Patented July 15, 1941 2,249,626

UNITED STATES PATENT OFFICE

2,429,626

LUBRICATING COMPOSITION

Elmer William Cook, New York, N. Y., and William David Thomas, Jr., Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application March 13, 1941, Serial No. 383,167

16 Claims. (Cl. 252—48)

This invention relates to lubricating oil compositions containing corrosion inhibitors.

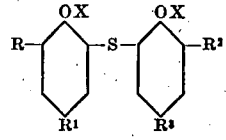
When lubricating oil is used under conditions of extremely hard surfaces such as heavy duty Diesel engines, tractor and airplane engines, a serious problem is presented due to the fact that the oil tends to form sludges which causes sticking on rings and also corrosive decomposition products are formed which present a serious corrosion problem with bearings, especially the new heavy duty alloy bearings such as silver-cadmium and copper-lead bearings.

It has been proposed to decrease the bad effect of sludging by adding metal salts of various organic acids which have a detergent action on the sludge. However, the addition of such metal salts has the very grave disadvantage that they greatly accelerate corrosion of bearings and this has seriously reduced their field of utility.

It has also been proposed in the past to use certain p-alkylphenol sulfides as corrosion inhibitors. These compounds do have considerable corrosion inhibiting power but are open to serious disadvantages. In the first place, the position on the benzene ring ortho to the hydroxy group is free and is hence active with a tendency for the compound to polymerize and to form sludge. Another very serious disadvantage is that the solubility in benzene hydrocarbons of some of the metal salts of these compounds is so low that they cannot be satisfactorily used alone in paraffin base lubricating oils such as Pennsylvania oils.

According to the present invention 2, 4-dialkylphenol sulfides are used in the form of their metal salts as bearing corrosion inhibitors and anti-sludging agents. These compounds show high solubility when the alkyl groups are sufficiently large, for example five carbon atoms or more; they do not decompose with heat, and give a protection against corrosion which is of a different order of magnitude than corrosion inhibitors which have hitherto been used. Even in such extreme tests as heating the lubricating oil to 340° F. and blowing air through it for days, the corrosion of bearing alloys is not increased and in many cases is less than 1% of that which results with standard so-called corrosion inhibitors.

While any of the 2, 4-dialkylphenol sulfides may be used, I have found that the 2, 4-diamylphenol sulfides are particularly useful. They are very cheap relatively, and in the form of their salts show complete solubility in Pennsylvania oils. However, other 2, 4-dialkylphenol sulfides may be used such as those obtained from p-amylphenol which has been condensed with the chlorinated residues of waxes and in which the alkyl radical in the 2-position may contain from 20–21 carbon atoms. Of course the sulfides may have different phenols. Essentially they are represented by the formula:



in which R, R^1, R^2, and R^3 are alkyl radicals and X is hydrogen or a metal.

Disulfides in which two phenol radicals are united through two sulfur atoms can also be used but it is not practical to use them in the form of their salts with strongly basic metals such as alkaline earth metals. However, salts of more weakly basic metals such as tin can be employed. The mono-sulfides are in general more effective than the corresponding disulfides, and are therefore preferred.

The products used in the present invention may be prepared in various ways, for example, by reacting the respective dialkyl phenol with sulfur dichloride in solution in carbon tetrachloride, ethylene chloride, or trichlorethylene, or other suitable solvent. The dialkylphenol sulfides and their methods of preparation are not claimed per se in the present application, forming the subject matter of our copending application, Serial No. 383,166, filed March 13, 1941.

The phenol sulfides are preferably used in the form of their salts such as tin, barium, or zinc salts. All of the salts are effective corrosion inhibitors but they will differ somewhat, and curiously enough they differ with the different alloys used. Thus, for example, with silver-cadmium alloys and most lubricating oils, the tin salts appear to give maximum protection. With other alloy bearings, barium and zinc salts are preferable. We have not determined the reason for this difference in effectiveness with the different salts when used with certain alloys. It should be

understood, however, that while the different metal salts differ among themselves, they are all effective corrosion inhibitors and sludge dispersors.

In addition to excellent dispersion characteristics, the compositions of the present invention reduce sludge formation. Probably this is due, at least in part, to the fact that the dialkylphenol sulfides of the present invention tend to wet bearing surfaces and thus to coat them with a thin film which removes the metal surface from actual contact of the bulk of the oil and it is believed that the metal of the bearing acts as a catalyst in sludge formation. The operation of compounds of the present invention is difficult to determine exactly and it is possible that other factors may be involved, and hence, the invention is not intended to be limited to any theory of action.

While the dialkylphenol sulfides of the present invention show uniformly good sludge dispersing powers, their corrosion inhibiting effect varies greatly with different oils and different bearings. Therefore, no one compound is best for all oils and all bearings. In some cases, more advantageous results are obtained from a mixture of different metal salts of the dialkylphenol sulfides. Thus, mixtures of the barium salts with zinc or tin salts are particularly effective and in some cases are more effective with certain oils than either alone.

The salts may be prepared either by direct action of the metal hydroxide or metal alcoholate, in the case of strongly basic metals, with the phenol sulfide, or in the case of some of the heavy metals by double decomposition of the sodium salt of the dialkylphenol sulfide and an alcoholic solution of the metal in question.

It is an important advantage of the present invention that the products can be used in very small quantities in lubricating oils. Thus the cost of protecting lubricating oils against corrosion in heavy duty service is negligible.

The products used in the present invention also have a further peculiar property in that they tend to render certain other compounds having corrosion inhibiting power, soluble in oil in which the other compounds will not dissolve when used alone. The reason why certain other compounds are rendered soluble when associated with the 2,4-dialkylphenol sulfides of the present invention has not as yet been completely determined and no theoretical explanation is therefore advanced.

While one of the outstanding fields of the present invention is in the protection of paraffin base and highly refined lubricating oils for which many known corrosion inhibitors are unsuitable, it should be understood that the present invention is not limited to paraffin base and highly refined lubricating oils entirely. On the contrary, the same desirable corrosion inhibiting and anti-sludging effect is to be noted with asphalt and naphthenic base lubricating oils although the advantage is not so outstanding because other corrosion inhibitors, even though less effective, can be used with such oils.

The invention will be described in greater detail in conjunction with the following specific examples.

Example 1

A solvent refined Mid-continent lubricating oil was subjected to the conventional Indiana oxidation test modified by suspending alloy bearing sections in the test oil samples. Loss of weight of the alloy bearing strips was taken as a measure of corrosion tendency of the lubricating composition. The test period was for 70 hours at 341° F., air being pumped through the lubricating compositions at the rate of 10 liters per hour. The corrosion effects are shown in the following table.

Table 1

Additive	Concentration	Bearing loss
	Percent	*Mgs.*
CADMIUM—SILVER BEARING		
None (control)		589
Barium diamylphenol monsulfide	0.3	21
Tin diamylphenol monosulfide	0.3	36
Zinc diamylphenol monosulfide	0.3	+3
COPPER—LEAD BEARING		
None (control)		127
Barium diamylphenol monosulfide	0.3	92
Tin diamylphenol disulfide	0.3	65
COPPER-SILVER-CADMIUM BEARING		
None (control)		193
Tin diamylphenol monosulfide	0.3	196
Zinc diamylphenol monosulfide	0.3	198
Barium diamylphenol monosulfide	0.3	17

In every case sludging was reduced materially as compared with the control and such sludge as was formed was soft and for the most part readily removed from the glass tube in which the test was carried out by a single wash with kerosene.

Example 2

A Pennsylvania oil of predominantly paraffin base was tested as described in Example 1. The corrosion inhibiting effects of the various products are shown in the following table.

Table 2

Additive	Concentration	Bearing loss
	Percent	*Mgs.*
CADMIUM—SILVER BEARING		
None (control)		500–1000
Tin diamylphenol monosulfide	0.3	533
Zinc diamylphenol monosulfide	0.3	83
Barium diamylphenol monosulfide	0.15	17
Zinc diamylphenol monosulfide	0.15	
Barium diamylphenol monosulfide	0.15	2
Tin diamylphenol monosulfide	0.15	
COPPER—LEAD BEARING		
None (control)		201
Zinc diamylphenol monosulfide	0.3	33
Barium diamylphenol monosulfide	0.3	50
Barium 2-dodecyl-4-tert. amylphenol monosulfide	0.5	136
COPPER-SILVER-CADMIUM BEARING		
None (control)		389
Barium diamylphenol monosulfide	0.3	16
Zinc diamylphenol monosulfide	0.3	43
Tin diamylphenol monosulfide	0.3	+11

In every case sludging was reduced materially as compared with the control and such sludge as was formed was soft, and for the most part, readily removed from the glass tube in which the test was carried out by a single wash with kerosene.

EXAMPLE 3

A Pennsylvania base oil highly refined by the aluminum chloride process was tested as described in Example 1. The corrosion inhibiting results are shown in the following table.

Table 3

Additive	Concentration	Bearing loss
CADMIUM—SILVER BEARING		
	Percent	*Mgs.*
None (control)		1556
Tin diamylphenol monosulfide	0.3	+11
Barium diamylphenol monosulfide	0.3	1505
Tin diamylphenol monosulfide	0.15	123
Barium diamylphenol monosulfide	0.15	
COPPER-SILVER-CADMIUM BEARING		
None (control)		135
Tin diamylphenol monosulfide	0.3	+2
Barium diamylphenol monosulfide	0.3	133

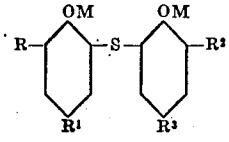
+ means gain.

In every case sludging was reduced materially as compared with the control and such sludge as was formed was soft, and for the most part, readily removed from the glass tube in which the test was carried out by a single wash with kerosene.

An examination of the specific examples will show that while in every case corrosion was no worse as compared with the control, it is not possible to correlate corrosion inhibitance with chemical structure. Thus, for instance, in Example 3 the barium compound did not show improved corrosion resistance over the control sample although corrosion was not increased. On the other hand, in Example 1 with the silver-cadmium bearing, the barium compound was the only one that showed high corrosion inhibiting tendencies. It is notable, however, that mixed compounds containing both barium and other metal salts show uniformly good results in all of the classes.

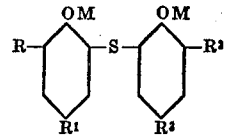
We claim:

1. A lubricating oil composition containing a 2,4-dialkylphenol sulfide having the following formula:



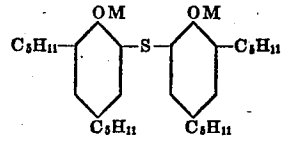
in which R, R^1, R^2 and R^3 are alkyl radicals and M is a metal, in amounts sufficient to exert sludge dispersing properties under heavy duty service without increasing bearing corrosion.

2. A paraffin base lubricating oil composition containing a 2,4-dialkylphenol sulfide having the formula:



in which R, R^1, R^2 and R^3 are alkyl radicals and M is a metal, in amounts sufficient to exert sludge dispersing properties under heavy duty service without increasing bearing corrosion.

3. A lubricating oil composition containing a 2,4-diamylphenol sulfide having the following formula:



in which M is a metal, in amounts sufficient to exert sludge dispersing properties under heavy duty service without increasing bearing corrosion.

4. A composition according to claim 1 in which M is tin.

5. A composition according to claim 2 in which M is tin.

6. A composition according to claim 3 in which M is tin.

7. A composition according to claim 1 in which M is barium.

8. A composition according to claim 2 in which M is barium.

9. A composition according to claim 3 in which M is barium.

10. A composition according to claim 1 in which M is zinc.

11. A composition according to claim 2 in which M is zinc.

12. A composition according to claim 3 in which M is zinc.

13. A composition according to claim 1 in which a mixture of dialkylphenol sulfide salts are used, part of them being a barium salt and part a different metal salt.

14. A composition according to claim 3 in which a mixture of diamylphenol sulfide salts are used, part of them being a barium salt and part a different metal salt.

15. A composition according to claim 3 in which a mixture of diamylphenol sulfide salts are used, part being the barium salt and part the zinc salt.

16. A composition according to claim 3 in which a mixture of diamylphenol sulfide salts are used, part being the barium salt and part the zinc salt.

ELMER WILLIAM COOK.
WILLIAM DAVID THOMAS, JR.