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2,813,828

## STABILIZED GREASE COMPOSITION CONTAINING A THIODIARYLAMINE AND A DIALKYL TELLURIDE OR SELANIDE

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No Drawing. Application April 25, 1955,  
Serial No. 503,809

14 Claims. (Cl. 252—33.3)

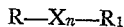
This invention is concerned with improved grease compositions. More particularly, it is directed to soap-base greases containing a combination of additive materials for improving the durability of the grease.

Greases are primarily subject to the degenerating influences of air and heat. The degradation of the ingredients present in grease compositions, especially due to these two influences, results in the formation of materials such as acids and the like which are corrosive to bearings and furthermore generate additional decomposition of certain of the grease ingredients. Numerous additives have been investigated for improving various properties of greases including their corrosion resistance, thermal stability, oxidation resistance and extreme pressure properties. It has been the experience of most investigators to find that the addition of many materials, while improving the grease composition with respect to a certain function thereof, simultaneously causes or increases a disadvantageous property of the grease. More specifically, certain corrosion inhibitors have been found to improve the corrosion resistance of the grease compositions but at the same time to cause the latter to have poorer oxidation (or bearing performance) properties.

As the temperature of bearing operation is elevated, the properties of the grease become more and more critical, since at these elevated temperatures, the degradation processes are accelerated. Moreover, additives which may have functioned at lower temperatures are often found to reverse their behavior when the composition is utilized for the lubrication of bearings operated at temperatures in the order of 250° F. and higher.

It is an object of the present invention to provide improved grease compositions. It is another object of this invention to provide greases having improved oxidation and corrosion characteristics. It is a further object of this invention to improve the oxidation (or bearing performance) properties of the greases which have been stabilized with respect to corrosion resistant properties. Other objects will become apparent during the following discussion.

Now, in accordance with the present invention, it has been found that greases comprising mineral oil gelled to a grease consistency with an alkali metal soap are unexpectedly improved with respect to their operating bearing lubrication life by the combined addition thereto of a thiodiaryllamine and a compound of the general formula



wherein R is an aliphatic radical, R<sub>1</sub> is a substituent of the group consisting of hydrogen atoms and aliphatic radicals, X is an element of the group consisting of selenium and tellurium and n is a whole integer less than 3, said compound containing at least 8 carbon atoms per molecule.

More particularly, it has been found that this combination of additive materials is especially useful in alkali metal soap greases which have been previously stabilized against corrosion by the addition of oil-soluble sulfonates and/or the presence of alkylphenoxypolyethoxy ethanols. Still more particularly, alkali metal soap greases containing the combination of oil-soluble petroleum sulfonates

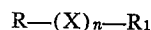
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together with the alkylphenoxypolyethoxy ethanols have been found to be improved in resistance to corrosion but their oxidation (or bearing performance) properties have been impaired by the presence of these combined additives. The present invention comprises the discovery that this disadvantageous property is unexpectedly overcome to a surprisingly great degree by the combined presence of the thiodiaryllamines and the dialkyl selenides or tellurides (or the corresponding mercaptans). This is especially unexpected in view of the fact that the use of the individual additives is of a relatively minor order but that when employing both of the materials together far more than an additive effect results.

The soaps which are utilized as the gelling agent for the subject grease compositions comprise the alkali metal soaps of fatty or hydroxy fatty acids wherein single acids or mixtures thereof may be employed, the acids predominating in members having carbon atom chain lengths of between about 12 and about 24 carbon atoms and preferably between about 16 and 22 carbon atoms. The alkali metal radical may be either sodium, lithium or potassium, or mixtures thereof, while the greatest response is found when modifying greases gelled with either soaps predominating in lithium 12-hydroxy stearate or soaps predominating in lithium stearate, or mixtures of said soaps. The proportion of soap utilized in the subject composition may vary depending upon the consistency desired, but should be sufficient to gel the lubricating oil to a grease consistency. Normally, the soap content will be within the range from about 5% to about 25% by weight of the composition.

### SELENIUM AND TELLURIUM COMPOUNDS

The selenium and tellurium compounds added for their synergistic stabilizing effect have the general configuration:



wherein R is an aliphatic radical, R<sub>1</sub> is a substituent of the group consisting of hydrogen atoms and aliphatic radicals, X is an element of the group consisting of selenium and tellurium and n is a whole number less than 3, i. e., 1 or 2, said compound containing at least 8 carbon atoms per molecule. Preferably, the constituents R and R<sub>1</sub> are aliphatic hydrocarbon radicals and the element X is selenium. The three principal groups of compounds falling within the general formula, as defined above, include dialkyl selenides, dialkyl diselenides and alkyl selenomercaptans as well as the analogous tellurium compounds and substituted or unsaturated analogs of the same. The following description of specific materials meeting the above requirements defines the classes contemplated:

#### Monoselenides (R<sub>1</sub>—Se—R<sub>2</sub>)

##### Normal (straight chain) monoselenides

Didecyl selenide, n—C<sub>10</sub>H<sub>21</sub>—Se—C<sub>10</sub>H<sub>21</sub>—n

Dicetyl selenide, n—C<sub>16</sub>H<sub>33</sub>—Se—C<sub>16</sub>H<sub>33</sub>—n

Dilauryl selenide, n—C<sub>12</sub>H<sub>25</sub>—Se—C<sub>12</sub>H<sub>25</sub>—n

##### Iso (branched chain) monoselenides

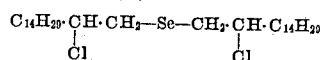
Diundecyl selenide, iso—C<sub>11</sub>H<sub>23</sub>—Se—C<sub>11</sub>H<sub>23</sub>—iso

Ditetradecyl selenide, iso—C<sub>14</sub>H<sub>29</sub>—Se—C<sub>14</sub>H<sub>29</sub>—iso

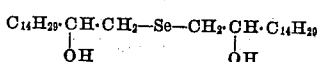
Diheptadecyl selenide, iso—C<sub>17</sub>H<sub>35</sub>—Se—C<sub>17</sub>H<sub>35</sub>—iso

##### Polar substituted monoselenides

###### Bis(beta-chlorocetyl) selenide



###### Bis(beta-hydroxy cetyl) selenide

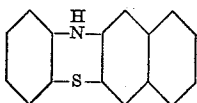




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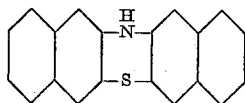
Thio-2,2'-dimethyldiphenylamine  
 Thio-4,4'-didecyldiphenylamine  
 Thio-4,4'-dihydroxydiphenylamine  
 Thio-3,3'-dibutyl diphenylamine

(Based on thiophenyl naphthylamine)



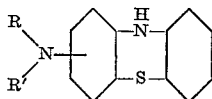
Thio-4-methylphenyl naphthylamine  
 Thiophenyl-6-ethyl naphthylamine  
 Thio-4-hydroxyphenyl naphthylamine

(Base on thiodinaphthylamine)



Thio-di- $\alpha$ -naphthylamine  
 Thio-di- $\beta$ -naphthylamine

A particularly effective type of additive comprises the amino thiodiphenylamines which have the general formula:



R and R' in the above formula may be substituents such as hydrogen, alkyl, aryl, heterocyclic or cycloparaffin groups. Species falling within this class are given below.

4-aminothiodiphenylamine  
 2-aminothiodiphenylamine  
 3-aminothiodiphenylamine  
 N-acetyl-2-aminothiodiphenylamine  
 N-benzyl-2-aminothiodiphenylamine  
 N-acetyl-4-aminothiodiphenylamine  
 Dimethyl-4-aminothiodiphenylamine

The proportion of both of these classes of materials to be incorporated in the subject grease compositions will vary depending upon the specific ingredients and upon the conditions to which the compositions will be subjected. Normally, this will be between about 0.1% and about 3% by weight of the total grease composition. Preferably the proportions utilized are in the range 0.25 to 2.5% by weight.

It has been found that it is necessary to include both of these types of additive materials in order to obtain the maximum bearing life. In the absence of either of the additives, as the working examples given hereinafter will show, the bearing life of the grease compositions is not satisfactory. The incorporation of either of the additives in the absence of the other somewhat increases the bearing life but still the grease compositions do not prolong the utility of the grease to the necessary extent.

As the working examples will demonstrate, the combination of these two materials produced an entirely unexpected magnitude of effect in extending the bearing life of greases and in overcoming the disadvantages which are created by the incorporation of other additives utilized for special purposes. The results are especially outstanding and surprising when the additives comprise oil-soluble sulfonates or alkylphenoxypolyethoxy ethanol or combinations of these materials. As Example I given hereinafter demonstrates, the incorporation of the latter two materials decreases the bearing life of the grease even though they may at the same time provide increased protection against corrosion. However, the addition of phenothiazine and dilauryl selenide to these greases containing the sulfonates and ethanol resulted not only in overcoming the degradation of the grease created by the incorporation of the two anti-corrosive materials but also,

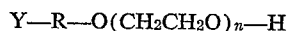
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surprisingly enough, substantially improved and prolonged the bearing life of the resulting composition. Thus, it will be seen that a primary purpose for the utilization of the present invention is the correction of the shortened bearing life occasioned by the inclusion of sulfonates and the phenoxy ethanol in alkali metal soap greases.

The sulfonates may be oil-soluble sulfonic compounds derived from the treatment of heavy hydrocarbon oils with strong sulfuric acid, followed by neutralization. Suitable sulfonic acids from which the salts are formed are well known in the art as possessing rust-proofing properties, and as set forth in expired U. S. Patent No. 1,630,101 granted to the Standard Oil Company of Indiana, May 24, 1927, and in other U. S. patents including Nos. 1,795,993, 2,923,367, 2,119,553, 2,182,992, 2,348,715 and 2,349,785. These sulfonates contain a polar type of molecule which is oil-soluble, and further, they possess the property of adhering to the metal to which they are applied, thereby preventing scuffing or pushing away of the oil films. Therefore, sulfonates keep the metal surfaces constantly covered with a film of the lubricant and also act as a rust-proofing agent.

Various soaps of the sulfonates may be used including metal soaps such as sodium, lithium and calcium sulfonates. Lithium petroleum sulfonate is found to be a very satisfactory rust-proofing agent. Many of the other metal sulfonates are well known in the art to act as rust-proofing agents when incorporated in a lubricating grease. However, lithium petroleum sulfonate, that is, the lithium soap of the product produced by reacting a lithium salt with the sulfonate resulting from the treatment of heavy hydrocarbon oils with strong sulfuric acid, is thought to be novel with the applicants. It has also been ascertained that organic amino oil-soluble sulfonates function satisfactorily as a rust-proofing agent when incorporated in lithium soap and sodium soap when the molecular weight of said sulfonates approach the molecular weight of the oil. Short chain molecules are not as soluble in oil as the larger chain molecules. When the sulfonate derived from the treatment of heavy hydrocarbon oils with strong sulfuric acid is treated with sodium hydroxide, there results a sulfonate molecule which may be a mono- or disubstituted sulfonated aromatic or aliphatic molecule. The alkali petroleum sulfonates and the synthetic hydrocarbon sulfonates which give the best results are those which have an average molecular weight of 300 to 500, thereby tending to make the sulfonate quite soluble in both naphthenic and paraffinic base oils.

The phenoxy ethanol have the general formula

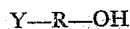


where R is an aromatic nucleus of the benzene, anthracene, phenanthrene, naphthalene or other condensed ring series, Y is an aliphatic, cycloaliphatic, arylaliphatic or aryl group having at least four carbon atoms, and n is a whole number between 3 and 10 (preferably 4). Representative of the compounds contemplated for use as rust-preventive additives in greases of this invention are substituted phenoxy tetraethoxy ethanol, substituted naphthoxy tetraethoxy ethanol, substituted anthroxy tetraethoxy ethanol, substituted phenanthroxy tetraethoxy ethanol, and the like, wherein at least one of the substituents in the aromatic nucleus is a group such as butyl, amyl, hexyl, octyl, dodecyl, tetradecyl, hexadecyl, oleyl or other alkyl group containing up to 30 carbon atoms; a cycloaliphatic group, such as cyclohexyl, octyl-cyclohexyl, lauryl-cyclohexyl, cetyl-cyclohexyl, butyl-cyclohexyl, etc.; bornyl, abietyl, decahydronaphthyl, tetrahydroabietyl, or other terpenic radical or a naphthenic radical; phenyl, benzyl, phenylethyl, phenylisobutyl or other aryl or arylaliphatic hydrocarbon group. The substituents above mentioned may have straight or branched chains and the aromatic nucleus of

the above-defined compounds may have more than one substituent which may either be the same or a different group. In general, when more than one substituent is present in the aromatic nucleus of the above compounds, at least one of the substituents will contain four or more carbon atoms; the remaining substituent or substituents may then optionally contain less than four carbon atoms and be represented by methyl, ethyl, propyl, isopropyl radicals, and the like.

It has been found, as a general rule, that the di- and poly-substituted compounds of the type described above are more effective in inhibiting rust formation when incorporated in greases than the mono-substituted compounds. The use of the former type compounds accordingly represents a preferred embodiment of this invention. In particular, the substituted phenoxy tetraethoxy ethanols are suitably employed as rust-preventive additives in the greases of the present invention. Of the various substituent groups, preference is accorded those compounds containing alkyl substituents.

The above-described compounds may be suitably prepared by condensing a phenolic compound corresponding to the formula:



with a compound of the type:



in which  $n$  is an integer between about 3 and 10, preferably 5,  $X$  is a halogen atom, said condensation taking place in the presence of an alkali to split out an alkali metal halide and thus yield the desired inhibitor.

The following examples illustrate the principles of the present invention but are meant only to be illustrative thereof and not limited thereto.

#### Example I

A grease prepared by gelling a 4:1 weight ratio of bis(2-ethylhexyl) sebacate and light mineral lubricating oil with lithium stearate was used as the primary grease to be modified by additives and is labeled grease A. Grease B was formed by incorporating in this grease 1.5% by weight of sodium petroleum sulfonates having an average molecular weight of about 470 and 1% by weight of octyl phenoxy tetraethoxy ethanol. Grease C was prepared by modifying grease B with the addition of 1% by weight of phenothiazine and 1% by weight of dilauryl selenide. The table given below lists the data obtained by utilizing these three greases in a high temperature bearing test at temperatures of 250 and 300° F. at 10,000 R. P. M.

TABLE I

	High Temperature Bearing Test 300° F., 10,000 R. P. M., Hours to failure	High Temperature Bearing Test 250° F., 10,000 R. P. M., Hours to failure
Grease A.....	157	1,018
Grease B.....	302	600
Grease C.....		1,587

#### Example II

A grease was prepared by gelling a medium viscosity mineral lubricating oil with lithium 12-hydroxy stearate. This grease was modified by the presence of 0.75% phenothiazine and 0.50% dilauryl selenide. These two greases were tested for comparative purposes in the same high temperature high speed bearing test utilized in Example I, the test temperature being 250° F. The unmodified grease composition had a bearing life of 1,118 hours, while the same composition improved by the presence of the two additives did not fail even after 2,100 hours of operation under the same conditions.

The following examples illustrate typical compositions of the present invention.

#### Example III

	Percent by weight
Sodium stearate .....	20
Ethyl octadecyl selenide .....	2.5
Thiophenyl naphthylamine .....	0.5
Poly (propylene oxide) average mol. wt. 1200 .....	77

#### Example IV

	Percent by weight
Sodium 12-hydroxy stearate .....	15
Dodecyl selenomercaptan .....	1.5
Thiodinaphthylamine .....	1.0
Mineral lubricating oil .....	82.5

#### Example V

	Percent by weight
Potassium stearate .....	24
Dicetyl telluride .....	0.5
4-aminothiodiphenylamine .....	1.5
Mineral oil .....	74

We claim as our invention:

1. A lubricating grease comprising a major amount of a mixed lubricating oil, said oil comprising a major amount of bis(2-ethylhexyl) sebacate and a minor amount of a mineral oil, a minor amount of lithium stearate sufficient to thicken said oil to a grease consistency, and 0.25-2% by weight each of sodium petroleum sulfonates, octylphenoxytetraethoxyethanol, dilauryl selenide and phenothiazine.
2. A lubricating grease composition comprising a major amount of a mineral lubricating oil, a minor amount sufficient to gel said oil to a grease consistency, of lithium hydroxy stearate, and 0.25-2% by weight each of sodium petroleum sulfonates, octylphenoxytetraethoxyethanol, dilauryl selenide and phenothiazine.
3. A lubricating grease comprising a major amount of a mineral lubricating oil, a minor amount of lithium stearate sufficient to gel said oil to a grease consistency, and from about 0.1% to about 3% by weight each of an alkali metal hydrocarbon sulfonate, an alkyl-substituted phenoxy polyethoxy ethanol, a dialkyl selenide and a thiodiphenylamine.
4. A lubricating grease comprising a major amount of a mixed lubricating oil, said oil comprising a major amount of bis(2-ethylhexyl) sebacate and a minor amount of a mineral oil, a minor amount of lithium stearate sufficient to thicken said oil to a grease consistency, and from about 0.1% to about 3% by weight each of an alkali metal hydrocarbon sulfonate, an alkyl-substituted phenoxy polyethoxy ethanol, a dialkyl selenide and a thiodiphenylamine.
5. A lubricating grease comprising a major amount of a mixed lubricating oil, said oil comprising a major amount of bis(2-ethylhexyl) sebacate and a minor amount of a mineral oil, a minor amount of lithium stearate sufficient to thicken said oil to a grease consistency, and from about 0.1% to about 3% by weight of phenothiazine and dilauryl selenide.
6. A lubricating grease comprising a major amount of mineral lubricating oil, a minor amount of lithium hydroxy stearate sufficient to thicken said oil to a grease consistency, and from about 0.1% to about 3% by weight each of phenothiazine and dilauryl selenide.
7. A lubricating grease comprising a major amount of a mixed lubricating oil, said oil comprising a major amount of an aliphatic ester of a dicarboxylic acid and a minor amount of a mineral lubricating oil, a minor amount of lithium soaps of fatty acids sufficient to thicken said oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dialkyl selenide and a thiodiphenylamine.
8. A lubricating grease comprising a major amount of a mineral lubricating oil, a minor amount of lithium soap

of hydroxy fatty acids sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dialkyl selenide and a thiodiphenylamine.

9. A lubricating grease comprising a major amount of a mixed lubricating oil, said oil comprising a major amount of an aliphatic ester of a dicarboxylic acid and a minor amount of a mineral lubricating oil, and a minor amount of a lithium soap sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dialkyl selenide and a thiodiphenylamine.

10. A lubricating grease comprising a major amount of a lubricating oil, a minor amount of a lithium soap sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dialkyl selenide and a thiodiphenylamine.

11. A lubricating grease comprising a major amount of a mineral lubricating oil, a minor amount of a lithium soap sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dialkyl selenide and a thiodiphenylamine.

12. A lubricating grease comprising a major amount of a lubricating oil, a minor amount of an alkali metal soap sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dialkyl selenide and a thiodiphenylamine.

13. A lubricating grease comprising a major amount of a lubricating oil, a minor amount of an alkali metal soap sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a dihydrocarbyl selenide and a thiodiarylamine.

14. A lubricating grease comprising a major amount of a lubricating oil, a minor amount of an alkali metal soap sufficient to thicken the oil to a grease consistency, and from about 0.1% to about 3% by weight each of a thiodiarylamine and a compound of the general formula



wherein R is an aliphatic radical, R<sub>1</sub> is a substituent of the group consisting of hydrogen atoms and aliphatic radicals, X is an element of the group consisting of selenium and tellurium and n is a full integer less than 3, said compound containing at least 8 carbon atoms per molecule.

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