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LUBRICATING OIL COMPOSITIONS

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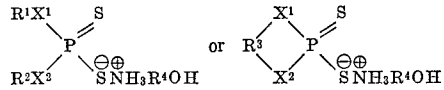
U.S. Cl. 252—32 FE 9 Claims

ABSTRACT OF THE DISCLOSURE

A lubricating oil composition having an ashless antiwear additive not giving rise to Cu/Pb bearing discolouration comprises a lubricating oil and 0.001 to 20.0% by weight based on the oil, of a mono hydroxy-amine salt of a dithiophosphoric acid, trithiophosphoric acid, or tetrathiophosphoric acid having the formula



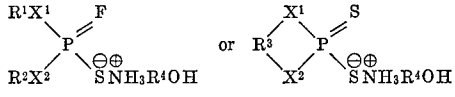
where R^1, R^2 and R^4 are hydrogen- and carbon-containing groups, R^3 is a divalent aromatic group, and X^1 and X^2 are oxygen or sulphur atoms. The monohydroxy-amine is preferably monoisopropanolamine, and the groups R^1 and R^2 are preferably C_1 to C_{25} alkyl.

This invention relates to lubricating oil compositions containing an amine salt of a thiophosphoric acid.

Certain amine salts of dithiophosphoric acid are known and they have use as ashless antiwear additives for lubricating oils. However it has been found that the use of certain amine salts results in a tendency to cause bearing discolouration.

We have now found a certain type of amine salts of thiophosphoric acids which are useful as ashless antiwear additives for lubricating oils and which do not give rise to copper/lead bearing discolouration.

According to the invention a lubricating oil composition comprises a lubricating oil and 0.001 to 20.0% by weight based on the oil, of a mono hydroxy-amine salt of a dithiophosphoric acid, trithiophosphoric acid, or tetraethiophosphoric acid having the formula



where

R^1, R^2 and R^4 are hydrogen- and carbon-containing groups, R^3 is a divalent aromatic group, and X^1 and X^2 are oxygen or sulphur atoms.

X^1 and X^2 are preferably the same i.e. both sulphur or both oxygen atoms, although they could be different. In practice it is preferable if X^1 and X^2 are both oxygen atoms.

The groups R^1 and R^2 can be aliphatic or aromatic, e.g. they may be the hydrocarbyl groups such as alkyl, aryl, alkaryl, or aralkyl. If alkyl the groups R^1 and R^2 preferably contain between 1 and 25 carbon atoms, e.g. propyl, n-hexyl, sec-octyl, isodecyl, tetradecyl or eicosyl. Suitable aryl groups include phenyl, naphthyl, and anthranyl. Suitable alkaryl groups are alkyl phenyl, the alkyl portion being C_1 to C_{18}, e.g. tolyl, xylyl, nonyl phenyl, dodecyl phenyl, octadecyl phenyl, dibutyl phenyl, butyl pentyl phenyl and dinonyl phenyl. Aralkyl groups which are suitable include benzyl, 2-phenyl butyl, and 2-phenyl ethyl. The groups R^1 and R^2 are usually, but need not be the same.

As an alternative to being hydrocarbyl, the groups R^1 and R^2 may contain oxygen atoms, e.g. they may be alkoxyalkyl, for instance methoxybutyl, or alkoxyaryl, e.g. ethoxyphenyl, or aryloxyalkyl, e.g. phenoxyethyl.

The group R^3 is aromatic, and it may be for example phenylene, bisphenylene or their alkylated derivatives in which case the thiophosphoric acid is derived from catechol, resorcinol, bisphenol or their alkylated derivatives or their thio analogues.

The groups R^1, R^2, and R^3 are preferably hydrocarbyl groups, i.e. contain no atoms other than carbon and hydrogen. If desired however these groups R^1, R^2 and R^3 may also be substituted by polar substituents, e.g. chloro, bromo, keto, ethereal, aldehydo or nitro atoms or groups. Preferably these polar substituents are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the group, e.g. they contain no more than 10% by weight of polar substituent based on the hydrocarbyl portion of the group.

The group R^4 is preferably a hydrocarbyl group, and is preferably a saturated aliphatic group e.g. alkylene. It may however be an arylene, aralkylene, or alkarylene group. Usually the amine salts used in the lubricating oil of this invention are derived from hydroxy-containing primary amines of the formula H_2NR^4OH, e.g. mono alkanolamines, for example mono ethanolamine, monopropanolamine, mono butanolamine, 6-amino-1-hexanol, and 5-amino-8-octanol. A particularly suitable alkanolamine salt is the isopropanolamine salt. The preferred chain length of R^4 is 1 to 20 carbon atoms, e.g. 1 to 10 carbon atoms.

Further examples of R^4 include cyclopentylene, cyclohexylene, phenylene, naphthylene, and anthracene.

The hydroxy-amine salts used in the oil composition of this invention may be prepared by reacting the thiophosphoric acid with the hydroxy-amine, the latter preferably being added to the former at an elevated temperature, e.g. 50° to 120° C., over a period of time e.g. about 30 minutes. The thiophosphoric acid can itself be prepared in situ, e.g. by reacting P_2S_5 with an alcohol or the corresponding thiol.

The reaction is preferably carried out in an inert atmosphere, e.g. under a nitrogen blanket.

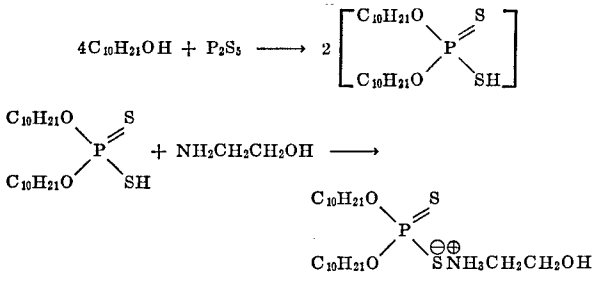
Approximately stoichiometric amounts of reactants should be used for the reactions.

Suitable lubricating oils to which the amine salts are added include animal, vegetable or mineral oils, for example petroleum oil fractions ranging from spindle oil to SAE 30, 40 or 50 lubricating oil grades; castor oil, fish oils, oxidised mineral oil or brightstocks. The lubricating oil may be a synthetic ester oil, e.g. diesters such as those prepared by esterifying carboxylic acids such as adipic or sebacic acid with monohydric alcohols, or complex esters obtained by the esterification of the polyhydric alcohol (e.g. a polyglycol) with a dibasic acid (e.g. sebacic or adipic acid) and a monohydric alcohol (e.g. 2-ethyl hexanol or a C_8 oxo alcohol).

The amount of amine salt added to the oil must be between 0.001 and 20.0% based on the weight of oil, and the preferred quantity added to the lubricating oil is between 0.01 and 10%, e.g. between 0.1 and 5% by weight, based on the weight of the lubricating oil.

EXAMPLE

The ethanolamine salt of isodecanol dithiophosphoric acid was prepared in accordance with the following equations:



44.4 g. P_2S_5 was slurried with 67.0 g. of a mineral lubricating oil (viscosity 150 SSU at 100° F.) using slow stirring. 132.6 g. (representing about 5% excess over stoichiometric) isodecanol was added to the mixture over four hours and the temperature was raised to 100° C. for one hour. A clear dark liquid was obtained. 24.4 g. ethanolamine was added slowly at 100° C. over 30 minutes (maximum temperature which was reached was 110° C.), and stirring was continued for a further hour to complete the reaction. The mixture was vacuum stripped (17" Hg) at 100° C. to remove excess isodecanol. The reaction was carried out under a nitrogen blank.

The mono isopropanolamine salt of isodecanol dithiophosphoric acid was prepared in the following manner:

63.0 g. P_2S_5 was added over two hours to 189.6 g. of isodecanol and 94.2 g. of a mineral lubricating oil (viscosity 150 SSU at 100° F.) heated to 60° C. The reaction mixture was heat soaked at 100° C. for three hours and vacuum stripped to remove H_2S. The liquid was cooled at 60° C. and 39.0 g. of mono isopropanolamine was added over one hour and the temperature was kept below 70° C. A clear amber coloured mobile liquid was obtained as the product of this reaction.

To a mineral lubricating oil having the following physical characteristics (viscosity 150 SSU at 100° F., 42 SSU at 210° F.) 1% by weight based on the weight of oil of the above prepared oil solutions of various alkanolamine dithiophosphates and other amine salts were added.

The Shell four ball test was carried out on the oil alone and the oil containing the above mentioned amount of various amine salts, for different loads. The results obtained were as follows:

	Weld load. kg.	Wear scar. kg.	(mm.) [1]
Base oil alone	124	30	1.00
		40	1.35
		60	2.50
Base oil plus mono ethanolamine salt of isodecanol dithiophosphoric acid	180	30	0.30
Base oil plus mono isopropanolamine salt of isodecanol dithiophosphoric acid	180	40	0.95
		60	1.10
		60	1.02
Base oil plus triethanolamine salt of isodecanol dithiophosphoric acid [2]	140	60	1.80
Base oil plus Primene 81R salt of hexylene glycol dithiophosphoric acid	185	60	1.20

[1] 1 hour at various loads.
[2] Very poor oil solubility.

Thus, it can be seen that the mono hydroxyamine salts of the invention give load bearing properties at least equivalent to those of a prior art additive (Primene 81–R salt), and better load bearing properties than those of another prior art additive (triethanolamine salt).

Measurement of Cu/Pb bearing protection

A bearing corrosion rig described by Staudt et al. (SAE 680538) was used to evaluate bearing weight loss and colour of Petter W1 bearings.

Base oil [1]	Bearing weight loss (mg.) [2]	Bearing colour
No additive	1,810	Clean.
Base oil plus 1 wt. percent mono isopropanolamine salt of isodecanol dithiophosphoric acid.	31	Do.
Base oil plus 1.4 wt. percent mono ethanolamine salt of isodecanol dithiophosphoric acid.	23	Do.
Base oil plus 1 wt. percent triethanolamine salt of isodecanol dithiophosphoric acid.	102	Brown.
Base oil plus wt. percent Primene 81–R salt of hexylene glycol dithiophosphoric acid.	53	Black.

[1] Base oil contains dispersant (polyamine) and VI improver (ethylene copolymer) to SAE 10W-30 with base oil.
[2] After 36 hours at 140° C.

Hence it can be seen that the monoalkanolamine salts of the invention give no bearing discolouration whereas the prior art additives either tarnish and give a high bearing weight loss (triethanolamine salt) or else blacken the copper/lead bearing (Primene 81–R salt).

ASTM D-130 Cu Corrosion

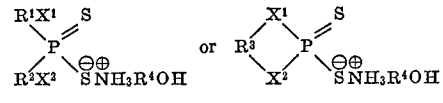
Dithiophosphoric acid	Amine	ASTM D-130 [1]
Isodecanol	Mono ethanolamine	1b
Do	Mono isopropanolamine	1b
Do	Triethanolamine	1b
Hexylene glycol (2-methylpentane-2,4-diol).	Primene 81R	2a

[1] 1% by weight of amine dithiophosphoric acid in a mineral lubricating oil having the following physical characteristics (viscosity 150 SSU at 100° F., 42 SSU at 210° F.).

It will be noted that in the ASTM copper corrosion test there is less corrosion of copper strip by lubricant compositions containing additives of the invention than compositions containing an additive of the prior art.

What is claimed is:

1. A lubricating oil composition comprising a lubricating oil and 0.001 to 20.0% by weight based on the oil, of a monoalkanol primary amine salt of a phosphoric acid selected from the group consisting of dithiophosphoric acid, trithiophosphoric acid, and tetrathiophosphoric acid, the salt having the formula



wherein in each formula R^1 and R^2 are alkyl of from 1 to 25 carbon atoms, alkyl phenyl wherein the alkyl portion has from 1 to 18 carbon atoms, phenyl, naphthyl, anthranyl, or phenyl alkylene wherein the alkylene portion has from 1 to 4 carbon atoms; R^3 is phenylene or bisphenylene; R^4 is alkylene of from 1 to 20 carbon atoms, and X^1 and X^2 are oxygen or sulfur.

2. A composition according to claim **1** wherein X^1 and X^2 are both oxygen atoms.

3. A composition according to claim **1** wherein R^1 and R^2 are both C_1 to C_{25} alkyl groups.

4. A composition according to claim **1** wherein R^1 and R^2 are both alkyl phenyl, the alkyl portion containing 1 to 18 carbon atoms.

5. A composition according to claim **1** wherein the monoalkanolamine is monopropanolamine.

6. A composition according to claim **1** wherein the monoalkanolamine is monoethanolamine.

7. A composition according to claim **1** wherein the phosphoric acid is isodecanol dithiophosphoric acid.

8. A composition according to claim 1 wherein the phsphoric acid is isodecanol dithiophosphoric acid.

9. A composition according to claim 1 wherein R^4 is alkylene of from 1 to 10 carbon atoms.

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U.S. Cl. X.R.

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