

UNITED STATES PATENT OFFICE

2,160,880

LUBRICANT

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6 Claims. (Cl. 87-9)

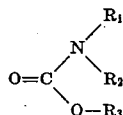
This invention relates to lubricants and, in particular, to addition agents imparting to lubricants improved properties.

Our invention has particular utility in preventing and/or inhibiting the corrosion of "hard metal" alloy bearings such as cooper-lead, cadmium-nickel, and cadmium-silver bearings which, to a large extent, have replaced soft metal bearings such as Babbitt metal in the trend toward internal combustion engines having high compression ratios and having increased acceleration and increased speed characteristics. The use of the "hard metal" bearings has created lubrication and corrosion problems, particularly in connection with "highly refined" oils, some of which may be very corrosive to the "hard metal" bearings.

By "highly refined" lubricating oils we mean viscous oils which have a minimum viscosity in the range of S. A. E. 10 oils and which have been subjected to such refining processes such as, for example, solvent extraction, that the paraffinicity of the oil is markedly increased. It has been found that highly refined lubricating oils cause corrosion to alloy bearings of the cadmium-silver type to the extent of 5mg./cm.² and even greater when such bearings are submerged for 25 hours or less in an air agitated oil which has been preoxidized at about 340° F. for 25 to 50 hours. The motor oils may be highly refined lubricating oils as such or mixtures of highly refined lubricating oils with less highly refined lubricating oils, or stated in another way, mixtures of corrosive oils and non-corrosive oils, examples of the latter being lubricating oil fractions from Winkler crude or crudes of the Winkler type.

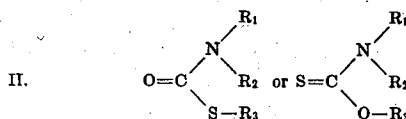
We have found that corrosiveness is inhibited and highly desirable properties are imparted to lubricating oils by adding thereto up to 1%, but preferably 0.05% to 0.75% of certain organic materials, particularly aliphatic or open chain organic compounds containing nitrogen, oxygen and/or sulfur.

Examples of compounds which may be used are the esters of amide derivatives of carbonic acid such as the carbamic acid derivatives having the general formula

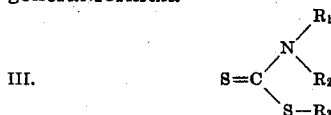


in which R₁ and R₂ may be hydrogen, an alkyl radical and/or an aryl radical and R₃ may be an alkyl radical, an aryl radical and/or a metal, such as ethyl carbamate, propyl carbamate, butyl carbamate, isoamyl carbamate, ethyl carbamic ethyl ester (ethyl urethane), urethane, methyl carbamic ethyl ester, diethyl carbamic ethyl ester, ethyl-butyl carbamic butyl ester, phenyl carbamate (phenyl urethane), phenyl carbamic

phenyl ester, diphenyl carbamic phenyl ester, tin salt of diamyl carbamic acid; the thiocarbamic acid derivatives having the general formula

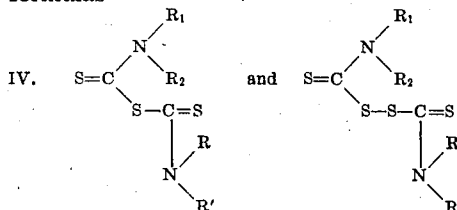


in which R₁ and R₂ may be hydrogen, an alkyl radical and/or an aryl radical and R₃ may be an alkyl radical, an aryl radical and/or a metal such as thio carbamic ethyl ester, butyl thio carbamic ethyl ester, diethyl thio carbamic ester, ethyl butyl thio carbamic ethyl ester, thiol carbamic phenyl ester, diphenyl thio carbamic phenyl ester; and the dithiocarbamic acid derivatives having the general formula



in which R₁ and R₂ may be hydrogen, an alkyl radical and/or an aryl radical, and R₃ may be an alkyl radical, an aryl radical and/or a metal such as dithiocarbamic ethyl ester, ethyl dithiocarbamic ethyl ester, diethyl dithiocarbamic ethyl ester, dithiocarbamate phenyl ester, phenyl dithiocarbamic phenyl ester, lauryl dithiocarbamate, tin diamyl dithiocarbamate.

Other compounds contemplated by our invention are the thiuram sulfides having the general formulas



in which R₁ and R₂ and R and R' are hydrogen and/or alkyl radicals or an alkylene radical and/or aryl radicals such as tetra methyl thiuram sulfide, tetra methyl thiuram disulfide, tetra ethyl thiuram sulfide, and di pentamethylene thiuram tetra sulfide.

Since these compounds are subjected to high temperature conditions it is highly desirable that compounds of the aforementioned type having boiling points of about 400° F. or greater be used.

The effectiveness of compounds of the above type as corrosion inhibitors is demonstrated by the following examples in which they were subjected to one or more different sets of conditions, each of which is more severe than those encountered in the actual operation of internal combustion engines.

Method I.—Cadmium-silver alloy bearings are

submerged in a highly refined oil to which the compound to be tested is added and the oil air-agitated and heated to about 341° F. At regular intervals the test strips are removed from the bath, washed free of oil and weighed to determine the loss in weight and then replaced in the bath for further testing.

Method II.—By this method a "highly" refined oil, to which the corrosion inhibitor is to be added, is preoxidized for either 25 hours or 50 hours by air agitating the same at about 341° F. The corrosion inhibitor and the weighed bearings are placed in the preoxidized oil and the oil air-agitated at about 341° F. The bearings are removed at periodic intervals, washed free of oil and the loss in weight determined.

Method III.—By this method the weighed bearings are placed in a "highly" refined oil containing the inhibitor which is air agitated at about 341° F. At periodic intervals the bearings are removed from the oil bath, washed free of oil and the loss in weight determined. Each time before being replaced in the oil bath the bearings are polished bright and reweighed and again tested for predetermined periods. This method differs from Method II in that the test is started with an unoxidized "highly" refined oil and the test bearings are polished at predetermined intervals.

In each of the above methods the oil used was a motor oil refined to such an extent that a loss in weight of more than 5 mg./cm.² is obtained in 25 hours or less on a cadmium-silver alloy bearing submerged in an air agitated oil at 340° F., which oil has been preoxidized for 25-50 hours at about 340° F.

In Table I are tabulated the results obtained with representative compounds when tested according to the above described test Method II.

Table I

Oil	Loss in mg./cm. ² in—	
	3 hrs.	24 hrs.
Control.....	4.3	43.0+
Control+.2% tetra methyl thiuram mono sulfide..	0.3	27.0
Control+.2% dipenta methylene thiuram tetra sulfide.	.0	7.5

In Table II are the results obtained with several representative compounds when tested according to the above described test Method III.

Table II

Oil	Loss in mg./cm. ² , periods		
	1st 24 hrs.	2nd 6 hrs.	3rd 16 hrs.
Control.....	3.6	5.0	20.5
Control+.2% ethyl thiourethane.....	.1	—	16.5
Control+.2% tin diamyl dithiocarbamate.....	.0	.0	.4
Control+.2% tetra methyl thiuram mono sulfide.....	.3	.1	.0
Control+.2% lauryl dithiocarbamate.....	.1	.0	1.5

While we have described in detail the use of the hereinbefore mentioned compounds as corrosion inhibitors in "highly" refined lubricating oils, we contemplate the use of up to 10% of these compounds in lubricating oils whether "highly" refined or not, for the purpose of improving the film strength thereof and to impart to lubricants improved extreme pressure characteristics.

These compounds may also be used to improve

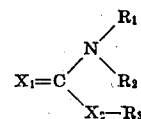
the lubricity and other desirable properties of lubricating oils.

Some of the hereinbefore named compounds may not be completely soluble in the lubricant, in which case effective results are obtained by suspending the inhibitor in the lubricant by means of a small amount of a peptizing agent such as aluminum naphthenate, aluminum stearate, etc.

We do not limit ourselves to the specific embodiments of our invention herein described except as defined by the appended claims.

We claim:

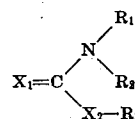
1. An improved lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% of a carbamic acid derivative having the general formula



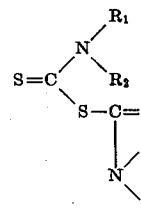
in which X₁ and X₂ are elements selected from the group consisting of oxygen and sulfur, R₁ and R₂ are selected from the group consisting of hydrogen, an alkyl radical, and an aryl radical and R₃ is selected from the group consisting of an alkyl radical, an aryl radical and a metal.

2. An improved lubricant comprising a lubricating oil and from about 0.05% to about 10% of tin diamyl dithiocarbamate.

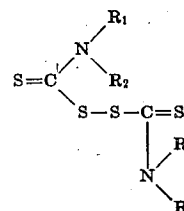
3. The method of lubricating an internal combustion engine provided with hard metal alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys which comprises applying to said bearings a lubricant comprising a highly refined mineral lubricating oil normally corrosive to said bearings and a small but corrosion inhibiting amount of an aliphatic hydrocarbon selected from the group consisting of carbamic acid derivatives having the general formula



in which X₁ and X₂ are elements selected from the group consisting of oxygen and sulfur, R₁ and R₂ are substituents selected from the group consisting of hydrogen, an alkyl radical, an aryl radical, and R₃ is a substituent selected from the group consisting of an alkyl radical, an aryl radical and a metal, a thiuram sulfide having the general formula



and a thiuram disulfide having the general formula



in which R₁, R₂, R and R' are substituents selected from the group consisting of an alkyl radical and an aryl radical.

4. The method of lubricating an internal combustion engine provided with hard metal alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys which comprises applying to said bearings a lubricant comprising a highly refined mineral lubricating oil normally corrosive to said bearings and a small but sufficient quantity of tin diamyl dithiocarbamate to inhibit the corrosion of said bearings by said highly refined lubricating oil.

5. The method of lubricating an internal combustion engine provided with hard metal alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys which

comprises applying to said bearings a lubricant comprising a highly refined mineral lubricating oil normally corrosive to said bearings and a small but sufficient quantity of lauryl dithiocarbamate to inhibit the corrosion of said bearings by said highly refined lubricating oil.

6. The method of lubricating an internal combustion engine provided with hard metal alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys which comprises applying to said bearings a lubricant comprising a highly refined mineral lubricating oil normally corrosive to said bearings and a small but sufficient quantity of a thiuram sulfide to inhibit the corrosion of said bearings by said highly refined lubricating oil.

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CERTIFICATE OF CORRECTION.

Patent No. 2,160,880.

June 6, 1939.

CLARENCE M. LOANE, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 55, for "carbante" read carbamate; same page, second column, line 13, after the word "carbamic" insert ethyl; line 28, for "dithiocarbamate" read dithiocarbamic; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of July, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.