

UNITED STATES PATENT OFFICE

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LUBRICANT

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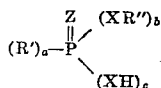
6 Claims. (Cl. 87-9)

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

My invention has particular utility in preventing and/or inhibiting the corrosion of "hard metal" alloy bearing 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 I 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.

My invention is practised by adding to highly refined lubricating oils up to 5%, but preferably from 0.0005 to 0.01 gram mols to 100 grams of oil of certain organic phosphorous compounds derived from phosphinic and phosphinous acids, said organic phosphorous compounds having the general formula

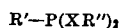


in which R' and R'' are hydrocarbon radicals such as alkyl, aryl, aralkyl or alkaryl or mixtures thereof and/or said hydrocarbon radicals having substituted mercapto, hydroxy, amino, alkyl substituted amino, thiocyno, isothiocyno, or halogen group or groups; X is oxygen, sulfur or selenium; Z is either absent or is oxygen, sulfur,

or selenium; and in which *a* is a whole number 1 or 2, *b* is a whole number 1 or 2 and *c* is either 0 or 1; and in which *a*+*b*+*c* is always equal to 3.

The above general formula comprises the mono and di esters of R-phosphinic acid and R-phosphinous acid and the esters of di-R-phosphinic acid and the esters of di-R-phosphinous acid.

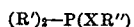
The following compounds are examples of the di esters of R-phosphinous acid having the general formula



in which R', R'' and X are as defined above:

Diethyl isoamyl thiophosphinite
Diamyl methyl phosphinite
Diethyl propylphosphinite
Diethyl phenylphosphinite
Diethyl phenylthiophosphinite
Diphenyl ethylphosphinite
Dithiophenyl ethylphosphinite
Di isobutyl phenylthiophosphinite
Diethyl chlor-phenylphosphinite

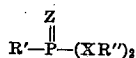
The following compounds are examples of the esters of the di R-phosphinous acid having the general formula



in which R', R'' and X are as hereinbefore defined:

Ethyl diphenylphosphinite
Ethyl diphenylthiophosphinite
Isopropyl diphenylthiophosphinite
Iso diphenylphosphinite
Amyl diamylphosphinite
Isoamyl dibutylthiophosphinite
Phenyl diphenylphosphinite
Phenyl diphenylthiophosphinite

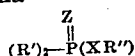
Listed below are specific examples of the di esters of R-phosphinic acid having the general formula



in which R', R'', X are as hereinbefore defined and Z is oxygen, sulfur or selenium:

Diethyl phenylphosphinate
Diethyl paratolylphosphinate
Dibutyl m-carboxy phenylphosphinate
Diethyl p-bromo phenylphosphinate
Dimethyl alpha hydroxy benzylphosphinate
Dibutyl alpha hydroxy isopropylphosphinate
Di isoamyl hydroxy methylphosphinate.

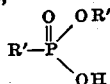
The esters of the di R-phosphinic acid having the general formula



in which R', R'', X are as hereinbefore defined and Z is oxygen, sulfur or selenium are illustrated by the following representative compounds:

- Ethyl phenylethylphosphinate
- Ethyl diphenylphosphinate
- Ethyl 4-methyl-4 carboxy diphenylphosphinate
- Butyl di-p-tolylthiophosphinate
- Methyl phenylmethylphosphinate
- Amyl phenylhydroxyethylphosphinate, etc.

Compounds such as ethyl phenylphosphinate, butyl isoamyl thiophosphinate are examples of the mono esters of the R-phosphinic acid having the general formula,



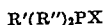
in which R' and R'' are as hereinbefore defined, contemplated within the scope of my invention.

Contemplated within the scope of my invention are also the mono esters of the R-phosphinous acid having the general formula



in which R' and R'' are as hereinbefore defined. Examples of such compounds are ethyl phenylphosphinite and phenyl butyl phosphinite.

In addition to the compounds hereinbefore mentioned my invention further contemplates the use of the isomers of the di R-phosphinous acid having the general formula



in which R', R'' and X are as hereinbefore defined. Examples of compounds falling within this class are:-

- Triphenyl phosphine oxide
- Tri-m-amino phenyl phosphine oxide
- Triphenyl phosphine sulfide
- Triphenyl phosphine selenide
- Chlorphenyl di-p-tolyl phosphine oxide
- Chlorphenyl di-p-tolyl phosphine selenide
- Methyl diphenyl phosphine oxide
- Dimethyl p-carboxy phenyl phosphine oxide
- Diethyl benzyl phosphine oxide.

As has been heretofore mentioned many of the recent models of automobiles now in use are equipped with bearings of the "hard metal" alloy type such as cadmium-silver alloy, cadmium-nickel alloy, nickel-lead alloy, etc. for the purpose of permitting increased speed characteristics and increased acceleration. In recent years mineral lubricating oils adapted for use in internal combustion engines have been given refining treatments, such as solvent extraction, which are more drastic than those of the past, for the purpose of increasing the viscosity index of such oils. While oils so refined give satisfactory performance in many respects, they have been found to cause more or less trouble in internal combustion engines equipped with bearings of the cadmium-silver type due to the corrosion of such alloys. This condition is remedied by the addition of very small amounts, such as 0.0005 to 0.01 gram mols per 100 grams of oil of any of the foregoing compounds or mixtures thereof to corrosive highly

refined motor oils will inhibit the corrosion of the hard metal alloy bearings.

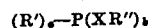
My invention further contemplates the use of the foregoing compounds in concentrations up to 10% in oils whether highly refined or not for the purpose of improving the film strength of said oils and to impart to lubricants improved extreme pressure characteristics. These compounds may also be used to impart other desirable properties to lubricating oils such as non-sticking ring properties and the like.

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

I do not wish to limit myself to the specific embodiments of my invention herein described except as defined by the appended claims.

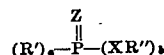
I claim:

1. A corrosion inhibited motor oil comprising a mineral lubricating oil and a small amount but not more than 5% of an ester of phosphinous acid having the general formula



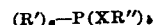
in which R' and R'' represent members selected from the group consisting of alkyl, aryl, aralkyl, alkaryl and halogen-substituted alkyl, aryl and aralkyl groups; X is an element selected from the group consisting of oxygen, sulfur and selenium; a and b are integers selected from the group of numbers consisting of 1 and 2; and in which a+b is always equal to 3.

2. A corrosion inhibited motor oil comprising a mineral lubricating oil and a small amount but not more than 5% of an ester of phosphinic acid having the general formula



in which R' and R'' represent members selected from the group consisting of alkyl, aryl, aralkyl, alkaryl and halogen-substituted alkyl, aryl and aralkyl groups; Z is an element selected from the group consisting of oxygen, sulfur and selenium; X is an element selected from the group consisting of oxygen, sulfur and selenium; a and b are integers selected from the group of numbers consisting of 1 and 2; and in which a+b is always equal to 3.

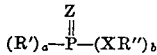
3. The method of preventing the corrosion of metal alloy bearings selected from the group consisting of cadmium-silver, cadmium-nickel, copper-lead alloys in the presence of highly refined lubricating oils in internal combustion engines which comprises adding an ester of phosphinous acid having the general formula



in which R' and R'' represent members selected from the group consisting of alkyl, aryl, aralkyl, alkaryl and halogen-substituted alkyl, aryl and aralkyl groups; X is an element selected from the group consisting of oxygen, sulfur and selenium; a and b are integers selected from the group of numbers consisting of 1 and 2; and in which a+b is always equal to 3, said esters being added in a small but sufficient quantity to inhibit the corrosion of said metal alloy bearings.

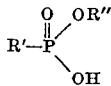
4. The method of preventing the corrosion of metal alloy bearings selected from the group consisting of cadmium-silver, cadmium-nickel and copper-lead alloys of the cadmium-silver al-

loy type in the presence of highly refined lubricating oils in internal combustion engines which comprises adding to such oils an ester of phosphinic acid having the general formula



in which R' and R'' represent members selected from the group consisting of alkyl, aryl, aralkyl, alkaryl and halogen-substituted alkyl, aryl and aralkyl groups; Z is an element selected from the group consisting of oxygen, sulfur and selenium; X is an element selected from the group consisting of oxygen, sulfur and selenium; a and b are integers selected from the group of numbers consisting of 1 and 2; and in which a+b is always equal to 3, said esters being added in small but sufficient quantities to retard the corrosion to said metal alloy bearings.

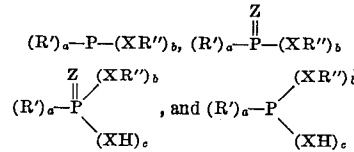
5. A corrosion inhibited motor oil comprising a mineral lubricating oil and a small amount but not more than 5% of a mono ester of a substituted phosphinic acid having the general formula



in which R' and R'' are radicals selected from

the group consisting of alkyl, aryl, aralkyl, alkaryl and halogen substituted alkyl and aryl radicals.

6. A corrosion inhibited motor oil comprising a mineral lubricating oil and an organic phosphorous compound selected from the group consisting of compounds having the general formulas



in which R' and R'' represent members selected from the group consisting of alkyl, aryl, aralkyl, alkaryl and halogen-substituted alkyl, aryl and aralkyl groups; Z is an element selected from the group consisting of oxygen, sulfur and selenium; X is an element selected from the group consisting of oxygen, sulfur and selenium; a and b are integers selected from the group of numbers consisting of 1 and 2; c is a number selected from the group of numbers consisting of 0 and 1; and in which a+b+c is always equal to 3, said organic phosphorous compound being added in small but sufficient quantities to inhibit corrosion by said mineral lubricating oil.

FREDERICK W. SULLIVAN, JR.

CERTIFICATE OF CORRECTION.

Patent No. 2,174,019.

September 26, 1939.

FREDERICK W. SULLIVAN, JR.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 75, and page 3, first column, line 1, claim 1, strike out the words "of the cadmium-silver alloy type; 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 31st day of October, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.