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LUBRICATING GREASE COMPOSITIONS

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The present invention relates to lubricating grease compositions and particularly to improvements in lubricating greases of the type which comprise lubricating oil thickened to grease consistency with a combination of high and low molecular weight soaps and salts. The invention relates also to a process for making lubricating greases of soft consistency and a stable physical structure having improved properties over the prior art compositions.

In the prior art, a number of suggestions have been made for combining the usual soaps, which are used to thicken lubricating oils in the preparation of greases, with certain low molecular weight compounds to improve high temperature properties, increase the yield value or thickening effect of a given soap content, and to secure other advantages. Such suggestions have been applied to various types of lubricating greases. A particular application of practical value has been the addition of such low molecular weight compounds to the alkali metal soap greases, particularly the soda base greases, and, to a lesser extent, to the lithium base greases. Lubricating compositions of this type are found to have superior stability at high temperatures, higher dropping points, a firmer consistency for a given soap or salt content and certain other useful properties. Along with the usual metal soaps of the higher fatty acids, it has been suggested that the corresponding metal salts of acetic acid, acrylic acid, crotonic acid, furoic acid, and other homologous and analogous compounds may be advantageously combined. The combination of salts of the low molecular weight acids with the conventional soaps has one common disadvantage in that when sufficient soap is employed to give them structural stability, the greases tend to be of hard consistency under some conditions, making them somewhat difficult to dispense in certain commercial types of grease dispensing equipment. This tends somewhat to limit the utility of the soap-salt type greases. An object of the present invention is to improve greases of this type in this respect without adversely affecting their desirable properties.

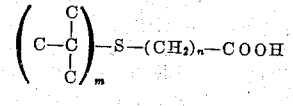
According to the present invention, by using a small amount of certain branched chain aliphatic acids containing sulfur or oxygen, greases of the type mentioned above may be materially improved. The quantities used are from about 1 to 10% by weight, based on the total composition, along with the usual quantities of fatty acid soap and low molecular weight salt. Using such acids as are described below, greases of softer consistency may be made with the same

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general properties of high temperature stability, high melting point, and the like. In effect, soaps of these branched chain sulfur- or oxygen-bearing acids are substituted for part of the conventional soap.

In general, the invention contemplates the use of small amounts of the soaps of branched chain sulfur- or oxygen-bearing acids along with the low molecular weight salts and the conventional metal soap of fatty acids. The latter conventional soaps are preferably those derived from the fatty acids of between 12 and 24 carbon atoms, especially those having between 14 and 20 carbon atoms. The soaps of the saturated long chain acids or those which are substantially saturated are normally preferred. However, soaps of the long chain unsaturated acids may be used for many purposes as the principal thickening ingredient. With such soap is combined preferably a somewhat smaller quantity of the preferred low molecular weight salt such as the acetate, propionate, acrylate, methacrylate, furoate, or the like. The metal ion is preferably but not necessarily the same as that of the principal soap. Proportions of 2 or 3 to 20 or 25% by weight of conventional soap, plus 1 to 15% of the low molecular weight salt may be used. These proportions are based on the total composition, the preferred range being between about 4 or 5 to 20% soap, 2 to 10% salt, or approximately in 1:1 molar ratio for most applications.

Greases thickened to a solid consistency with the combination of soap and salt mentioned above, have fairly good properties, but according to the present invention a superior texture and better softness and stability may be secured by combining 1 to 10%, preferably 2 to 6% by weight, based on the total composition, of a high molecular weight branched aliphatic chain sulfur-bearing soap. A suitable soap for this latter purpose is one which is prepared by neutralizing with an appropriate metal base an acid of the following general type:



wherein m and n are of such value that the total number of carbon atoms is between about 10 and about 20. The sulfur atom may be positioned at various points in the chain, but the composition preferably has at least two tertiary carbon atom groups and may have several branched groups of this character.

The acids of the type exemplified in the above formula may be prepared by reacting aliphatic mercaptans, preferably branched chain substantially saturated aliphatic mercaptans, with a suitable acidogenic material, preferably an aliphatic unsaturated acidogenic material such as acrylonitrile. The mercaptans themselves may be obtained from various sources, a preferred source being by the reaction of polyolefins with hydrogen sulfide. For example, diisobutylene, triisobutylene, polypropylene and analogous polymers and copolymers of appropriate molecular weight (about 8 to 16 carbon atoms, preferably) may be converted to mercaptans and reacted with acrylonitrile or equivalent acidic or acidogenic materials, as pointed out more fully below. The soaps (or salt) of such mercaptan type acids may be formed by neutralization with a suitable metal base in an obvious manner.

The soap, the low molecular weight salt, and the salt of the branched chain sulfur-bearing acid may all be formed simultaneously by combining the acids first, preferably in the presence of a quantity of mineral lubricating oil, and then co-neutralizing the various acids with a saponifying agent. Thus, there may be combined in mineral oil a commercial mixture of hydrogenated fish oil acids varying from about 14 to 22 carbon atoms in chain length and of an average of about 18 carbon atoms, together with acrylic, glycollic or furoic acid as a low molecular weight acid, and with a sulfur bearing acid described more fully below but having about 12 to 18 carbon atoms. This combination of acids may be neutralized with sodium hydroxide to produce a grease containing all three soaps (salts) which is a very satisfactory product. Alternatively, the low molecular weight acid may, in effect, be added to the other ingredients by first adding the corresponding aldehyde which, when treated with a stronger alkaline base such as sodium hydroxide, simultaneously with the neutralization of the other acids, undergoes the well-known Cannizzaro reaction. Thus from furfural may be obtained the corresponding furoic acid salt and furfural alcohol. This aspect of the process has previously been covered in a copending application, Serial Number 60,615, filed November 17, 1948, by Morway, one of the present inventors, and a co-inventor Kolfenbach, now U. S. Patent 2,516,137, issued July 25, 1950, where there is disclosed a process for preparing greases containing furoic acid salts and analogous products, by using the Cannizzaro reaction. The Cannizzaro reaction is equally useful in the present case, the product being beneficially modified, however, by the addition of the high molecular weight, branched chain, sulfur- (or oxygen-) bearing salt which gives the lubricant the desirable soft consistency and other properties mentioned above.

Another aspect of the present invention involves the preparation of the sulfur-bearing acids. An aliphatic unsaturated nitrile having the unsaturation adjacent the nitrile group, such as acrylonitrile, methacrylonitrile, ethacrylonitrile, etc., may be reacted with a branched chain aliphatic mercaptan derived as suggested above or from any other suitable source to produce a sulfur-bearing acid of the type desired for preparing the salt referred to above. The alcohols may be used in place of the mercaptans if desired, although the sulfur-bearing compounds are preferred. The mercaptan or alcohol should preferably have at least 2 tertiary carbon atoms. Thus, by reacting acrylonitrile or methacrylonitrile with an aliphatic mercaptan having about 15 carbon atoms, preferably using a small quantity of $NaOCH_3$ or other alkoxide as a catalyst, an exothermic reaction takes place at ordinary temperatures. This reaction should be controlled, keeping the temperature of the mixture preferably below about 45° C. for example. The thionitrile thus formed is thereafter hydrolyzed to the sodium soap or salt of the acid by adding an alcoholic-aqueous NaOH solution. If the soap of another metal is desired, the solution is acidified, e. g., with HCl. Upon acidification in a conventional manner, the acid is produced, although if desired the sodium salt may be employed directly in the grease, in which event, acidification is not necessary.

The sulfur-bearing acid derived as above, in proportions of about 1 to 10 parts, preferably 2 to 5 parts by weight, is combined with 2 to 20, preferably 3 or 4 to 15, parts of saponifiable fatty acid and 1 to 15, preferably 2 to 10 parts of the low molecular weight acid.

The sulfur-bearing acids, or their salts, may also be formed directly in the grease by incorporating the nitrile and the mercaptan and hydrolyzing with sodium hydroxide or other appropriate strong base. In this case, ammonia is evolved while the sulfur-bearing salt (or soap), the conventional soap, and the low molecular weight salt are all being formed in situ.

As previously noted, the low molecular weight acid may be a saturated acid such as acetic or propionic acid, an unsaturated acid such as acrylic acid, or a cyclic or heterocyclic acid such as furoic acid. Alternatively, acidogenic ingredients may be used which will result in the production of such acids. For example, the appropriate aldehydes may be used which are subjected to the Cannizzaro reaction.

The various acids are preferably mixed together as a solution or slurry in at least a part of the lubricating oil, usually a mineral base lubricating oil. The quantity of oil used initially during soap and salt formation may be varied rather widely. Preferably, it is of about the same order as the added acids and should usually be less than the total quantity of oil used in the final grease so that a further quantity of oil may be worked into the soap-salt composition later. The acidic ingredients are then saponified or co-neutralized in the presence of the oil, and the remainder of the oil desired in the finished product is added after neutralization is substantially complete. Thereafter, the whole mixture is cooked in the usual manner, for example to a temperature of 300 to 500° F. or more. When cooking is completed, other conventional ingredients such as an antioxidant, e. g., phenyl alpha naphthylamine, metal deactivators, tackiness agents, load bearing compounds, and the like, may be added. The product may be cooled rapidly by using a continuous cooler or may be allowed to stand for cooling in pans in a conventional manner. Preferably, the grease is stirred or homogenized after cooling and it is then ready for packaging.

It will thus be appreciated that a distinct feature of the present invention is the use of sulfur-bearing salts which are preferably derived from branched chain aliphatic acids having a total of about 10 to about 20 carbon atoms per molecule and containing at least one atom of sulfur. A greater sulfur content is permissible and may be highly desirable where the lubricating grease is expected to perform extreme pressure functions. In such cases, sulfurized mercaptans or acids may

be used. In other cases, an acid containing one sulfur atom in the chain is quite satisfactory. The high molecular weight Oxo-acids, i. e., those of 8 or more carbon atoms which contain branching in the hydrocarbon chain or the acids or salts derived from such Oxo-alcohols by reaction with acrylonitrile similar to that of the mercaptans to form ether linkages rather than thio linkages, have the branched chain characteristics desired and are quite useful.

These sulfur-bearing or oxygen-bearing acids may be prepared also by reacting the C_8 or higher Oxo alcohols (or other branched chain alcohols) or mercaptans, with lactones, such as β-propiolactone. They may be formed also by reacting salts of mercaptans or alkoxides with halo-nitriles or halo-acids, e. g., chloroacetonitrile, β-chloropropionic acids, etc.

The invention may be more fully understood by reference to the following specific examples:

Example I

As a preliminary step to the preparation of a grease according to the present invention, the following ingredients were combined and subjected to the Cannizzaro reaction to form a sodium furoate:

10.00 parts furfural
3.18 parts NaOH
30.00 parts mineral lubricating oil, 55 S. U. S. viscosity at 210° F.

Proportions are given by weight.

After the Cannizzaro reaction was substantially completed, the following ingredients were added:

10.00 parts fatty acids (hydrogenated fish oil acids of predominately 18 to 20 carbon atoms)
5.00 parts C_{15} branched chain sulfur-bearing acid (having the formula shown in Example II)
2.00 parts NaOH
1.00 part phenyl alpha naphthylamine
38.82 parts mineral lubricating oil as above

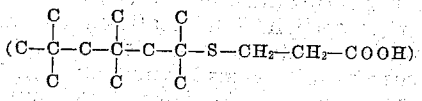
After the Cannizzaro reaction was carried out to completion, the resulting alcohol was partly evaporated during neutralization of the two high molecular weight acids. The temperature of the mass was then raised while adding about half of the second quantity of mineral oil. At 300° F., the remainder of the oil was added and the mass was further heated, with continued stirring, to a temperature of 450° F. During this period, most of the furfuryl alcohol evaporated although a small amount probably polymerized in the grease. After heating was completed, the antioxidant (phenyl alpha naphthylamine) was added and thereafter the grease was allowed to cool. After cooling, the composition was homogenized to a smooth uniform product, by stirring, in the grease kettle. The product had the following properties:

Appearance—Excellent, smooth homogeneous grease
Unworked penetration—220 mm./10
Worked penetration (60 strokes)—230 mm./10
Worked penetration (100,000 strokes fine hole worker plate)—273 mm./10
Dropping point, ° F.—500+

Example II

Another composition was prepared of the following ingredients:

15.0% sulfur-bearing high molecular weight acid



6.0% furoic acid [1]
5.2% NaOH
1.0% phenyl alpha naphthylamine
72.8% mineral lubricating oil, 55 S. U. S. viscosity at 210° F.

[1] May be formed from furfural by Cannizzaro reaction.

The product of Example II was a very soft semi-fluid grease notwithstanding the relatively high content of sodium salt of a C_{15} acid. Apparently, the sulfur-bearing acid alone is not an adequate grease thickening ingredient and the composition requires at least a modest proportion of the fatty acids of the usual type to form a firm and stable grease. This is true whether the low molecular weight salts are used or not. Without the latter, larger quantities of fatty acid soaps usually are needed.

The low molecular weight acids should have a molecular weight in the acid radical of not more than about 160 and preferably not more than about 120. The best compositions apparently are those which contain all three acid salt or soap ingredients, namely, the conventional long chain fatty acid soap, the salt of low molecular weight, and the soap of the branched chain sulfur- or oxygen-bearing aliphatic acid of 10 to 20 carbon atoms. While the alkali metal soaps and salts of these acids are preferred, and specifically the soda or lithium compounds, other metals may be used and a mixture of the soaps of one metal, salts of another metal, and the sulfur-bearing soap of either, both or a third and different metal may be combined. Ordinarily, and preferably as a matter of convenience, the soaps and salts are formed in situ by reacting a single metal base therewith, and they are therefore most easily formed simultaneously. Simultaneous neutralization is not preferred, however, when the Cannizzaro reaction is employed, in which case the low molecular weight salt should, of course, be prepared first. However, for economy, the sodium salt or a concentrated aqueous solution may be employed with no degradation in the quality of the product.

While, in general, the sulfur-bearing acid has a preferred molecular content of about 15 carbon atoms, suitable acids may be prepared by reacting aliphatic unsaturated nitriles, or the like, of 3 to about 10 carbon atoms with branched chain aliphatic mercaptans of 8 to about 18 carbon atoms, the reactants being so selected that the resulting acid will have not more than 20 nor less than 10 carbon atoms, as previously stated.

The usual or conventional modifiers or additives such as antioxidants, metal deactivators, tackiness or stringiness agents, extreme pressure compounds, and the like, may be employed, as in well understood by those skilled in the art. The lubricating oil is preferably a mineral base oil, but may be a synthetic ester or polyglycol oil in many cases. Where the Cannizzaro reaction is used, the oil which is present during the reaction should be a hydrocarbon or substantially hydrocarbon product since esters are hydrolyzed under the conditions of the Cannizzaro reaction. In such cases, esters may be added after the soap and salt forming reactions are substantially completed.

What is claimed is:

1. A lubricating grease composition comprising a major proportion of lubricating oil thickened to a grease consistency with a combination of a metal soap of fatty acids having between 12 and 24 carbon atoms, a metal salt of an organic acid having a molecular weight below about 160, and a metal soap of a branched chain aliphatic carboxylic acid having between about 10 and about 20 carbon atoms, of which at least 2 carbon atoms are tertiary and having at least one thioether linkage in the chain.

2. A lubricating grease composition comprising a major proportion of lubricating oil and a minor proportion of a thickener, said thickener consisting essentially of an alkali metal soap of fatty acid having between 12 and 24 carbon atoms, an alkali metal salt of an organic acid of molecular weight below about 160, and an alkali metal salt of a branched chain aliphatic carboxylic acid having between 10 and 20 carbon atoms, of which at least 2 carbon atoms are tertiary and having at least one thioether linkage in the chain.

3. Composition as in claim 2 wherein the alkali metal is sodium.

4. Composition as in claim 2 wherein the alkali metal is lithium.

5. Composition as in claim 1 wherein the metal is an alkaline earth metal.

6. Composition as in claim 1 wherein the acid of molecular weight below 160 is a heterocyclic acid.

7. Composition as in claim 1 wherein the acid of molecular weight below 160 is furoic acid.

8. A lubricating grease composition comprising a major proportion of mineral base lubricating oil thickened to a grease consistency with a thickener consisting essentially of 2 to 20% by weight, based on the total composition, of a metal soap of fatty acid, said acid having a molecular chain length within the range of 12 to 24 carbon atoms, 1 to 15% of a metal salt of organic acid which has a molecular weight below about 160, and 1 to 15% of metal soap of branched chain aliphatic carboxylic acid having between 10 and 20 carbon atoms and one thioether linkage in the chain.

9. Composition as in claim 8 wherein the metals are alkali metals.

10. Composition as in claim 8 wherein all of the metals are the same metal.

11. Composition as in claim 8 wherein the metals are alkaline earth metals.

12. Composition as in claim 8 wherein all the metals are sodium.

13. Composition as in claim 8 wherein all the metals are lithium.

14. The process of preparing a lubricating grease composition which comprises simultaneously forming a soap, a low molecular weight salt, and a salt of high molecular weight sulfur bearing aliphatic acid, by reacting a combination of fatty acid, an aldehyde having a low molecular weight radical corresponding to said first mentioned salt, and a branched chain aliphatic carboxylic acid having at least one thioether linkage in the chain, with a saponifying compound of metal base to convert said fatty acid to soap, convert said aldehyde to acid and alcohol and thence said last mentioned acid to salt, and convert said aliphatic carboxylic acid to salt in the presence of a lubricating oil, thereby thickening said oil to grease consistency.

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