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LUBRICATING OIL

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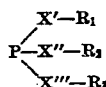
8 Claims. (Cl. 87-9)

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 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, 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 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./cm². 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 corrosion of hard metal alloy bearings of the cadmium-silver type in the presence of highly refined lubricating oil can be inhibited by adding to the oil up to 2%, but preferably 0.05% to 0.75%, of certain organic phosphorous materials, particularly the aryl and alkyl derivatives of thiophosphites having the general formula



in which X' is S and X'' and X''' are either O or S, and in which R₁, R₂ and R₃ are either hydrogen, and/or an alkyl radical and/or an aryl radical, and at least one of which is an alkyl radical or an aryl radical.

Further, our invention contemplates the use of the mono-, di- and tri-alkyl or aryl thiophosphites or mixtures thereof, the thiophosphites being the mono-, di- or tri-thiophosphite.

Further, our invention contemplates the use of an alkyl and/or an aryl thiophosphite in which one or more of the alkyl and/or aryl radicals have a substituted, hydroxy, mercapto, halogen, alkoxy, aryloxy, thiocyno, iso-thiocyno, amino, alkyl substituted amino, etc. group or groups.

Specific examples of some of the thiophosphites falling within the scope of our invention are:

Mono and/or di and/or tri propyl mono-, di- or tri-thiophosphite 15

Mono and/or di and/or tri butyl mono-, di- or tri-thiophosphite

Mono and/or di and/or tri amyl mono-, di- or tri-thiophosphite 20

Mono and/or di and/or tri hexyl mono-, di- or tri-thiophosphite

Mono and/or di and/or tri phenyl mono-, di- or tri-thiophosphite

Mono and/or di and/or tri cresyl mono-, di- or tri-thiophosphite 25

Dibutyl phenyl mono-, di- or tri-thiophosphite

Amyl dicresyl mono-, di- or tri-thiophosphite and the above with the hereinbefore mentioned substituted groups, for example, mono-, di-, or tri-(chlorophenyl), tri-thiophosphites or mixtures and the mono-, di-, or tri-(chlorobutyl) tri-thiophosphites or mixtures thereof. 30

Although the alkyl and/or aryl thiophosphites in general may be employed we prefer to use the alkyl and/or the aryl thiophosphites having 3 to 6 carbon atoms in each alkyl since the same are the most effective corrosion inhibitors.

The effectiveness of compounds of the above type as corrosion inhibitors is demonstrated by the following test in which they 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 (preoxidized for 25 hours at 341° F.) with and without the addition of the compound to be tested and the oil air agitated while maintained at a temperature of 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 baths and further tested. 50

In this test 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.

Using this method the following results were obtained.

Oil	Periods of submergence	
	6 hrs.	16 hrs.
Control	Loss in weight (mg./cm. ²)	Loss in weight (mg./cm. ²)
Control+0.2% triphenyl tri-thiophosphite	Corrosion started... 0.0	8.1 0.2

The above results clearly show the corrosion inhibiting effect of small amounts of triphenyl tri thiophosphite in a highly refined lubricating oil.

The effectiveness of the thiophosphites in inhibiting the corrosion of bearing metal alloys of the cadmium-silver type is further demonstrated by another test. In this test weighed bearings of the cadmium-silver alloy are placed in vessels containing a "highly refined" oil with and without the inhibitor. The oil in each vessel is air agitated and maintained at a temperature of about 341° F. At periodic intervals the bearings are removed from the vessels, washed free of oil and the loss in weight determined. The bearings are then repolished bright, reweighed and again tested for another predetermined period. The control oil used in this test was the same type used in the hereinbefore mentioned test.

Using the above test the following data were obtained:

Oil	Periods			
	1st 24 hrs.	2nd 6 hrs.	3rd 16 hrs.	4th 6 hrs.
Control	Loss in mg./cm. ² 0.6	Loss in mg./cm. ² 5.4	Loss in mg./cm. ² 27.2	Loss in mg./cm. ² 11.7
Control+0.2% tri-amyli tri-thiophosphite	0.1	0.5	6.7	7.9

The above data definitely show the high inhibiting effect of the alkyl thiophosphite.

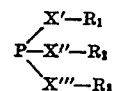
Although most of the compounds mentioned hereinbefore are oil soluble some may not be completely soluble in the lubricant. We have obtained satisfactory results by suspending the inhibitor in the lubricant by means of a small amount of a peptizing agent, such as aluminum naphthenate, aluminum stearate, etc.

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

We claim:

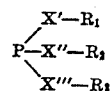
1. The method of preventing corrosion to hard metal alloy bearings in the presence of highly refined lubricating oils normally corrosive to such bearings in internal combustion engines which comprises adding to said lubricating oils in an amount sufficient to inhibit such corrosion an

organic phosphorous compound having the general formula



in which X' is sulfur, X'' and X''' are elements selected from the group consisting of oxygen and sulfur and R₁, R₂ and R₃ are substituents selected from the group consisting of hydrogen, alkyl radicals and aryl radicals, at least one of which is selected from the group consisting of alkyl radicals and aryl radicals.

2. A lubricating oil non-corrosive to hard metal alloy bearings comprising a mineral lubricating oil normally corrosive to said bearings and an organic phosphorus compound having the general formula



in which X' is sulfur, X'' and X''' are elements selected from the group consisting of oxygen and sulfur and R₁, R₂ and R₃ are substituents selected from the group consisting of hydrogen, alkyl radicals and aryl radicals, at least one of which is selected from the group consisting of alkyl radicals and aryl radicals, said phosphorus compound being added in a small but sufficient quantity to inhibit the corrosion of said hard metal alloy bearings.

3. A lubricating oil non-corrosive to hard metal alloy bearings comprising a mineral lubricating oil normally corrosive to said bearings and an alkyl thiophosphite having 3 to 6 carbon atoms in each alkyl radical, said alkyl thiophosphite being added in a small but sufficient quantity to inhibit the corrosion to said hard metal alloy bearing.

4. A lubricating oil as described in claim 3 in which the alkyl thiophosphite is tri-amyli tri-thiophosphite.

5. A lubricating oil non-corrosive to hard metal alloy bearings comprising a mineral lubricating oil normally corrosive to said bearings and an aryl thiophosphite, said aryl thiophosphite being added in a small but sufficient quantity to inhibit the corrosion to said hard metal alloy bearing.

6. A lubricating oil as described in claim 5 in which the aryl thiophosphite is tri-phenyl tri-thiophosphite.

7. 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 in internal combustion engines which comprises adding to said lubricating oils an alkyl thiophosphite having 3 to 6 carbon atoms in each alkyl radical in a small but sufficient amount to inhibit said corrosion.

8. 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 in internal combustion engines which comprises adding to said lubricating oils an aryl thiophosphite in a small but sufficient quantity to inhibit said corrosion.

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DISCLAIMER

2,191,996.—*Bernard H. Shoemaker and Clarence M. Loane*, Hammond, Ind. LUBRICATING OIL. Patent dated February 27, 1940. Disclaimer filed April 20, 1942, by the assignee, *Standard Oil Company (Indiana)*.

Hereby enters this disclaimer to claims 3 and 4 in said specification.

[*Official Gazette May 19, 1942.*]