The grease may be a lime base grease in which a calcium soap is used, a barium soap grease or a sodium soap grease. Such greases are well known in this art.

This invention also contemplates the addition of such inhibitors to gasoline. When so incorporated they have the property of stabilizing the gasoline against gum formation. Inhibitors of various compositions are now used and the manner of incorporation of inhibitors in gasoline is well known. The amount of inhibitor to be added to the gasoline will depend upon the nature of the gasoline and the gum content. Usually it will be found that from .5% to 3% of the inhibitor may be usefully employed.

The foregoing description and examples are not intended to be limitations of my invention, it being understood that various changes and modifications may be made therein without departing from the spirit of the appended claims.

I claim:

1. A mineral lubricating oil composition comprising a lubricating oil fraction and a compound of the general formula RSR'SR where R is one of the groups taken from the class consisting of an aryl, alkyl aryl and substituted aryl, alkyl aryl groups, and where S is sulfur and R' is a low molecular weight alkyl group taken from the group consisting of methyl and ethyl groups, said compound being present in an amount sufficient to inhibit oxidation of said oil.

2. A mineral lubricating oil composition comprising a lubricating oil fraction and a compound of the general formula RSR'SR where R is one of the groups taken from the class consisting of an aryl, alkyl aryl and substituted aryl, alkyl aryl groups, and where S is sulfur and R' is ethylene, said compound being present in an amount sufficient to inhibit oxidation of said oil.

3. A mineral lubricating oil composition comprising a lubricating oil fraction and a compound of the general formula RSR'SR where R is one of the groups taken from the class consisting of an aryl, alkyl aryl and substituted aryl, alkyl aryl groups, and where S is sulfur and R' is methylene, said compound being present in an amount sufficient to inhibit oxidation of said oil.

4. A mineral lubricating oil composition comprising a lubricating oil fraction and a small proportion of methylene bis phenyl sulfide,

$$C_6H_5—SCH_2S\ C_6H_5$$

said compound being present in an amount sufficient to inhibit oxidation of said oil.

5. A mineral lubricating oil composition comprising a lubricating oil fraction and a small proportion of methylene bis tolyl sulfide,

$$CH_3C_6H_4SCH_2S\ C_6H_4CH_3$$

said compound being present in an amount sufficient to inhibit oxidation of said oil.

6. A mineral lubricating oil composition comprising a lubricating oil fraction and a small proportion of ethylene bis phenyl sulfide,

$$C_6H_5S\ CH_2CH_2S\ C_6H_5$$

said compound being present in an amount sufficient to inhibit oxidation of said oil.

7. A mineral lubricating oil composition comprising a lubricating oil fraction and a small proportion of ethylene bis tolyl sulfide,

$$CH_3C_6H_4S\ CH_2CH_2SC_6H_4CH_3$$

said compound being present in an amount sufficient to inhibit oxidation of said oil.

PHILIP SUBKOW.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,278,224	Subkow	Mar. 31, 1942
2,282,710	Dietrich	May 12, 1942
2,346,153	Denison et al.	Apr. 11, 1944