Patented Apr. 11, 1939 2,154,097

UNITED STATES PATENT OFFICE

2,154,097

LUBRICATING OIL

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No Drawing. Application November 27, 1936 Serial No. 112,993

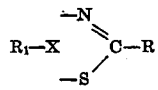
3 Claims. (Cl. 87—9)

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

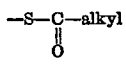
This invention has particular utility in improving the lubricating properties of lubricating oils and/or in preventing or inhibiting the corrosion of "hard metal" alloy bearings such as copper-lead, cadmium-nickel and cadmium-silver bearings which, to a large extent, have replaced soft metal bearings,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

As used herein "highly refined" lubricating oil means viscous oils which have a minimum viscosity of S. A. E. 10 oils, or higher, and which have been subjected to such refining processes 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 hard metal type such as cadmium-silver alloy bearings to the extent of about 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.

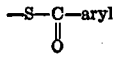
I have found that the corrosion of hard metal alloy bearings of the cadmium-silver type in the presence of highly refined lubricating oils can be inhibited by adding to the said oil up to 2%, but preferably 0.05% to 0.75% of certain organic compounds, particularly the bivalent radical substituted five membered ring compounds having sulfur and nitrogen in the ring, said compounds having the general formula



in which X is a benzo radical or arylene derivative thereof and in which R is hydrogen or alkyl or aryl or —SH or —S— alkyl or —S— aryl or

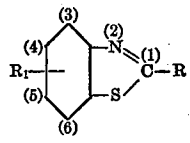


or

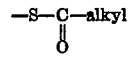


or —NH_2 or —NH— alkyl or —N— alkyl or mixtures thereof and/or R_1 may be hydrogen or alkyl or halogen or amino or mercapto or alkyl substituted amino or substituted mercapto or substituted benzothiazole group or groups and/or mixtures thereof.

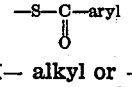
Specific examples of the benzothiazoles having the general formula



in which R is hydrogen or alkyl or aryl or —SH or —S— alkyl or —S— aryl or



or



or —NH_2 or —NH— alkyl or —N— alkyl or mixtures thereof and/or R_1 may be hydrogen or alkyl or halogen or amino or mercapto or alkyl substituted amino or substituted mercapto or substituted benzothiazole group or groups and/or mixtures thereof are:

Mercapto benzothiazole
1-butyl benzothiazole
3-hexyl benzothiazole
6-octyl benzothiazole
1-3-dibutyl benzothiazole
4-5-dipropyl benzothiazole
1-phenyl benzothiazole
1-butyl amino benzothiazole
1-butyl mercapto benzothiazole
1-mercapto-3-hexyl benzothiazole
1-mercapto-4-5-diamyl benzothiazole
1-mercapto-6-phenyl benzothiazole
1-mercapto-5-chlor benzothiazole
1-mercapto-3-butyl-5-chlor benzothiazole
1-amino-5-hexyl benzothiazole
1-5 dimercapto benzothiazole
1-5 dimercapto-3-amyl benzothiazole
1-mercapto-5-butyl amino benzothiazole
Benzothiazole thio glycollic acid
Benzothiazole thio benzoic acid

And the naphthothiazole derivatives of the above such as:

Mercapto naphthothiazole
Amino naphthothiazole
Hexyl naphthothiazole
Phenyl naphthothiazole

In addition to the above compounds I have found that the benzo derivatives of the thio (AA) diazoles which are known as the piazothioles are effective corrosion inhibitors.

The effectiveness of compounds of the above type as corrosion inhibitors is demonstrated by

the following test in which oils to which the inhibitor has been added were subjected to conditions which are more severe than those encountered in the actual operation of internal combustion engines.

Weighed cadmium-silver alloy bearings were submerged in samples of a highly refined oil with and without the addition of the compound to be tested and the oil air agitated while maintained at a temperature of about 341° F. At regular intervals the cadmium-silver alloy bearings were removed from the bath, washed free of oil, and weighed to determine the loss in weight. The bearings were then replaced in the oil and further tested. 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 the air agitated oil at about 340° F., which oil has been preoxidized for 25 to 50 hours at about 340° F.

The following results were obtained on cadmium-silver alloy bearings when tested in the foregoing manner.

Oil	Duration of test		
	25 hrs.	50 hrs.	100 hrs.
	Loss in weight (mg/cm.²)		
Control	2.5	35.0	105.0
Control+.2% mercapto-benzothiazole	0.0	0.0	0.4

The above data definitely show the high inhibiting effect of the mercapto benzothiazole.

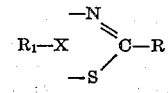
Although I prefer to use the compounds of the hereinabove type which are completely oil soluble, equally effective results are obtained with those which are not completely soluble in the lubricant by suspending the inhibitor in the lubricant by means of a small amount of a peptizing agent, such as aluminum naphthenate, aluminum stearate and the like.

While I have described my invention by using preferred examples thereof I do not wish to be limited by the same except as defined by the appended claims.

I claim:

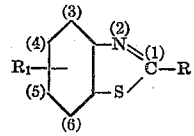
1. The method of preventing corrosion of bearing metal alloys selected from the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of highly refined lubricating oils normally corrosive to said bearing metal alloys in internal combustion engines which comprises adding to said lubricating oils a mercapto benzothiazole in a small but sufficient quantity to effect the retardation of said corrosion to said bearing metal alloys.

2. The method of preventing corrosion of hard metal alloy bearings in the presence of highly refined lubricating oils normally corrosive to said hard metal alloy bearings in internal combustion engines which comprises adding to said lubricating oils a bivalent radical substituted five-membered ring compound having sulfur and nitrogen in the ring and having the general formula



in which X is a radical selected from the group consisting of a benzo radical and an arylene derivative of a benzo radical, R is a substituent selected from the group consisting of hydrogen, an alkyl radical, an aryl radical and R_1 is a substituent selected from the group consisting of hydrogen, an alkyl radical, an amino group and a mercapto group, said compound being added to said lubricating oil in a small but sufficient quantity to effectively inhibit the corrosion to said hard metal alloy bearings.

3. The method of preventing corrosion of hard metal alloy bearings in the presence of highly refined lubricating oils normally corrosive to said hard metal alloy bearings in internal combustion engines which comprises adding to said lubricating oils a benzothiazole having the general formula



in which R is a substituent selected from the group consisting of hydrogen, an alkyl radical and an aryl radical, and R_1 is a substituent selected from the group consisting of hydrogen, an alkyl radical, an aryl radical, a mercapto group and an amino group, said benzothiazole being added to said lubricating oil in a small but sufficient quantity to effectively inhibit the corrosion of said hard metal alloy bearings.

CLARENCE M. LOANE.