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LUBRICATING GREASE

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ABSTRACT OF THE DISCLOSURE

A lubricating grease of improved properties is prepared by forming an aluminum complex soap in a paraffin oil by sequentially reacting an aluminum alkoxide with an aromatic carboxylic acid and then with a higher fatty acid, followed by blending with an isobutylene polymer and a low viscosity paraffin oil.

FIELD OF THE INVENTION

The field of art to which the invention pertains includes the field of lubricating greases, particularly greases containing an aluminum complex soap and isobutylene polymer.

BACKGROUND AND SUMMARY OF THE INVENTION

The formulation of lubricating grease compositions is a sophisticated art involving the blending of mineral oil, thickening agent and additive materials under carefully controlled temperature and blending conditions. A large number of different formulations and processes have been developed to meet the wide variety of requirements for industrial lubrication with the trend being directed toward the production of multipurpose greases. Various complex soap greases have been developed and notable among these are the aluminum complex greases. Modern manufacturing processes involve the in situ preparation of the aluminum complex thickener by adding the reactive components directly to a mineral oil while processing through a temperature and milling cycle designed to blend the components into a smooth, homogenous grease.

Aluminum complex thickening agents are generally prepared from the reaction of an aluminum alkoxide, such as aluminum isopropoxide, with a duality of organic acids. In this regard, see "Manufacture and Properties of Aluminum Complex Greases," by J. L. Dreher, T. H. Koundakjian and C. F. Carter, published in the NLGI Spokesman, July 1965. A typical manufacturing procedure is described wherein hydrogenated tallow acids and benzoic acid are dissolved in a portion of the oil at a temperature of about 180° F. and aluminum isopropoxide is then added with vigorous agitation at a temperature of about 200–225° F. Thereafter, water is added to liberate remaining portions of isopropanol and the temperature is increased to 310–330° F. As the grease is cooled, additives and the remainder of the oil are added. The thickener concentration for such greases ranges from 5.5 to 8.5 weight percent.

In Polishuk U.S. Pat. 3,591,505, an aluminum complex grease is prepared by sequentially reacting the less reactive of two carboxylic acids with aluminum alkoxide followed by reaction with the more reactive acid. Thus, stearic acid is first reacted followed by reaction with benzoic acid to complete the formation of the aluminum thickener.

The complexity of grease formulation is increased when other components are added which affect its physical properties. Thus, it is known to add a material such as an isobutylene polymer to increase the viscosity index and decrease the affect of temperature on viscosity. Such polymers comprise relatively long, slender molecules which tend to ball-up at low temperature with little resistance

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to flow, but apparently straighten out at high temperature thereby impeding flow and increasing the viscosity, with the result that viscosity is relatively stable. See, in this regard, Oswalt U.S. Pat. 3,211,650 and Warung German Pat. 1,955,951. The presence of such a polymer adds further complications to grease formulation. In the Oswalt patent, the thickening agent is obtained by saponifying hydroxy stearic acid with lime and the patentee requires that a naphthenic oil be used, having a viscosity of about 90–120 SUS at 100° F. The isobutylene polymer has an average molecular weight of about 17,500–18,500. In the Warung patent, the polymer is added to a grease thickened with a complex soap containing calcium, aluminum, barium or lithium. However, when combined with such complex soap, one of the complexing acids is required to have 5 or less carbon atoms, exemplified by acetic acid. Here also, at least a portion of the lubricating oil is a naphthenic base neutral oil, but the patentee requires that all the oil have a viscosity ranging from 350–650 SUS at 100° F. Other references of interest include U.S. Pat. Nos. 2,599,553; 2,654,710; 2,719,826; 2,768,138; 3,211,650; 3,290,244; 3,453,211; 3,574,111; British Pat. 1,099,620 and an article entitled "Physical and Chemical Properties of Complex Soap Greases," by A. T. Polishuk, Lubrication Engineering, February 1963.

The present invention provides a lubricating grease composition incorporating an aluminum complex soap and isobutylene polymer. The grease has excellent structural stability and effective multipurpose properties over a very wide range of operational requirements. The grease is low-bleeding and very cohesive. It is water resistant, temperature resistant and is compatible with and retains its consistency in the presence of greases with different soap bases. The grease is prepared by a unique process which enable a higher thickener content as compared to conventional greases, aiding in obtaining the foregoing desirable characteristics.

In particular, a lubricating grease composition is provided comprising a major amount of lubricating oil, an amount sufficient to form a grease of an aluminum complex soap, and about 1–20 weight percent of an isobutylene polymer. One of the acid groups used to form the aluminum soap is an aromatic carboxylic acid, exemplified by benzoic acid, and the other group is a higher fatty acid, such as containing a major amount of stearic acid. The aluminum complex soap is formed in a paraffin neutral oil and the isobutylene polymer has a molecular weight of about 9,000–25,000, perferably greater than 18,500 and less than 20,000. There is thus provided a novel grease formulation in which isobutylene polymer is combined with an aluminum complex soap having an aromatic carboxylate component, the combination carried by a paraffin neutral oil. Rust corrosion inhibitors and oxidation inhibitors, as known, can be added.

A unique process for the foregoing formulation is provided wherein an aluminum alkoxide and an aromatic carboxylic acid are dissolved in a paraffin neutral oil having a viscosity of about 250–340 SUS at 100° F., heated to about 80–175° F. for a time sufficient to blend the components. A higher fatty acid is then added to the heated mixture, and then the isobutylene polymer is added along with additional paraffin neutral oil, followed by heating to about 240–400° F. No water need be added, the aluminum complex being formed to constitute about 15–21 weight percent of the grease composition, a much higher concentration than generally obtainable. However, lower, and even higher levels, e.g., 5–30 percent can be produced to provide any desired consistency.

DETAILED DESCRIPTION

The initial steps of the preparation of a lubricating grease of this invention involve the addition of an aluminum alkoxide and an aromatic carboxylic acid to a portion of the base oil. The alcohol precursor of the alkoxide can contain from 1 to about 22 carbon atoms, e.g., methanol, ethanol, propanol, butanol, pentanol, heptanol, nonanol, dodecanol, hexadecanol, eicoxanol, dodesanol, isomeric forms and mixtures thereof. In prior grease formulations, water is added to replace a portion of the alkoxide component with hydroxyl anion. However, in a preferred form of the present invention, as detailed hereinafter, the grease is formulated without the addition of water, hydroxyl ion being produced only by water generated by reaction of the components. It is preferred that the alcohol precursor of the aluminum alkoxide have from 1 to 4 carbon atoms. Examples include aluminum methoxide, aluminum ethoxide, aluminum propoxide, aluminum isopropoxide, aluminum butoxide, aluminum sec-butoxide, and the like, aluminum isopropoxide being particularly preferred.

Aromatic carboxylic acids which can be used in the preparation of the present lubricating grease include benzoic acid, the toluic acids, benzoic acid substituted with one or more alkyl groups such as ethyl, propyl or butyl groups, benzoic acid containing other substituents such as amine, halogen such as chlorine, bromine and iodine, naphthoic acids, and the like. It is preferred to use unsubstituted benzoic acid.

The aluminum alkoxide and aromatic carboxylic acid are first agitated in a portion of the lubricating oil base while heating to a temperature in the range of about 80–175° F. Thereafter, higher fatty acids are added to complete the formation of the complex aluminum salt. The higher fatty acids contain from about 12 to about 22 carbon atoms and are preferably hydrogenated to decrease their saturation. Examples of suitable fatty acids include lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxy stearic acid, arachioic acid, oleic acid, linoleic acid, pentadecanoic acid and margaric acid. Phenyl-substituted fatty acids such as phenyl decanoic acid and naphthenic acids containing at least 12 carbon atoms may also be employed. As indicated, it is preferred that the acids be hydrogenated so as to be substantially saturated. A mixture of acids is conveniently used and it is preferred that such mixture contain a major amount, i.e., greater than 50%, of stearic acid.

The ratios of aluminum alkoxide to carboxylic acid reactants should be controlled so that there are about 0.8–1.2 mols of each acid to each mol of aluminum alkoxide, and preferably there is a 1:1:1 ratio. An amount of lubricating oil which is equivalent to about 35–50% of the total weight of the grease can conveniently be utilized as the initial reaction medium. As the reaction between the higher fatty acids and aluminum isopropoxide-aromatic carboxylic acid complex proceeds, the mass of the material thickens and additional lubricating oil is added blended with a portion of the isobutylene polymer, as hereinafter detailed. The amount added is about one fourth of the remaining fluid components. At this point, one may add water to react with the remaining alkoxide portion of the aluminum alkoxide. However, it is preferred that no water be added; some water is generated from the reaction which reacts with the alkoxide to produce hydroxyl anion.

The resultant aluminum complex soap will be a mixture of aluminum soap molecules containing on an average of one aromatic carboxylic acid anion, one higher fatty acid anion and one hydroxyl ion per atom of aluminum. It will be appreciated that all individual soap molecules in a given complex soap are not the same but that the foregoing composition is an average. For example, one soap molecule may contain 2 fatty acid anions and one aromatic carboxylic acid anion while another may contain 2 aromatic carboxylic acid anions and one higher fatty acid anion, while still another may contain an hydroxyl anion, an aromatic carboxylic acid anion and a higher fatty acid anion, and so forth. Thus, any given aluminum soap preparation will contain a mixture of all these various molecules and the properties of any given soap preparation will be average properties of the mixture of the molecules present.

As above indicated, along with the addition of oil following the reaction with the fatty acids, there is also added a desired amount of isobutylene polymer, about 1–20 weight percent, based on the weight of the formulating grease. The isobutylene polymer as added has a molecular weight of about 15,000–25,000, but as the grease formulation is agitated and milled, some breakdown may occur so that the polymer contained in the final grease formulation can have an average molecular weight of about 9,000–25,000. Generally, it is preferred to add about 7–9 weight percent of isobutylene polymer having a molecular weight, at the time of addition, of greater than 18,500 and less than 20,000.

After the addition of a portion of the polyisobutylene oil blend, the mass is heated to about 250–400° F. to remove any excess unreacted moisture produced by the saponification reactions. The grease is then cooled, passed through a colloid mill to achieve complete dispersion of the complex aluminum soap and graded to the proper consistency with the remaining portion of the lubricating oil. The total oil added after the fatty acids comprise about 25–35 weight percent of the grease. The polymer-oil blend can also contain a corrosion inhibitor and an oxidation inhibitor. Any prior art components for these purposes can be utilized. Examples of rust corrosion inhibitors include lead naphthenate, calcium sulphonate, barium sulphonate, sodium nitrite and tallow dimaine dioleate. Examples of oxidation inhibitors include butylated hydroxy toluene, phenyl alpha naphthylamine, phenyl beta naphthylamine and styrenated diphenylamine. Generally about 0.1–2 weight percent of each inhibitor can be included.

In a broader aspect of the present invention, base oils which can be used to form the lubricating grease can include lubricating oils of naphthenic base, paraffinic base and mixed base mineral oils, and the like, as well as synthetic oils, such as alkylene polymers, polysiloxanes, dicarboxylic acid ester type oils, or liquid esters of phosphorus acids, and the like. It is preferred that the entire lubricating oil be a paraffinic neutral oil and further that a relatively low viscosity oil be utilized. In particular, it is preferred that the oil used to initially support the formation of the complex soap be a paraffin neutral oil having a viscosity of about 250–340 SUS at 100° F., and having a viscosity index of about 70–90, and that the added oil to dilute the mixture be a paraffin neutral oil having a viscosity of about 100–190 SUS at 100° F. and a viscosity index of about 90–110.

The amount of aluminum alkoxide, aromatic carboxylic acid and higher fatty acid added should be sufficient to provide about 15–21 weight percent of aluminum complex soap in the grease formulation, which amount is substantially higher than generally obtainable and can be attributed to the formulation procedure as above outlined. This concentration can be obtained by reacting about 5–7 weight percent of the aluminum alkoxide, calculated as aluminum isopropoxide, with about 3–4 weight percent of the aromatic carboxylic acid, calculated as benzoic acid, and about 7–10 weight percent of the higher fatty acid, calculated as stearic acid.

The following examples, in which all parts are by weight, will illustrate the invention.

Example 1

A grease processing kettle was charged with 40.90 parts of a solvent refined paraffin neutral oil having a viscosity of 300 SUS at 100° F. and a viscosity index of 85, and 6.13 parts of an aluminum isopropoxide (a tri-oxy-aluminum tri-isopropoxide sold under the trade name Kolate No. 7013 by Agrashell, Inc.) was added followed by 3.63 parts of benzoic acid. The two components were allowed to blend and react while the mass was heated to 125° F. At this temperature, 8.34 partst of hydrogenated tallow fatty acid was added to complete the reaction and complete the formation of the complex aluminum soap. The fatty acids, comprising about 65% stearic acid, about 27.5% palmitic acid, about 3% myristic acid and minor quantities of pentadecanoic acid, margaric acid, and oleic acid, had the following characteristics:

Free fatty acid (calculated as oleic acid)	99–103%
Acid No.	197–205
Saponification No.	200–206
Iodine value	1–5
Titre	56–61°

The foregoing characteristics are based on a number of determinations.

Following the addition of the fatty acids, a thickening of the mass occurred and approximately one-fourth of the remaining fluid components of the grease were added to keep the mass in a soft plastic consistency. These fluid components comprise a blend of 32 parts of solvent refined neutral oil and 8 parts of polyisobutylene having a molecular weight of about 19,000. The material was then heated to about 320° F. removing excess moisture produced by the reaction. The grease was then cooled, passed through a colloid mill and graded to the proper consistency by the addition of the remaining fluid components. Rust and oxidation inhibitors were then added (0.5 part of tallow diamine dioleate and about 0.5 part of 30% lead naphthenate).

The grease had a clear amber color and a smooth, adhesive texture. It was tested for rust protection according to ASTM 1743 and passed, for oxidation stability according to ASTM D942 (100 hours, 5 pounds maximum) and passed, and for bleed stability according to ASTM D1742, with no bleeding. The grease was found to have a dropping point, in accordance with ASTM D566, of 500° F., a consistency (worked penetration) according to ASTM D217 of 280 and a shell roll stability change (100 hours at 150° F.) of 8 points softer.

Example 2

For comparison purposes, the preparation of Example 1 was repeated but using a molar equivalent of acetic acid in place of the benzoic acid. The formulated grease was tested for dropping point, consistency and shell roll stability in direct comparison with the grease of Example 1, the following table setting forth a comparison of these properties.

Test	With benzoic acid	With acetic acid
Dropping point, ° F	500	320
Consistency (worked penetration)	280	346
Shell roll stability, pts. change	8	44

Referring to the foregoing results, it will be seen that the substitution of acetic acid for benzoic acid results in a deterioration of the measured properties.

I claim:

1. A lubricating grease composition, comprising:
a major amount of paraffinic neutral lubricating oil;
an amount sufficient to form a grease of an aluminum complex soap, said soap being formed by reacting an aluminum alkoxide having 1–22 carbon atoms in each organic group with a higher fatty acid and an aromatic, benzene-nucleus, carboxylic acid, said aluminum alkoxide being sequentially first reacted with said aromatic carboxylic acid and then with said higher fatty acid; and

about 1–20 weight percent of an isobutylene polymer having an average molecular weight of about 9000–25,000.

2. The invention according to claim **1** in which said lubricating oil comprises about 35–50 weight percent of a paraffin neutral oil having a viscosity of about 250–340 SUS at 100° F. and about 25–35 weight percent of a paraffin neutral oil having a viscosity of about 100–190 SUS at 100° F.

3. The invention according to claim **1** in which said isobutylene polymer has a molecular weight of greater than 18,500 and less than 20,000.

4. The invention according to claim **1** in which the amount of said amount of aluminum isobutylene complex soap in said composition is about 15–21 weight percent.

5. The invention according to claim **1** in which said amount of aluminum complex soap in said composition is about 15–21 weight percent formed by reacting about 5–7 weight percent of aluminum isopropoxide sequentially with about 3–4 weight percent benzoic acid and then about 7–10 weight percent hydrogenated higher fatty acid, said higher fatty acid comprising major amounts of stearic acid, and the amount of said isobutylene polymer in said composition is about 7–9 weight percent.

6. The invention according to claim **1** in which said grease is formed without the addition of water.

7. A method of preparing a grease composition, comprising, in sequence:
dissolving an aluminum alkoxide having 1–22 carbon atoms in each organic group and an aromatic, benzene-nucleus carboxylic acid in a paraffinic neutral lubricating oil to form a mixture thereof;
heating said mixture to react said alkoxide with said carboxylic acid;
adding a higher fatty acid to said reacted mixture and reacting said fatty acid with said reacted mixture; and
adding about 1–20 weight percent of an isobutylene polymer having an average molecular weight of about 9,000–25,000.

8. The invention according to claim **7** in which additional lubricating oil is added subsequent to addition of said higher fatty acid.

9. The invention according to claim **7** in which said isobutylene polymer has a molecular weight of greater than 18,500 and less than 20,000.

10. The invention according to claim **8** in which said first mentioned oil comprises a paraffin neutral oil having a viscosity of about 250–340 SUS at 100° F., and constitutes about 35–50 weight percent of said grease composition, and said additional oil is a paraffin neutral oil having a viscosity of about 100–190 SUS at 100° F. and constitutes about 25–35 weight percent of said grease composition.

11. The invention according to laim **7** in which about 5–7 weight percent of said aluminum alkoxide, as aluminum isopropoxide, and about 3–4 weight percent of said aromatic carboxylic acid, as benzoic acid, is added to said lubricating oil to form said mixture, and about 7–10 weight percent of said higher fatty acid is added to said heated mixture, said fatty acid being hydrogenated and comprising major amounts of stearic acid.

12. The invention according to claim **11** in which said lubricating oil comprises a paraffin oil having a viscosity of about 250–340 SUS at 100° F. and constitutes about 35–50 weight percent of said grease composition, and including adding an additional amount of paraffin oil subsequent to the addition of said higher acid, said additional amount of paraffin oil having a viscosity of about 100–190 SUS at 100° F. and constituting about 25–35 weight percent of said grease, the amount of said isobutylene polymer being about 7–9 weight percent.

13. The invention according to claim **12** including the steps of heating said mixture of components comprising

the first mentioned lubricating oil, aluminum alkoxide and aromatic carboxylic acid to about 80–175° F. for a time sufficient to blend said components, and heating said grease after addition of said additional oil to about 250–400° F. for a time sufficient to remove excess moisture produced by the reaction.

14. The invention according to claim **13** in which the alkoxide portion of said aluminum alkoxide contains from 1 to 4 carbon atoms.

15. The invention according to claim **13** in which said grease is formed without the addition of water.

16. The invention according to claim **15** in which said aluminum alkoxide is aluminum isopropoxide.

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