

UNITED STATES PATENT OFFICE

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LUBRICANT

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164,310

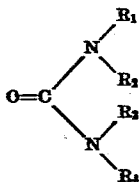
16 Claims. (Cl. 252-47)

This invention relates to lubricants and, in particular, to addition agents imparting to lubricants improved properties. This application is a division of our co-pending application Ser. No. 108,832 filed November 2, 1936, now issued as Patent No. 2,160,880 of June 6, 1939.

Our invention has particular utility in preventing and/or inhibiting the corrosion of "hard metal" alloy bearings such as copper-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 5 mg./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.

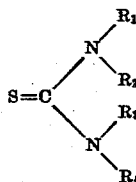
We have found that corrosiveness is inhibited and highly desirable properties are imparted to lubricating oils by adding thereto up to 1%, but preferably 0.05% to 0.75% of certain organic materials, particularly aliphatic or open chain organic compounds containing nitrogen, oxygen and/or sulfur, such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



in which R₁, R₂, R₃ and R₄ may be either hydrogen, an alkyl radical, an alkylene radical, and/or an aryl radical such as

Urea
Phenyl urea
Diethyl diphenyl urea
Di alpha naphthyl urea
Di-O-tolyl urea
Mono-O-tolyl urea;

the thio ureas having the general formula



in which R₁, R₂, R₃ and R₄ may be either hydrogen, an alkyl radical, an alkylene radical or an aryl radical such as

Thio urea
Di octyl thio urea
Di butyl thio urea
Di cetyl thio urea
Allyl thio urea
Phenyl thio urea
Di phenyl thio urea
Phenyl allyl thio urea.

Since these compounds are subjected to high temperature conditions it is highly desirable that the 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 several representative compounds using test Method I above described.

Table I

Oil	Loss in mg./cm. ² in—	
	24 hrs.	72 hrs.
Control.....	11.0	93.5
Control+0.05% urea.....	0.0	0.0
Control+0.1% dibutyl thiourea.....	0.0	0.9
Control+0.1% diphenyl thiourea.....	0.0	17.1
Control+0.1% thiourea.....	0.0	0.0
Control+0.05% thiourea.....	0.0	0.0

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

Table II

Oil	Loss in mg./cm. ² in—	
	3 hrs.	24 hrs.
Control.....	4.3	43.0
Control+diethyl diphenyl urea.....	2.1	20.6
Control+0.2% di o-tolyl urea.....	0.4	1.6
Control+0.2% o-tolyl urea.....	0.9	3.8
Control+allyl thiourea.....	2.4	—
Control+0.1% thiourea.....	0.0	6.6

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

Table III

Oil	Loss in mg./cm. ²		
	Periods		
	1st 24 hrs.	2d 6 hrs.	3d 16 hrs.
Control.....	3.6	5.0	20.5
Control+phenyl allyl thiourea.....	0.1	0.0	0.0

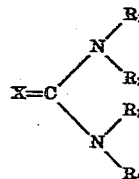
While we have described in detail the use of the hereinbefore mentioned compounds as corrosion inhibitors in "highly" refined lubricating oils, we contemplate the use of up to 10% of these compounds in lubricating oils whether "highly" refined or not, for the purpose of improving the film strength thereof 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. A corrosion inhibited lubricating oil adapted for use in the presence of hard metal alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys comprising a highly refined mineral lubricating oil normally corrosive to such alloys and a small but sufficient amount to inhibit the corrosion of said alloy bearings of an organic compound having the general formula



in which X is an element selected from the group consisting of oxygen and sulfur, and R₁, R₂, R₃ and R₄ are substituents selected from the group consisting of hydrogen, alkyl radicals, alkylene radicals and aryl radicals.

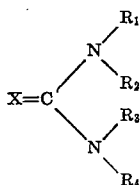
2. A corrosion inhibited lubricating oil adapted for use in the presence of hard metal alloy bearings of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys which comprises a highly refined mineral lubricating oil normally corrosive to bearings of said type and an urea, said urea being added in small but sufficient amounts to inhibit the corrosion of said alloy bearings.

3. A corrosion inhibited lubricating oil as described in claim 2 in which the urea is O-tolyl urea.

4. A corrosion inhibited lubricating oil adapted for use in the presence of hard metal alloy bearings of the class consisting of cadmium-silver, cadmium-nickel and copper-lead alloys which comprises a highly refined mineral lubricating oil normally corrosive to bearings of said type having added thereto a thiourea in small but sufficient quantities to inhibit the corrosion of said alloy bearings.

5. The method of preventing the corrosion of hard metal alloy bearings having the corrosion susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys, by highly refined mineral lubricating oils which comprises adding to said oils normally corrosive to said alloy bearings

in corrosion inhibiting amounts an organic compound having the general formula



in which X is an element selected from the group consisting of oxygen and sulfur, and R₁, R₂, R₃ and R₄ are substituents selected from the group consisting of hydrogen, alkyl radicals, alkylene radicals and aryl radicals.

6. A lubricant consisting of a mineral lubricating oil normally corrosive to alloys having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys, and copper-lead alloys, and a hydrocarbon substituted thiourea added in amounts sufficient to render said mineral lubricating oil non-corrosive to said alloys.

7. The method of preventing the corrosion of alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys, and copper-lead alloys, by highly refined mineral lubricating oils normally corrosive to said alloys which comprises adding to said oils a hydrocarbon substituted thiourea in small but corrosion inhibiting proportions.

8. A lubricant consisting of a mineral lubricating oil normally corrosive to alloys having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys, and copper-lead alloys, and an alkyl thiourea added in amounts sufficient to render said mineral lubricating oil non-corrosive to said alloys.

9. The method of preventing the corrosion of alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys, and copper-lead alloys by highly refined mineral lubricating

oils normally corrosive to said alloys which comprises adding to said oils an alkyl thiourea in small but corrosion inhibiting proportions.

10. A lubricant consisting of a mineral lubricating oil normally corrosive to alloys having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys, and copper-lead alloys and thiourea added in amounts sufficient to render said mineral lubricating oil non-corrosive to said alloys.

11. The method of preventing the corrosion of alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys, and copper-lead alloys by highly refined mineral lubricating oils normally corrosive to said alloys which comprises adding to said oils thiourea in small but corrosion inhibiting proportions.

12. A lubricant as described in claim 8 in which the alkyl thiourea is dibutyl thiourea.

13. The method of preventing the corrosion of alloy bearings as described in claim 9 in which the alkyl thiourea is dibutyl thiourea.

14. The method of preventing the corrosion of alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys by highly refined mineral lubricating oils normally corrosive to said alloys, which comprises adding to said oils an urea in small but corrosion inhibiting proportions.

15. The method of preventing the corrosion of alloy bearings as described in claim 14 in which the urea is O-tolyl urea.

16. The method of preventing the corrosion of alloy bearings having the corrosive susceptibility of alloys of the class consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys by highly refined mineral lubricating oils normally corrosive to said alloys, which comprises adding to said oils a thiourea in small but corrosion inhibiting proportions.

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