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LUBRICANT CONTAINING SELENIUM COMPOUNDS

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The present invention relates to lubricating oils compounded with selenium-containing compounds, such as dialkyl selenides, which attack silver and like metals, thereby decreasing the effectiveness of the selenium compound in lubricating oils. In order to prevent the loss of effectiveness of the selenium compounds by attack on silver and like metals, certain protective agents such as 2-mercapto-4,6,6-trimethylthiazine are added to the lubricating oils.

As is well known, the present-day problems involved in the lubrication of internal combustion engines are extremely complex and difficult to overcome due mainly to the great load imposed on the bearings, the high engine speeds, and the elevated operating temperatures. To avoid rapid deterioration resulting from such severe operating conditions, lubricating oils have been compounded with various improving or stabilizing agents. Of the various lubricating oil compounding agents, a group of highly effective additives is the selenium-containing organic compounds. For example, aliphatic mono-, di-, and higher poly-selenides, seleno-mercaptans, metal seleno-mercaptides, etc. are highly effective oxidation inhibitors. Unfortunately, oils compounded with such selenium-containing compounds are adversely affected by silver and like metals. The deleterious action involves a direct attack of the metal by selenium, resulting in a rapid discoloration of the metal surface and formation of metal selenides and the subsequent sloughing off of these metal selenides during engine operation. As the selenium of the selenium-containing compounds attacks the metals during engine operation, the effectiveness of the selenium compounds as addition agents in lubricating oils is considerably decreased. For example, when a selenium compound is added to a lubricating oil to inhibit oxidation, the effectiveness of the selenium compound is considerably decreased as the selenium-containing compound attacks the metal. Also, when the selenium-containing compound attacks the metals in an engine, there is a substantial loss of bearing metal and a pitting of bearing surfaces.

Thus, it may readily be seen that when the selenium of a selenium-containing oxidation inhibitor attacks metals of bearing surfaces, etc., there is a two-fold loss to the system, namely, a reduction in the effectivenss of the selenium-containing compound as an oxidation inhibitor and a loss of sensitive metal from the bearing surfaces during engine operation. It is apparent that in spite of the long desire to lubricate silver bearings with lubricants compounded with selenium compounds, it has been impractical to do so in view of the aforementioned difficulties.

Because of these difficulties with lubricants containing selenium compounds, there is a tendency to eliminate the highly effective selenium-containing additives from the Diesel lubricating oils, thereby losing the remarkable benefits of these additives. For example, heretofore, it has been undesirable to use these effective selenium anti-oxidants in lubricants employed for engines containing silver bearings, such as in certain railroad Diesel engines containing silver wrist pin bushings. Alternative practices have been to eliminate the selenium-containing additives from the oil, allowing the oil to deteriorate more rapidly through oxidation; or include the selenium-containing additives, allowing the oil to deteoriate less rapidly through oxidation with a consequent selenium attack on the silver wrist pin bushings. Because of the presence of the silver in many aircraft engines, it has not been feasible to use the highly effective selenium-containing aviation oil additives.

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Therefore, it is an object of this invention to provide a selenium compound-containing lubricant which is stable to sensitive metals such as silver, whereby the effectiveness of the selenium compounds as oxidation inhibitors is not reduced by the reaction of the selenium compounds with the sensitive metal surfaces.

In the attainment of these objects, the present invention concerns the combination of a lubricant compounded with selenium compounds, and a silver-protective agent which greatly minimizes attack on silver by the selenium compounds, whereby the essential functions of the selenium compounds are maintained at maximum activity.

Now, through the use of the silver-protective agents in accordance with the present invention, lubricating oils compounded with selenium-containing additives can be used in Diesel oils, aviation oils, and any other oils where selenium attack on sensitive metals is a problem, to provide a stable lubricant having selenium compounds of increased effectiveness. While the outstanding advantages of the action of the silver protective agents in lubricants containing selenium compounds is particularly apparent in heavy-duty motor oils, the inventive combination finds application in turbine oils, gear oils, such as for use in hypoid gears, cutting oils, soluble oils, greases, etc.

The silver protective agents include 2-thio- thiazine compounds of which 2-mercapto-thiazine is the simplest member. Also included are the derivatives of said simplest member, wherein the mercapto-hydrogen may be replaced by a hydrolyzable group, and where there may be short-chain saturated and unsaturated aliphatic groups substituted on the ring carbon atoms. The short-chain saturated and unsaturated aliphatic groups which may be substituted on the ring include the following: methyl, ethyl, propyl, butyl, octyl, ethenyl, propenyl, butenyl, octenyl, etc. It is pre-

ferred that the thiazine ring contain not more than 4 substituents having a total of not more than 16 carbon atoms. It is preferred that each substituent group on the thiazine ring contain not more than 4 carbon atoms. By "short-chain aliphatic groups" is meant aliphatic groups containing not more than 8 carbon atoms.

The hydrolyzable group is one which may react on hydrolysis to yield hydrogen in the mercapto group, and includes cationic salt-forming atoms and radicals including metals (e. g., sodium, potassium, barium, calcium, zinc, aluminum, etc.), groups obtained by salt formation with amines (e. g., trimethylamine, n-butylamine, dodecylamine, ammonia, etc.), amide radicals (e. g., cyclohexylamide radical and organic carboxyl and thionyl radicals such as benzoic and diethyl dithiocarbonyl radicals).

Examples of 2-thio-thiazine compounds are: 2-mercapto-4,6,6-trimethyl thiazine; zinc salt of 2-mercapto-4,6,6-trimethyl thiazine; 2-mercapto-1,3-dihydrothiazine; 3-mercapto - 2,4,1-thiazine; 2 - mercapto-4-methyl thiazine; 2 - mercapto - 4-ethyl thiazine; 2-mercapto-4,6-dimethyl thiazine; 2 - mercapto-4-isobutenyl-6,6-dimethyl thiazine; 4,6,6 - trimethyl thiazine - 2 - cyclohexyl sulfenamide; and the butyrate ester of 2-mercapto-thiazine. Examples of 2-thio-thiazine compounds also include the reaction products obtained by reacting a 2-mercapto-thiazine with the following: carboxylic acids, alpha-beta unsaturated ketones, esters, olefins, nitriles, organometallic compounds, sulfonyl halides, ethylene oxide, anhydrides and acyl halides.

Because of the greater effectiveness obtained, it is preferred to use 2-mercapto-4,6,6-trimethyl thiazine to prevent selenium attack on silver.

The 2-thio-thiazines embraced in this invention vary in effectiveness in minimizing the loss of the effectiveness of the selenium compounds; some of the 2-thio-thiazines, for example, are effective when used in amounts as low as 0.001% (by weight of total composition). Certain of the 2-thio-thiazines have only limited solubility in the lubricating oil and are effective at that solubility. All of the 2-thio-thiazines having sufficient solubility are effective when they are used in amounts as great as 5.0%. However, it is preferred that the compounds of this invention be used in amounts sufficient to substantially reduce the corrosion of silver. For example, it is preferred to use amounts of from 0.1% to 3.0 %. The major proportion of the lubricating composition of the present invention is the lubricating oil or base oil.

Beneficial effects of inhibiting selenium attack on silver and like metals may be obtained by using 2-thio-thiazole compounds in conjunction with the 2-thiazine compounds.

Examples of 2-thio-thiazoles are: 2-mercapto-benzothiazole, N-cyclohexyl 2-benzothiazyl sulfenamide; dodecyl amine salt of mercaptobenzothiazole; zinc salt of mercapto-benzothiazole; 2-mercapto-5-methyl thiazole; 2-mercapto-5-ethyl thiazole; 2-mercapto-4-methyl thiazole; etc.

Suitable base oils include a wide variety of lubricating oils such as naphthenic base, paraffin base, and mixed base mineral oils, other hydrocarbon lubricants, e. g., lubricating oil derived from coal products, and synthetic oils, e. g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers, dicarboxylic acid esters and liquid esters of acids of phosphorus. Synthetic oils of the alkylene oxide-type polymer which may be used include those exemplified by the alkylene oxide polymers (e. g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing alkylene oxides, e. g., propylene oxide, in the presence of water or alcohols, e. g., ethyl alcohol, and esters of alkylene oxide-type polymers, e. g., acetylated propylene oxide polymers prepared by acetylating propylene oxide polymers containing hydroxyl groups.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethyl-hexyl alcohol, dodecyl alcohol, etc. Examples of dicarboxylic acid ester synthetic oils include di-butyl adipate, di-hexyl adipate, di-2-ethyl-hexyl sebacate, di-n-hexyl fumarate polymer, etc.

Synthetic oils of the type of liquid esters of acids of phosphorus include the esters of phosphoric acid, e. g., tricresyl phosphate; the esters of phosphonic acid, e. g., di-ethyl ester of decane phosphonic acid or other such esters as obtained by reacting alkyl phosphonyl chlorides with hydroxyl-containing compounds such as phenols and aliphatic alcohols, and with olefin oxides such as propylene oxide, as described in Jensen et al., U. S. patent application No. 86,856, now abandoned.

The improved lubricant of the present invention is used where the effectiveness of selenium compounds as lubricant additives is decreased by the attack on metals by the selenium of the selenium compounds. In order to evaluate the silver protective agents of this invention for their effectiveness in inhibiting reduction of activity of selenium compounds, lubricants containing the selenium compounds and the protective agents were subjected to a "silver strip" test which was performed as follows:

A silver metal strip having the dimensions of 2½" x ¾" x $\frac{1}{32}$" was first cleaned with a wire brush until the strip was highly polished. The strip was weighed and the weight recorded. This highly polished silver strip was then placed in a 600 ml. beaker in such a manner that the strip was completely immersed when 300 g. of the oil being tested was poured into the beaker. The oil was stirred at a temperature of 300° F. for twenty hours, at which time the silver strip was removed and cleaned, first with chloroform, then with petroleum ether. The appearance of the strip was noted. Those strips which had been severely attacked were quite black. The tested silver strip was washed in a concentrated solution of cadmium chloride containing 10% of potassium cyanide to remove the selenide film adhering to the strip. After the strip had been washed with this cadmium chloride-potassium cyanide solution and dried, it was weighed. The difference in weight of the original strip and the strip after the cadmium chloride wash was noted and recorded as the weight lost due to reaction with the selenium compound.

In addition to being especially effective as protective agents for silver, the protective agents of this invention are effective in protecting other selenium-sensitive metals from selenium attack. Such other selenium sensitive metals include copper, aluminum, and alloys of copper and aluminum.

The following are illustrative of various selenium-containing oxidation inhibitors reactive with silver: alkyl selenides (e. g., didodecyl mono-

selenide, octadecyl methyl monoselenide, octadecyl ethyl monoselenide, octyl dodecyl monoselenide, di-eicosyl monoselenide, dioctyl diselenide, di-eicosyl diselenide, dilauryl diselenide, dioctadecyl diselenide, and the various mono- and polyselenides prepared by reacting sodium or other alkali metal mono- or polyselenides with halogenated, e. g., chlorinated hydrocarbons, such as decyl chloride, dodecyl chloride, tetradecyl chloride, octadecyl chloride, heptadecyl chloride, chlorinated lubricating oil and chlorinated wax); selenomercaptans (e. g., methyl selenomercaptan, octyl selenomercaptan, dodecyl selenomercaptan, tetradecyl selenomercaptan, hexadecyl selenomercaptan, octadecyl selenomercaptan, eicosyl selenomercaptan, paraffin wax selenomercaptan, phenyl methyl selenomercaptan, phenyl octyl selenomercaptan, phenyl dodecyl selenomercaptan, phenyl octadecyl selenomercaptan, cyclohexyl selenomercaptan, octyl cyclohexyl selenomercaptan, octadecyl cyclohexyl selenomercaptan, etc.); metal selenomercaptan (e. g., the barium, calcium, sodium, zinc, strontium, aluminum, cadmium, nickel, lead and thallium salts of the above selenomercaptans).

Some of the above-indicated additives are more vigorous in their attack on silver than others, and, consequently, such attack is more difficult to minimize. However, the silver-protective agents are advantageously used, even with the more active selenium additives.

The agents of this invention may be used in lubricating oils containing, in addition to the selenium compounds, other additives such as polyvalent metal phenates (e. g., calcium cetyl phenate), metal organo-sulfonates (e. g., calcium petroleum sulfonate), polyvalent metal salts of acids of phosphorus, such as phosphates (e. g., calcium cetyl phosphate), phosphonates (e. g., calcium white oil phosphonate), thiophosphates (e. g., calcium cetyl thiophosphates), phenols (e. g., 2,6-di-tertiary-butyl-4-methylphenol), etc.

The lubricant compositions of this invention may also contain other agents which are advantageously present, such as oiliness agents, blooming agents, viscosity index improvers, pour point depressants, peptizing agents, etc.

For the purpose of the tests described hereinbelow, the silver protective agents of this invention were incorporated in a California solvent refined S. A. E. 30 paraffinic base oil containing calcium petroleum sulfonate, sulfurized calcium cetyl phenate and a didodecyl monoselenide.

Table I below presents data obtained in the "silver strip test."

Table I

Protective Agent	Amount of Protective Agent Used in Lubricating Oil (Percent by weight)	Silver Strip Test—Weight Loss (Milligrams)
None		98.0
2-Mercapto-4,6,6-trimethyl thiazine	0.3	43.3

Table II below presents the results obtained when freshly polished silver strips were immersed for 30 minutes at a temperature of 300° F. in a California solvent refined S. A. E. 30 paraffinic base oil containing calcium petroleum sulfonate, sulfurized calcium cetyl phenate and 0.2% by weight of various selenium compounds

with and without 2 - mercapto - 4,6,6 - trimethyl thiazine as a silver protective agent. The darker the appearance of the silver strip, the more pronounced the attack on the silver by the selenium compound.

Table II

Selium Compound Added	Amount of 2-mercapto-4,6,6-trimethyl thiazine added (Percent by weight)	Visual Appearance
1. Didodecyl monoselenide		Deep dark brown.
2. Didodecyl monoselenide	0.3	Very light yellow.
3. Didodecyl diselenide[1]		Light gray.
4. Didodecyl diselenide[1]	0.3	Clean surface.
5. Dioctadecyl diselenide		Black.
6. Dioctadecyl diselenide	0.3	Brownish green.
7. Octadecyl selenomercaptan		Gray.
8. Octadecyl selenomercaptan	0.3	Light brownish gray.
9. Zinc octadecyl selenide		Dark brownish gray.
10. Zinc octadecyl selenide	0.3	Very light brownish green.

[1] 0.4% by weight of selenium compound present.

We claim:

1. A lubricant consisting essentially of a major portion of a selenium-containing lubricating oil composition corrosive to silver, and a small amount, sufficient substantially to inhibit the formation of silver selenide resulting from the selenium attack on silver, of a 2-mercapto-thiazine wherein not more than four of the ring carbons contain aliphatic groups each of which has not more than 4 carbon atoms.

2. A lubricant consisting essentially of a major portion of a selenium-containing lubricating oil composition which is corrosive to silver, and a small amount, sufficient substantially to inhibit the reaction between the selenium of said lubricating oil composition and silver, a 2-mercapto-thiazine wherein not more than four of the ring carbons contain short chain aliphatic groups, said aliphatic groups containing a total of no more than 16 carbon atoms.

3. A lubricating oil composition at least 95% of which is composed of an admixture of an oil of lubricating viscosity and lubricating oil additives having present selenium which reacts with silver-wearing surfaces, and a small amount, sufficient substantially to inhibit the reaction between the selenium and silver, of a 2-mercapto-thiazine wherein not more than four of the ring carbons of the said mercapto-thiazine contain short chain aliphatic carbons.

4. A lubricant consisting essentially of a major portion of a selenium-containing lubricating oil composition which attacks silver directly to form silver selenide, and a small amount, sufficient substantially to reduce the selenium attack on silver, of a 2-mercapto-thiazine wherein not more than 4 of the ring carbons contain short-chain aliphatic groups.

5. A lubricant consisting essentially of a major portion of a selenium-containing lubricating oil composition which attacks silver-wearing surfaces to form silver selenide, and a small amount, sufficient substantially to reduce the selenium attack on silver, of a 2-mercapto-4,6,6-trimethyl thiazine.

6. A selenium-containing lubricating oil composition which forms silver selenide on silver-wearing surfaces, and a small amount, sufficient substantially to reduce this silver selenide formation, of a 2-mercapto-thiazine wherein not more than four of the ring carbons contain short

chain aliphatic groups, said aliphatic groups containing a total of not more than 16 carbon atoms.

7. A selenium-containing lubricating oil composition which forms silver selenide on silver-wearing surfaces, and a small amount, sufficient substantially to reduce this silver selenide formation, of a 2-mercapto-thiazine wherein not more than 4 of the ring carbons contain short-chain aliphatic groups.

8. A selenium-containing lubricating oil composition which forms silver selenide on silver-wearing surfaces, and a small amount, sufficient substantially to reduce this silver selenide formation, of 2-mercapto-4,6,6-trimethyl thiazine.

9. A lubricant composition comprising a major proportion of an oil of lubricating viscosity, a selenium compound which attacks silver-wearing surfaces to form silver selenide, and a small amount, sufficient substantially to reduce the selenium attack on silver, of a 2-mercapto-thiazine wherein not more than four of the ring carbons contain short chain aliphatic groups.

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