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LUBRICANT CONTAINING COPPER CORROSION INHIBITOR

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This invention relates to additives for synthetic base ester type lubricants. More particularly, this invention is directed to additives that inhibit copper corrosion in sulfur-containing synthetic oils.

It has been found that some sulfur-containing ester base lubricants, such as thiodibutyrate esters compare favorably with other well known and well used ester base lubricants, such as sebacate esters of equivalent molecular weight, with respect to viscosity and viscosity-temperature properties. It has also been found that the thioether esters are considerably less volatile than the standard lubricating esters. However, these sulfur-containing thioether ester base oils cause considerable copper corrosion, whereas the other well known and well used non-sulfur-containing ester base lubricants have shown no such corrosion problems, and because of this the use of the thioether esters, at present, is strictly limited. The copper corrosion problem encountered with the use of the thioether ester lubricants is further complicated by the fact that known copper corrosion inhibitors have proven unsuccessful in inhibiting copper corrosion encountered with the thioether ester base lubricants. The advantage of the present invention is that the additives herein disclosed when incorporated in the thioether ester base lubricants materially reduce and in most cases eliminate the copper corrosion which is caused by these thio esters, thereby making such synthetic lubricants available for general use without the problem of encountering copper corrosion.

The thio esters to which the corrosion inhibitors of the present invention are added are broadly described as esters of hydrocarbyl carboxylic acids containing at least one thioether linkage. They are high molecular weight materials of lubricating oil characteristics derived from alcohols, which are usually aliphatic alcohols containing one or more hydroxyl radicals and carboxylic acids, which are usually aliphatic acids containing one or more carboxylic acid radicals and containing one or more thioether linkages. The thioether acids usually have the general formula:

$$HO_2CR—S—RCO_2H$$

wherein R is a divalent aliphatic hydrocarbyl radical containing 1 to 14 carbon atoms, but may also be thioether monoacids of the formula:

$$R'SRCOOH$$

wherein R' is a monovalent hydrocarbyl radical containing 1 to 14 or more carbon atoms and R is a divalent radical as previously defined. The acid moiety of these thioether esters usually contain 6 to 18 carbon atoms, preferably from 6 to 14. The aliphatic alcohols from which the thioether esters are formed usually contain at least 4

carbon atoms and up to 20 or more carbon atoms. Alcohols containing 6 to 18 carbon atoms are most commonly used. Ether alcohols such as $C_2H_5—O—C_2H_5—OH$ and $C_2H_5—O—C_2H_4—O—CH_2CH_2—OH$ or thioether alcohols such as $C_2H_5—S—C_2H_5—OH$ may also be used in the formation of the aliphatic thioether diesters of organic di-carboxylic acids making up the lubricating base in the composition of the present invention.

The alkyl esters of aliphatic thioether dicarboxylic acids have the following general formula:

$$R'O_2CR—S—RCO_2R'$$

wherein R is a divalent aliphatic hydrocarbyl radical containing from 1 to 18 carbon atoms and preferably from 2 to 14 carbon atoms, and R' is a monovalent hydrocarbyl radical containing 3 to 12 carbon atoms and preferably 3 to 8 carbon atoms. Examples of these are the following: di-2-ethylhexylthiodibutyrate, di-isooctyl thiodibutyrate, di-2-ethylhexyl-β,β'-thiodipropionate, di-isooctyl-β,β'-thiodipropionate, and di-2,2,4-trimethylpentyl thiodibutyrate.

An example of one method of preparing such aliphatic esters of thioether acids is by refluxing the acids with an excess of the appropriate alcohols in the presence of a water entrainer.

The inhibitors for copper corrosion used in the present invention are borate esters having the following general formula:



wherein R'' may be either the same or different organic radicals selected from the group consisting of alkyl, aryl, alkaryl, aralkyl and halo, nitro and carbonyl substitutes thereof, containing 6 to 15 carbon atoms.

The borate inhibitors of the present invention are usually present in an amount of from about 0.5 to 5.0 weight percent with concentrations of between 1.0 and 3.0 weight percent being preferred.

Examples of the copper corrosion inhibitors of the present invention are di-(nonylphenyl) mono-o-nitrophenyl borate, di-(nonylphenyl) mono-o-formylphenyl borate, mono-nonylphenyl di-p-chlorophenyl borate, di-(nonylphenyl) mono-o-acetylphenyl borate, tri-o-carbomethoxyphenyl borate, di-p-tertiary-butylphenyl mono-o-carbomethoxyphenyl borate.

Finished lubricant compositions containing the anti-corrosive additive of the present invention may also contain other well-known additives such as VI improvers, anti-oxidants, extreme pressure additives, and anti-foam agents.

The effectiveness of the anti-corrosive additive of the present invention was demonstrated in the bomb copper corrosion test, which is a rather severe test, described in military specification MIL–C–7118A, Federal Specification VV–L–791–5314 as an accelerated test, designed to evaluate lubricants under high temperature oxidizing conditions. The results of the bomb copper corrosion test are listed below in Table I.

Table I

Ex.	Base oil	Additive(s) (weight percent)	P.s.i. drop	Appearance		Rating
				Sample	Strip	
1	Di-n-octylisosebacate		0	Unchanged	No stain	Pass.
2	Di-2-ethylhexyl-β,β'-thiodipropionate.		29	Solid; yellow brown and green.	Brown stain above interface.	Fail.
3	Diisooctylthio-dibutyrate		0	Green	Dark brown stain	Do.
4	Di-2,2,4-trimethyl-pentyl-thiodibutyrate.		0	do	do	Do.
5	Diisooctyl-β,β'-thio dipropionate	Zinc dialkyldithio-phosphate (2.7)	94	Yellow with white crystals.	do	Do.
6	Di-2-ethylhexylthio-dibutyrate	N,N-disalicylidene-1-2-diaminopropane (1.0).	0	Black	Black stain	Do.
7	do	Di-(nonylphenyl)-mono-o-formylphenyl borate (1.4).	0	Light brownish yellow.	Light brown stain	Pass.
8	Di-2-ethylhexyl-β,β'-thiodipropionate.	Di-(nonylphenyl)mono-o-nitrophenyl borate (2.5).	0	Unchanged	Unchanged	Do.
9	Di-2-ethylhexylthio-dibutyrate	Di-p-tertiarybutylphenyl mono-o-carbomethoxyphenyl borate.	0	Yellow	Light gray stain	Do.

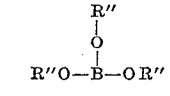
From the above data it can be seen that while synthetic ester base oils do not cause copper corrosion (Example 1) the uninhibited thio esters do cause much copper corrosion (Examples 2, 3 and 4). In addition, the above data demonstrate that conventional copper corrosion inhibitors are ineffective in preventing copper corrosion by the thio esters (Examples 5 and 6) whereas when the inhibitors of the present invention are added without conventional copper corrosion inhibitor they all pass the bomb copper corrosion test (Examples 7–9).

We claim:

1. A lubricating composition consisting essentially of a synthetic thioether ester base lubricant having the following general formula:

$$R'O_2CR—S—RCO_2R'$$

wherein R is a divalent aliphatic hydrocarbyl radical containing from 1 to 18 carbon atoms and R' is a monovalent hydrocarbyl radical containing 3 to 12 carbon atoms and a copper corrosion inhibitor having the following general formula:



wherein two of said R''s represent alkylphenyl radicals each having from 6 to 15 carbon atoms and the third R'' represents a radical selected from the group consisting of formylphenyl and carbomethoxyphenyl radicals having from 6 to 15 carbon atoms, said inhibitor being present in an amount between 0.5 and 5.0 weight percent.

2. A lubricating composition consisting essentially of a synthetic thioether ester base lubricant having the following general formula:

$$R'O_2CR—S—RCO_2R'$$

wherein R is a divalent aliphatic hydrocarbyl radical containing from 1 to 18 carbon atoms and R' is a monovalent hydrocarbyl radical containing 3 to 12 carbon atoms and 0.5 to 5.0 weight percent of di-(nonylphenyl) mono-o-formylphenyl borate.

3. A lubricating composition consisting essentially of a synthetic thioether ester base lubricant having the following general formula:

$$R'O_2CR—S—RCO_2R'$$

wherein R is a divalent hydrocarbyl radical containing from 1 to 18 carbon atoms and R' is a monovalent hydrocarbyl radical containing from 3 to 12 carbon atoms and 0.5 to 5.0 weight percent of di-p-tertiarybutylphenyl mono-o-carbomethoxyphenyl borate.

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