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LUBRICATING GREASES CONTAINING SALTS OF DIBORO ACIDS WITH AMINES

William R. Siegart, Wappingers Falls, and Norman R. Odell and Fred C. Toettcher, Fishkill, N.Y., and Edward L. Kay, Akron, Ohio, assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

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This invention relates to lubricating greases and to a novel class of additives therefor. More particularly, it relates to lubricating greases containing amine salts of tetra-covalent diboro acids.

Amine salts of tetra-covalent diboro acids are disclosed and claimed as novel compounds in copending application Serial No. 83,176, of Edwin C. Knowles and Edward L. Kay, filed of even date herewith. We have found, in accordance with the present invention, that these compounds are employed with particular advantage in lubricating greases thickened with hydroxy fatty acid soaps, wherein they impart greatly increased dropping points and other advantages, differently from their effect in lubricating greases generally, including greases thickened with conventional fatty acid soaps.

The amine salts of tetra-covalent diboro acids employed in accordance with the present invention are compounds represented by the following general formula:

$$R'''R''R'\overset{+}{N}HB(OR)_2\overset{-}{O}\overset{-}{B}(OR)_3$$

wherein R is a hydrocarbyl radical containing 1 to 24 carbon atoms, R′ is an aliphatic hydrocarbyl or hydroxy substituted aliphatic hydrocarbyl radical containing one or more carbon atoms and preferably at least 8 to about 30 carbon atoms and R″ and R‴ are hydrogen, aliphatic hydrocarbyl or hydroxy substituted aliphatic hydrocarbyl radicals containing 1 to 24 carbon atoms. The preferred compounds are those wherein R′ is a tertiary aliphatic hydrocarbyl group containing from 8 to 24 carbon atoms and R″ and R‴ are hydrogen.

The term hydrocarbyl radical when used herein denotes a monovalent hydrocarbon radical.

Suitable compounds of the above class include the following: octylamine salt of pentamethoxy diboro acid, dodecylamine salt of penta-n-propoxy diboro acid, dodecylamine salt of penta-secondary-butoxy diboro acid, tertiary dodecylamine salt of penta-benzyloxy diboro acid, tertiary dodecylamine salt of penta(nonylphenoxy) diboro acid, hexyldecylamine salt of tri-n-propoxy-di-isopropoxy-diboro acid, dodecylamine salt of tri-n-propoxy-di-pentabutoxy diboro acid, octylamine salt of tri-n-propoxy-di-beta-chloro-ethoxy diboro acid and tertiary hexyldecylamine salt of tri-(nonylphenoxy)-n-di-propoxy diboro acid.

Formation of the amine salts of tetra-covalent diboro acids takes place readily over a wide range of conditions. The tetra-covalent diboro acids may be prepared by merely mixing together a diborate ester and alcohol in equimolecular proportions at room temperature in the presence or absence of a solvent, and then reacting the product with the theoretical amount of amine, on the basis of one amine group to each molecule of tetraboric acid ester. Where the reaction is highly exothermic, the reaction mixture is preferably cooled during the reaction.

The lubricating greases to which this invention relate are those containing metal soaps of high molecular weight hydroxy fatty acids in sufficient proportions to provide at least a substantial thickening effect. The metal component may be any metal which is suitable for forming soaps as thickening agents in lubricating greases generally, including sodium, potassium, lithium, calcium, barium, strontium, aluminum, magnesium, zinc, etc. The alkali metals and alkaline earth metals comprise a preferred class of metals for this purpose. The hydroxy fatty acid soap will usually be present in the composition in amounts from about 3 to about 15 percent by weight, although somewhat smaller or larger amounts are also suitable, such as amounts as low as about 2 percent by weight and as high as about 30 percent by weight of the composition.

The diboro acid-amine salts are ordinarily employed in these lubricating greases in amounts in about the range 0.1–10 percent by weight, although somewhat larger or smaller amounts may be employed if desired. They are most suitably employed in amounts in about the range 0.5–5 percent by weight of the grease composition.

Suitable soap forming acid materials which may be employed in the production of these greases include hydroxy fatty acids containing from about 12 to about 24 carbon atoms per molecule and one or more hydroxy groups separated from the carboxylic group by at least one carbon atom, and the glycerides and other esters of such acids. The preferred acids are substantially saturated acids containing from about 16 to about 22 carbon atoms and one or two hydroxy groups per molecule. Such materials may be obtained from naturally occurring glycerides, by hydroxylation of fatty acids, by hydrogenation of ricinoleic acid or castor oil, or otherwise by processes such as the catalytic oxidation of hydrocarbon oils and waxes which have been extracted and fractionated to the desired molecular range. Mixtures of hydroxy acids together with unsubstituted fatty acids may be very suitably employed, wherein the hydroxy fatty acid comprises at least about one third of the fatty acid mixture.

Lubricating oils employed in the greases include conventional mineral oils and synthetic oils, such as high molecular weight ethers, esters, silicones, etc. Suitable mineral oils include both paraffinic and naphthenic oils and blends thereof, having viscosities in the range from about 80 seconds Saybolt Universal at 100° F. to about 225 seconds Saybolt Universal at 210° F. A particularly suitable class of synthetic lubricating oils comprises synthetic dicarboxylic acid esters, such as di-2-ethylhexyl sebacate, (di-secondary amyl) sebacate, di-2-ethylhexyl azelate, etc., and polymers obtained by condensing dicarboxylic acids with glycols as disclosed in U.S. 2,628,-974, as well as the sulfur analogs of such esters. Other synthetic oils which may be employed in accordance with this invention include the silicone polymers, including dialkyl silicone polymers such as dimethyl silicone polymer, diethyl silicone polymer, and mixed aryl-alkyl silicone polymers such as phenyl methyl silicone polymer, having viscosities in the lubricating oil viscosity range.

The grease preparation may be carried out in any suitable manner. The diboro acid-amine salt may be added either during the grease preparation or it may be incorporated into the preformed grease by heating a mixture of the grease and diboro acid-amine salt at a moderately elevated temperature with stirring, preferably followed by milling. It is conveniently added during the grease preparation when the mixture has cooled to about 200° F.

The lubricating greases of this invention may also contain other additives of various types such as are commonly employed in lubricating greases, such as extreme pressure agents, anti-corrosives, anti-oxidants, etc., as well as other thickening agents, such as finely divided solids having grease forming properties.

The following example is given for the purpose of further disclosing the invention.

EXAMPLE I

A lubricating grease representing a preferred embodiment of this invention having the following composition in percent by weight:

Lithium 12-hydroxystearate	7.1
Amine salt of diboro acid	3.0
Lubricating oil	Remainder

The lubricating oil is a mixture in a 3:1 ratio by weight respectively of 2-ethylhexyl sebacate and a refined paraffinic distillate oil having a Saybolt Universal viscosity of about 100 seconds at 100° F.

The amine salts of diboro acids are prepared as described in the said copending application. For example, the amine salt of penta(nonylphenoxy) diboro acid is obtained in the following manner: 110 grams of nonylphenol (0.5 mol) is added to 459 grams of tetra-nonylphenoxy) diborate (0.5 mol). Adduct or complex formation is indicated by an increase in temperature of the mixture from 27° C. to 35° C. Thereafter, 100 grams of tertiary alkyl (C_{12}–C_{15}) primary amine (0.5 mol) is added to the mixture, this amine being a commercial product sold under the trade name of "Primene 81–R." A further temperature increase from 25° C. to 70° C. is observed. The product is distilled to remove the solvent, and tertiary alkyl (C_{12}–C_{15}) primary amine-penta(nonylphenoxy) diborate is obtained.

The grease preparation is carried out by saponifying Hydrofol acids 200 with a small excess of lithium hydroxide in the presence of a major proportion of the mineral oil contained in the grease, and thereafter blending in the ester oil. The saponification is accomplished by heating the mixture for 1½ hours at about 317° F. The saponification mixture is then heated up to 400° F. while adding 2-ethylhexyl sebacate and circulating the mixture through a shear valve at 75 pounds pressure drop while the temperature is maintained at 400° F. The mixture is then cooled to 200° F. during about 2½ hours while additional amounts of mineral oil and 2-ethylhexyl sebacate are added. The grease is finally drawn and finished by milling in a Premier colloid mill. Diboro acid-amine salt is incorporated into the base grease thus obtained by heating a mixture of the grease and the amine salt in suitable proportions by weight at 150° F. for 30 minutes with stirring, and then milling with one pass through a Premier colloid mill at 0.002 inch clearance.

The following table shows the effect of the diboro acid-amine salt upon the dropping point of a grease obtained as described above.

Table I

Diboro acid-amine salt:	Dropping point, ASTM, ° F.
None	366
Amine salt of penta(nonylphenoxy) diboro acid	491

In addition to the increased dropping points obtained with diboro acid-amine salts, these compounds also produce large improvements in the water absorption properties of hydroxy fatty acid soap thickened greases which normally undergo objectionable penetration changes due to water absorption.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency by a metal hydroxy fatty acid soap and containing about 0.1–10 percent by weight of the class of amine salts of diboro acids represented by the formula:

$$R'''R''R'\overset{+}{N}HB(OR)_2\overset{-}{O}$$
$$|$$
$$(OR)_3$$

wherein R is a hydrocarbyl radical containing 1–24 carbon atoms, R′ is selected from the class consisting of aliphatic hydrocarbyl and hydroxy substituted aliphatic hydrocarbyl radicals containing 1–30 carbon atoms, and R″ and R‴ are selected from the class consisting of hydrogen, aliphatic hydrocarbyl and hydroxy substituted aliphatic hydrocarbyl radicals containg 1–24 carbon atoms.

2. A lubricating grease according to claim 1 wherein R′ is a tertiary aliphatic hydrocarbyl group containing 8–24 carbon atoms and R″ and R‴ are hydrogen.

3. A lubricating grease according to claim 1 wherein the said hydroxy fatty acid soap is a lithium soap.

4. A lubricating grease according to claim 1 wherein the said amine salt of diboro acid is a tertiary alkyl (C_{12}–C_{15}) primary amine salt of penta(nonylphenoxy) diboro acid.

5. A lubricating grease according to claim 1 wherein the said lubricating oil is a mineral oil.

6. A lubricating grease according to claim 1 wherein the said lubricating oil is a dicarboxylic acid ester.

References Cited in the file of this patent

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