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## LUBRICANT

Clarence M. Loane, Whiting, and Bernard H. Shoemaker, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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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 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 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 corrosion of hard metal alloy bearings can be inhibited and highly desirable properties can be imparted to the lubricating oil by adding thereto up to 2% but preferably 0.05% to 0.75% of certain organic materials, particularly the aliphatic and aromatic poly thiocyanates and the aliphatic and aromatic poly isothiocyanates having the general formulas

I. $R(SCN)_n$ and

II. $R(NCS)_n$

respectively in which R is an aliphatic group or aromatic group and $n$ is a whole number greater than one.

Examples of the poly thiocyanates which we may use are:

Dithiocyano ethane
Dithiocyano propane
Dithiocyano butane
Dithiocyano heptane
Trithiocyano heptane
Dithiocyano octane
Trithiocyano octane
Dithiocyano dodecane
1,2,4 trithiocyano benzene
Para phenylene dithiocyanate
Ortho phenylene dithiocyanate
Meta phenylene dithiocyanate

Examples of the poly isothiocyanates which may be used are:

Di isothiocyano propane
Di isothiocyano butane
Di isothiocyano heptane
Tri isothiocyano heptane
Ocetene di isothiocyanate
Tri isothiocyano octane
Dodecene di isothiocyanate
1,2,4 tri isothiocyano benzene
Para phenylene di isothiocyanate
Ortho phenylene di isothiocyanate
Meta phenylene di isothiocyanate

Our invention also contemplates the use of the polymers obtained by heating mustard oil with an aqueous solution of potassium acetate, or by heating mustard oil with dilute hydrochloric acid.

We have also found that certain metallo poly thiocyanates may be used effectively. Compounds such as potassium ferri thiocyanate and ammonium ferri thiocyanate are examples of the type of metallo poly thiocyanates we prefer to use. The metallo poly thiocyanates are best dissolved in the oil by adding, for example, KSCN to a slightly acidified $FeCl_3$ solution and extracting the aqueous solution with ether. The ether extract is then added to the oil and the ether removed by blowing. Since these compounds impart color to the oil they are preferably used where discoloration of the oil is not detrimental to its use.

Since these compounds are subjected to high temperature conditions it is highly desirable that the compound 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 test in which they were subjected to a set of conditions, which is more severe than those encountered in the actual operation of internal combustion engines. The compounds were tested by the following 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.

In the above test the oil used was a motor oil refined to such an extent that a loss in weight of more than 5 mg. per 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.

Using the above described test the following results were obtained.

| Oil | Periods | | | | |
|---|---|---|---|---|---|
| | 1st 24 hrs. | 2nd 6 hrs. | 3rd 16 hrs. | 4th 6 hrs. | 5th 16 hrs. |
| | Loss in mg/cm$^2$ | | | | |
| Control | 3.6 | 5.0 | 20.5 | ------- | ------- |
| .2% ethylene dithiocyanate | 0.9 | 0.0 | 2.9 | 11.9 | ------- |
| .2% dodecene dithiocyanate | 0.0 | 0.0 | 0.7 | 1.3 | 26.5 |
| .2% octene dithiocyanate | 0.1 | 0.0 | 0.9 | 6.6 | ------- |
| Mustard oil potassium acetate polymer | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Mustard oil HCl polymer | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| .2% 9KSCN·Fe(SCN)$_3$ | 0.1 | 1.1 | 3.6 | 1.0 | ------- |
| .2% $x$(NH$_4$SCN) . Fe(SCN)$_3$ | 0.5 | 1.2 | 2.5 | 0.9 | ------- |

While we have described in detail the use of the hereinbefore mentioned compounds as corrosion inhibitors in highly refined lubricating oils, our invention is not limited thereto, but contemplates the use of up to 10% of these compounds in lubricating oils for the purpose of improving the film strength thereof, reduce engine wear and to impart to lubricants improved extreme pressure characteristics. These compounds may also be used to improve the lubricity and other properties of lubricating oils.

Some of the foregoing 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 extreme pressure lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% of an organic compound having the general formula $R(Y)_n$ in which R is a substituent selected from the group consisting of an aliphatic group, an aromatic group and a metal, Y is a radical selected from the group consisting of a thiocyano radical and an isothiocyano radical and $n$ is a whole number greater than 1.

2. An improved extreme pressure lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% of a polythiocyanate having the general formula $R(SCN)_n$ in which R is a substituent selected from the group consisting of an aliphatic group, an aromatic group and a metal and $n$ is a whole number greater than one.

3. An improved extreme pressure lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% of a polyisothiocyanate having the general formula $R(NCS)_n$ in which R is a substituent selected from the group consisting of an aliphatic group, an aromatic group and a metal and $n$ is a whole number greater than one.

4. An improved extreme pressure lubricant comprising mineral lubricating oil and a polythiocyanate having the general formula $R(SCN)_n$ in which R is an aliphatic group and $n$ is a whole number greater than 1, said aliphatic polythiocyanate being added in amounts sufficient to impart extreme pressure properties to said lubricating oil.

5. An improved extreme pressure lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% dodecene dithiocyanate.

6. An improved extreme pressure lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% octene dithiocyanate.

7. An improved extreme pressure lubricant comprising mineral lubricating oil and a polythiocyanate having the general formula $R(SCN)_n$ in which R is an aromatic group and $n$ is a whole number greater than 1, said aromatic polythiocyanate being added in amounts sufficient to impart extreme pressure properties to said lubricating oil.

8. An improved extreme pressure lubricant comprising a mineral lubricating oil and an aliphatic polyisothiocyanate having the general formula $R(NCS)_n$ in which R is an aliphatic group and $n$ is a whole number greater than 1, said aliphatic polyisothiocyanate being added in amounts sufficient to impart extreme pressure properties to said lubricating oil.

9. An improved extreme pressure lubricant comprising a mineral lubricating oil and an aromatic polyisothiocyanate having the general formula $R(NCS)_n$ in which R is an aromatic group and $n$ is a whole number greater than 1, said aromatic polyisothiocyanate being added in amounts sufficient to impart extreme pressure properties to said lubricating oil.

10. An improved extreme pressure lubricant comprising a mineral lubricating oil and from about 0.05% to about 10% mustard oil potassium acetate polymer.

11. The method of preventing the corrosion of bearing metal alloys having the corrosive susceptibility of alloys of the group consisting of cadmium-silver, cadmium-nickel and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines which comprises adding to said lubricating oil a substantial amount but less than 2% of an organic compound having the general formula $R(Y)_n$ in which R is a substituent selected from the group consisting of an aliphatic group, an aromatic group and a metal, Y is a radical selected from the group consisting of a thiocyano radical and an isothiocyano radical and $n$ is a whole number greater than 1.

12. The method of preventing the corrosion of bearing metal alloys having the corrosive sus-

ceptibility of alloys of the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines, which comprises adding to said lubricating oil a substantial amount, but less than 2%, of a polyisothiocyanate having the general formula $R(NCS)_n$ in which R is a hydrocarbon group selected from the group consisting of an aliphatic group and an aromatic group and $n$ is a whole number greater than 1.

13. The method of preventing the corrosion of bearing metal alloys having the corrosive susceptibility of alloys of the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines which comprises adding to said lubricating oil a substantial amount but less than 2% of a polythiocyanate having the general formula $R(SCN)_n$ in which R is a hydrocarbon selected from the group consisting of an aliphatic group and an aromatic group, and $n$ is a whole number greater than one.

14. The method of preventing the corrosion of bearing metal alloys having the corrosive susceptibility of alloys of the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines which comprises adding to said lubricating oil a substantial amount, but less than 2%, of an aliphatic polythiocyanate having the general formula $R(SCN)_n$ in which R is an aliphatic group and $n$ is a whole number greater than 1.

15. The method of preventing the corrosion of bearing metal alloys having the corrosive susceptibility of alloys of the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines which comprises adding to said lubricating oil a substantial amount, but less than 2%, of an aromatic polythiocyanate having the general formula $R(SCN)_n$ in which R is an aromatic group and $n$ is a whole number greater than 1.

16. The method of preventing the corrosion of bearing metal alloys having the corrosive susceptibility of alloys of the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines which comprises adding to said lubricating oil a substantial amount, but less than 2%, of an aliphatic polyisothiocyanate having the general formula $R(NCS)_n$ in which R is an aliphatic group and $n$ is a whole number greater than 1.

17. The method of preventing the corrosion of bearing metal alloys having the corrosive susceptibility of alloys of the group consisting of cadmium-silver alloys, cadmium-nickel alloys and copper-lead alloys in the presence of a highly refined lubricating oil in internal combustion engines which comprises adding to said lubricating oil a substantial amount, but less than 2%, of an aromatic polyisothiocyanate having the general formula $R(NCS)_n$ in which R is an aromatic group and $n$ is a whole number greater than 1.

CLARENCE M. LOANE.
BERNARD H. SHOEMAKER.