This invention pertains to the use of a stabilized dispersion of calcium oxide or hydroxide to enhance the anti-wear characteristics of an aluminum soap grease composition. The anti-wear characteristics of aluminum soap (e.g., aluminum stearate and aluminum benzoate stearate) greases can be enhanced by dispersing calcium oxide or hydroxide therein, the dispersion being stabilized by a polyvalent metal sulfonate (e.g., calcium petroleum sulfonate).

Aluminum soap thickened greases are beneficially used where it is essential to have grease compositions of high water-resistance. Normal aluminum soaps (e.g., aluminum stearate) have a mild resistance to emulsification in water, but the normal aluminum soap greases are not beneficially used at high temperatures, such as above 160° F. Particularly effective aluminum soaps which can be used to produce grease compositions having combined characteristics of high water-resistance and high melting points are the complex aluminum soaps, e.g., basic aluminum benzoate stearate.

In addition to the thickening agents, numerous secondary agents are incorporated in grease compositions to improve their resistance to oxidation, to improve their extreme pressure properties, to enhance their anti-wear characteristics, etc.

It is a primary object of this invention to produce aluminum soap grease compositions having enhanced anti-wear characteristics. It is an object of this invention to set forth a new class of anti-wear agents for grease compositions.

It is another object of this invention to prepare grease compositions having inhibited wear characteristics. It is also an object of this invention to provide a high-melting, water-resistant grease composition having enhanced anti-wear characteristics.

These and further objects of this invention will be apparent from the following description and the appended claims.

According to this invention, it has been found that the anti-wear characteristics of aluminum soap grease compositions can be enhanced by incorporating therein a dispersion of lime, said dispersion stabilized by a polyvalent metal sulfonate.

The grease composition of this invention comprises, in particular, an oil of lubricating viscosity, an aluminum soap thickening agent, calcium oxide and/or hydroxide, and a polyvalent metal sulfonate.

Suitable lubricating oils useful as base oils in the preparation of the greases thickened according to this invention include a wide variety of oils such as naphthenic base, paraffin base and mixed base mineral oils, synthetic oils, e.g., alkylene oxide polymers such as polypropylene oxide polymers, and other hydrocarbon lubricants, e.g., lubricating oils derived from coal products. Other synthetic oils include esters of alkylene oxide type polymers, e.g., acetylated propene oxide polymers prepared by acetylating propene oxide polymers containing hydroxyl groups, dicarboxylic acid esters, polyhydric alcohol and liquid esters of acids of phosphorus and silicon.

Although the anti-wear characteristics of aluminum soap greases in general are enhanced by incorporating therein stable dispersions of calcium oxide and/or hydroxide, the anti-wear characteristics of grease compositions are particularly enhanced by dispersions of calcium oxide and/or hydroxide.

The aluminum soaps used herein to thicken lubricating oils to the consistency of a grease include the normal aluminum soaps (e.g., aluminum stearate) and complex basic aluminum soaps (e.g., aluminum benzoate stearate).

By "complex basic aluminum soaps" is meant that the aluminum soap molecule contains at least one hydroxyl anion for each aluminum cation, and at least two disimilar anions substantially hydrocarbonaceous in character. By "substantially hydrocarbonaceous anions" is meant those anions which are composed mainly of hydrogen and carbon, and include such anions which contain, in addition, minor amounts of substituents such as oxygen, nitrogen, etc.

The complex basic aluminum soaps are described in the Hotten-Echols patent application, Serial No. 112,584, filed August 26, 1949, now abandoned. The organo anions of the complex aluminum soaps are generally oleophilic (i.e., groups derived from or residues of acids which are oil-soluble); however, one of the organo anions has a greater solubility in lubricating oil than another organo anion. For purposes of simplification, the organo anions of greater oil solubility will be designated as "relatively oleophilic" anions, and the organo anions of lesser oil solubility will be designated as "relatively oleophobic" anions.

In order to characterize further the organo anions of the aluminum soaps of this invention, characteristic properties of each of the organo anions are noted as follows:

The aluminum di-soaps of each of the organo anions (i.e., the aluminum di-soaps of the oleophilic anion and the aluminum di-soaps of the oleophobic anion) are insoluble in water. For example, in the aluminum benzoate stearate example of this invention, the aluminum di-soap of the benzoate anion (i.e., aluminum benzoate) and the aluminum di-soap of the stearate anion (i.e., aluminum di-stearate) are insoluble in water. The aluminum di-soaps of the more soluble organo anions (i.e., the relatively oleophobic anions) are soluble in a petroleum hydrocarbon lubricating oil (e.g., a California solvent-refined paraffinic oil having a viscosity of 485 SUS at 100° F.) in an amount of at least 5% at 400° F. That is, at 400° F., 5% of the aluminum soap of the oleophilic organo anion will form a true solution in a petroleum hydrocarbon lubricating oil. On the other hand, the aluminum soaps of the less soluble organo anions (i.e., the relatively oleophobic anions) are soluble in a petroleum hydrocarbon lubricating oil in an amount of less than 1% at 400° F. That is, at 400° F., less than 1% (from 0% to about 1%) of aluminum soap containing the oleophobic anions will dissolve in a petroleum hydrocarbon lubricating oil to form a true solution.

Furthermore, the aluminum soaps of the relatively oleophobic anions melt at a temperature above 400° F., and the aluminum soaps of the relatively oleophilic anions melt at a temperature less than 350° F.

The complex aluminum soaps of this invention are polymeric in structure, that is, the complex aluminum soaps have more than one aluminum atom and at least two disimilar organo anions throughout the polymeric structure. It is possible for the complex aluminum soaps to contain as many as 1,000 or more monomeric...
units, each monomeric unit containing one aluminum atom having all of its valences satisfied by at least one hydroxyl group and two organo anions. Thus, it is readily understood that aluminum has a valence of +3, it is not meant herein to limit the complex aluminum soap of this invention to one containing only three specific anions. In the over-all average, the valence bonds of the aluminum atoms can be directed to more than three specific anions, that is, to more than one hydroxyl group and more than two organo anions. The average molecule in the soap may contain a plurality of relatively oleophilic anions or a plurality of relatively oleophobic anions per aluminum atom. For example, it may be advantageous in some instances to use a complex aluminum soap as exemplified by aluminum benzoate-stearate-caprylate.

Suitable relatively oleophilic anions are anions of alliphatic (saturated and unsaturated), aromatic, aralkyl, and cycloaliphatic carboxylic acids. The acids must be sufficiently hydrocarbonaceous in character to impart the desired oil solubility. Thus, the alliphatic (saturated and unsaturated) carboxylic acids may contain from 8 to about 30 carbon atoms, preferably from 12 to 18 carbon atoms. The aliphatic substituent in the various cyclic carboxylic acids may contain at least 4 carbon atoms on the alliphatic group attached to the ring. The aralkyl, arylcarboxylic acids and aromatic carboxylic acids preferably contain a total of about 16 carbon atoms. The relatively oleophilic anion may be an alkyl phenol containing at least 4 carbon atoms in the alkyl group, preferably 15 carbon atoms in the alkyl group; e.g., cetyl phenol. It is preferred that the organo-substituted acids of sulfur and phosphorus contain at least 14 carbon atoms, and more especially at least 20 carbon atoms, in the organo substituent. The oleophilic anion acids may contain various substituents, such as hydroxy, amino, alkoxy, e.g., methoxy, and like radicals, so long as the anion remains substantially hydrocarbonaceous in character.

Examples of the carboxylic acids from which the oleophilic anions are derived are: caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxy stearic acid, arachidic acid, melissic acid, oleic acid, linoleic acid, butyl benzoic acid, 2,4-decadiynoic acid, cetyl benzoic acid, decyloxybenzoic acid, phenyl butyric acid, phenyl hexanoic acid, phenyl decanoic acid, cetyl benzenesulfonic acid, a di-decylcetyl benzenesulfonic acid (e.g., a di-polypropylene benzenesulfonic acid), an alkanephosphonic acid having at least 24 carbon atoms in the alkane group, cetyl thiophosphonic acid, naphtenic acid, etc. Of these, stearic acid, hydroxy stearic acids, naphtenic acids of molecular weight above about 250, and alkyl benzenesulfonic acids having at least 20 carbon atoms in the alkyl substituents are preferred. The relatively oleophilic anions are substantially hydrocarbon in structure and may be selected from anions of alliphatic (saturated and unsaturated), aromatic, aralkyl, alkaryl and cycloaliphatic mono- and poly-carboxylic acids. Acids having up to two carboxyl groups are preferred, the monocarboxylic acids being especially preferred. For the desired properties, aliphatic monocarboxylic acids of 4 to 7 carbon atoms are employed. When the monocarboxylic acid contains 2 carboxyl groups, the acid contains from 8 to 11 carbon atoms, and in some cases up to 20 carbon atoms, so long as the anion resulting therefrom is relatively oleophilic as compared to the oleophilic anion employed. The alkyl groups of the arylaralkyl carboxylic acids contain no more than 3 carbon atoms. Thus, the aralkyl and the arylaralkyl carboxylic acids contain a total of not more than 9 carbon atoms, preferably a total of 7 carbon atoms.

Suitable oleophobic anions are derived from benzoic acid, methyl benzoic acid, ethyl benzoic acid, tolacic acid, phenyl acetic acid, phenyl propionic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, salicylic acid, carboxy methyl cellulose, polyacrylic acid, etc. Of these, the benzoic, azelaic and tolacic acids are preferred. Examples of aliphatic soaps which are effective thickening agents for grease compositions according to this invention include aluminum laurate, aluminum oleate, aluminum stearate, aluminum benzoate oleate, aluminum benzoate 12-hydroxy stearate, aluminum toluate stearate, aluminum benzoate naphthenate, aluminum benzoate hydrogent rotorin, aluminum benzoate sulfonate, aluminum azelate stearate, aluminum phosphate benzoate stearate, aluminum benzoate hydroxy stearate, etc.

Polyvalent metal sulfonates are used to stabilize the dispersions of calcium oxide and hydroxide. These polyvalent metal sulfonate dispersants include calcium and barium salts of sulfonic acids derived from petroleum, polypropylene, polybutylene, and benzene or naphthalene alkylated with high molecular weight, oil-soluble hydrocarbon groups. The molecular weight of the hydrocarbon used in the preparation of the sulfonic acid ranges from about 350 to about 900. By "petroleum sulfonate" is meant the mahogany sulfonates, as described in U. S. Patent 2,450,635.

Examples of suitable hydrocarbonaceous radicals which can be coupled to alkylate benzene or naphthalene are the following: dodecane, hexadecane, eicosane, tricountane radicals; radicals derived from petroleum hydrocarbons, such as white oil, wax, or olefin polymers (e.g., polypropylene and polybutylene, etc.). The sulfonic acids used in preparing the sulfonates of this invention also include the oil-soluble sulfonic acids obtained from petroleum, such as "mahogany acids," and the synthetic sulfonic acids prepared by various methods of synthesis (e.g., sulfonic acids prepared by reacting a chlorinated white oil with benzene, using hydrofluoric acid as a catalyst, then treating the resulting white oil alkylated benzene with chlorosulfonic acid or fuming sulfuric acid to form a white oil benzene sulfonic acid).

The dispersants (i.e., the polyvalent metal sulfonates) are used in amounts of 0.1% to 10% by weight of the total composition. However, because grease compositions containing from 0.5% to 2% of the dispersants markedly improve anti-wear characteristics, it is preferred to use these latter amounts. The amount of calcium oxide and hydroxide which can be stably dispersed in the lubricating oil depends upon the effectiveness of the particular dispersants used. On a percentage basis depending on the particular oil used, from 0.02% to 7% by weight of oxide or hydroxide can be dispersed in the lubricating oil composition.

In addition to the above considerations, the type of base oil of the grease will influence the amount of calcium oxide and hydroxide which is dispersible in the oil. For example, a polyvalent metal sulfonate is more soluble in a base oil of high aromatic or naphthenic content than in a base oil having only a minor aromatic or naphthenic content. Therefore, a greater amount of calcium oxide or hydroxide can be dispersed in an oil of high aromatic content.

In preparing the grease compositions of this invention, it is preferred to initially prepare a stable dispersion of calcium oxide or hydroxide in a lubricating oil. This dispersion of calcium oxide and/or hydroxide in lubricating oil is then incorporated into an aluminum soap-thickened grease in amounts sufficient to enhance the anti-wear characteristics and the dispersant action employed. The dispersion of calcium oxide and/or hydroxide in lubricating oil can be prepared by the method outlined in the Lindstrom and Woodruff patent application Serial No. 203,783. (filed December 30, 1950, now Patent No. 2,676,928. That is, colloidal dispersions (colloidal suspensions) of calcium oxide and/or hydroxide in lubricating oils can be obtained by the use of dihydrolic alcohols, e.g.,
ethylene glycol. Calcium oxide or hydroxide is dissolved (or dispersed) in a dihydric alcohol. The dihydric alcohol solution (or dispersion) is then thoroughly blended with lubricating oil to form a dispersion of calcium oxide or hydroxide in lubricating oil, which dispersion is then stabilized by a dispersant (e.g., a polyvalent metal sulfonate). The dihydric alcohol is removed by distillation, and the mixture is filtered to remove undispersed calcium oxide or hydroxide.

As set forth in the Woodruff et al. patent application Serial No. 218,284, filed March 29, 1951, the filtration rate of dispersions of calcium oxide or hydroxide in lubricating oils can be increased by the use of alpha-hydroxy acids (e.g., glycolic acid, lactic acid, etc.) (or the calcium salts of these acids) in the preparation of the dispersions.

It is desirable that the alpha-hydroxy acids (or the calcium salts thereof) be present in an amount such that the molar ratio of alpha-hydroxy acids (or the calcium salts thereof) to the calcium oxide (or hydroxide) dispersed has a value from about 0.1 to about 4.0.

The grease compositions of this invention can be prepared in the usual manner, for example, an aluminum soap and a lubricating oil can be heated, with agitation, then cooled to room temperature and the stabilized dispersion of calcium oxide and/or hydroxide in a lubricating oil can be incorporated into the aluminum soap grease. On the other hand, a stabilized dispersion of calcium oxide and/or hydroxide in oil may be incorporated into the grease prior to the heating step.

The data presented herein in Table I illustrate the effectiveness of a stable dispersion of calcium oxide for enhancing the anti-wear characteristics (increasing the film strength) of a grease composition thickened with basic aluminum benzoate stearate. A calcium petroleum sulfonate was used as a dispersant to stabilize the calcium oxide dispersion. The film strength data were obtained with a slightly modified Almen test machine as described on page 145 in "Lubricants and Lubrication" by Clower, published by McGraw-Hill Book Co. in 1939. In the present test, the drill-rod journal was prepared from bronze. The data show the weight loss, in milligrams, of the bronze journal under a constant load of 8 pounds for a period of 5 minutes.

Table I

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Grease &quot;A&quot; (Per cent by Weight)</th>
<th>Grease &quot;B&quot; (Per cent by Weight)</th>
<th>Lime Dispersion</th>
<th>Almen Wear (Brass or Steel), Mils Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>596-2B</td>
<td>100</td>
<td></td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>630-4T</td>
<td>94</td>
<td>10</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>630-27C</td>
<td>94</td>
<td>10</td>
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<td></td>
</tr>
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<td>95</td>
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</tr>
<tr>
<td>918-26C</td>
<td>90</td>
<td>10</td>
<td>65.8</td>
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</tr>
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<td>918-26D</td>
<td>90</td>
<td>10</td>
<td>40.9</td>
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<tr>
<td>918-26E</td>
<td>90</td>
<td>10</td>
<td>25.8</td>
<td></td>
</tr>
</tbody>
</table>

1. Grease "A" contained 12.5% by weight of basic aluminum benzoate stearate, 23.5% by weight of a California solvent-refined paraffinic base oil having a viscosity of 480 SUS at 210°F, and 54.7% by weight of a California solvent-refined paraffinic base oil having a viscosity of 70 SUS at 300°F.
2. Grease "B" contained 11% aluminum stearate and 89% of a California solvent-refined paraffinic base oil having a viscosity of 100 SUS at 100°F. A dispersion in oil of 2.5% calcium oxide stabilized with 30% calcium petroleum sulfonate, the dispersion containing 4.5% sodium glycolate used as an aid in the filtering step in the preparation of the dispersion.
3. A dispersion in oil of 2.5% calcium oxide stabilized with 30% calcium petroleum sulfonate, the dispersion containing 4.5% sodium glycolate used as an aid in the filtering step in the preparation of the dispersion.
4. A dispersion in oil of 1.4% calcium oxide stabilized with 20% calcium petroleum sulfonate. In the preparation of this dispersion, nothing was used to aid the filtration.
5. The average of 2 test results.
6. The average of 3 test results.

Not only are the stabilized dispersions of calcium oxide and hydroxide effective anti-wear agents for aluminum soap greases, but the calcium salts of alpha-hydroxy acids also enhance the anti-wear characteristics of aluminum soap greases.

In addition to the components already noted herein, other agents may be incorporated into the greases such as rust inhibitors, oxidation inhibitors, corrosion inhibitors, extreme pressure agents, other anti-wear agents, etc.

1. A grease composition comprising a major proportion of an oil of lubricating viscosity, and aluminum soap in an amount sufficient to thicken said oil to the consistency of a grease, from about 0.02% to about 7% by weight of an inorganic material selected from the group consisting of calcium oxide and calcium hydroxide, and from 0.1% to 10% by weight of an oil-soluble alkaline earth metal sulfonate, wherein said aluminum soap is a basic complex aluminum soap having at least two unlike organo anions, one of said organo anions being selected from the group consisting of aromatic monocarboxylic acid anions containing from 1 to 3 non-aromatic carbon atoms, and another of said organo anions being selected from the group consisting of monoalkyl aliphatic acid anions containing from 8 to 30 carbon atoms.

2. A grease composition comprising a major proportion of an oil of lubricating viscosity, a complex basic aluminum soap in an amount sufficient to thicken said oil to the consistency of a grease, from about 0.02% to about 7% by weight of an inorganic material selected from the group consisting of calcium oxide and calcium hydroxide, and from 0.1% to 10% by weight of an oil-soluble alkaline earth metal sulfonate, wherein said aluminum soap contains at least two unlike organo anions, one of said organo anions, the relatively oleophobic anion, being selected from the group consisting of aromatic carboxylic acid anions containing from 1 to 3 non-aromatic carbon atoms, and another of said organo anions, the relatively oleophilic anion, being selected from the group consisting of monoalkyl aliphatic acid anions containing from 8 to 30 carbon atoms, the mole ratio of said oleophobic anions to said relatively oleophilic anions having a value from about 0.2 to about 5.0.

3. The grease composition of claim 2, wherein the aluminum soap is a complex basic aluminum soap containing a plurality of anions derived from monoalcohols carboxylic acids, at least one of said carboxylic acids being an aromatic carboxylic acid containing from 1 to 3 non-aromatic carbon atoms, and another of said carboxylic acids being an aliphatic carboxylic acid containing from 12 to 18 carbon atoms.

4. The grease composition of claim 2, wherein the aluminum soap is aluminum benzoate stearate and wherein in the inorganic material is calcium oxide.

5. The grease composition of claim 2, wherein the aluminum soap is aluminum benzoate stearate and wherein in the inorganic material is calcium hydroxide.

6. The grease composition of claim 2, wherein the alkaline earth metal sulfonate is a calcium petroleum sulfonate.

7. A grease composition comprising a major proportion of an oil of lubricating viscosity, a complex basic aluminum soap in an amount sufficient to thicken said oil to the consistency of a grease, from about 0.02% to about 7% by weight of inorganic material selected from the group consisting of calcium oxide and calcium hydroxide, and from about 0.1% to about 10% by weight of an alkaline earth metal sulfonate, wherein said aluminum soap having at least two unlike organo anions, one of said organo anions, the relatively oleophobic anion, being selected from the group consisting of aromatic carboxylic acid anions containing from 1 to 3 non-aromatic carbon atoms, and another of said organo anions being selected from the group consisting of aliphatic acid anions containing from 8 to 30 carbon atoms, the mole ratio of said aromatic carboxylic acid anions to aliphatic acid anions having a value from 0.2 to about 5, said grease composition having incorporated therein a calcium salt of an alpha-hydroxy acid.
8. The composition of claim 7, wherein the alphahydroxy acid is glycolic acid.

9. The grease composition of claim 7, wherein the mole ratio of the said calcium salt of alphahydroxy acid to said inorganic material has a value from about 0.1 to about 4.0.

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