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COMPLEX BASIC ALUMINUM SOAP GREASES

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This invention pertains to a grease composition having the combined characteristics of high water resistance and high melting point, which characteristics are obtained in a grease composition containing a complex basic aluminum soap, e. g. basic aluminum benzoate stearate, as the primary thickening agent.

This application is a continuation-in-part of Hotten et al. application Serial No. 112,584, filed August 26, 1949 (and now abandoned).

In the field of lubrication, it has been the object of a long-time search to find a lubricating composition which would have a high melting point and at the same time be resistant to the effects of water. In the past, high melting point greases have been obtained by using, for example, sodium soaps as thickeners in grease compositions, which sodium soap greases have not been very resistant to emulsification in water; and high water-resistant grease compositions have been obtained by using, for example, calcium soap greases as thickening agents, which calcium soap greases have not had sufficiently high melting points.

If a soda base grease (which imparts high melting point to a grease composition) and a lime base grease (which imparts high water resistance to a grease composition) are blended together, the desired characteristics of high water resistance and high melting point are not obtained. The ratio of lime soap to soda soap required to obtain water resistance is so high that the melting point of the mixed grease is greatly reduced.

Some degree of satisfaction has been obtained in the preparation of a grease containing a lithium soap as the thickening agent; however, such products are usually expensive for many of the uses, and also lithium soap greases usually have less resistance to oxidation than is required in certain phases of lubrication.

Various other grease thickeners which have been heretofore proposed are disadvantageous in that they may improve one property of a grease at the expense of other desirable properties or are insufficiently effective to be commercially satisfactory or are too expensive. For example, some complex soaps are excessively fibrous when cold and quite syneretic when hot, both properties leading to poor retention in bearings. Others suffer from hardening on aging and/or deteriorate in the presence of water. Still others become gelatinous in bearing tests.

Industry has long realized that it would be highly efficient and highly acceptable to obtain one grease composition embodying the combined characteristics of high melting point and low water emulsibility. The solution to this problem has been attempted by numerous investigators in the lubrication art. For example, the grease composition containing the lithium soap as the thickening agent as noted hereinabove is a step in this direction, but the disadvantages of expense, oxidation instability, and excessive changes in texture and consistency on working and on heating in numerous cases outweigh the advantages.

It is an extreme advantage to be able to use one grease composition which has the combined characteristics of high melting point and high resistance to emulsification in water. Heretofore, it has been a problem in the lubrication industry to prepare lubricants which are particularly suitable to a certain specific job. For example, high melting point lubricants, e. g., a high dropping point grease, are used for lubricating automotive wheel bearings, steel mill equipment, high speed motors, universal joints, rocker arms of airplane motors, etc.; while highly water-resistant lubricants (e. g., a grease characterized by low solubility and low emulsibility in water) are used for lubricating water pumps, automotive motor chassis, valves, etc.

Now, by the use of the grease composition of this invention, it is possible to obtain one grease which has the combined characteristics of high water resistance and high melting point, as well as oxidation resistance. Such a grease has a wide variety of applications, particularly where both water and high temperatures are encountered, such as in steel mill rollers and transfer table bearings, paper mill roll bearings, automotive wheel bearings under winter and flood conditions including use in amphibious military vehicles, high temperature cannery equipment, exposed control surface bearings for aircraft, etc.

It is therefore an object of this invention to provide new aluminum complex soaps which are especially suitable as thickening agents to produce grease compositions having high resistance to water emulsibility and high melting points.

In accordance with this invention, it has been found that a high melting, high water-resistant grease may be obtained by incorporating in a lubricating oil a complex basic aluminum soap.

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 dissimilar anions substantially organic in character (i. e., substantially hydrocarbonaceous in character), the aluminum di-soaps of said organo anions being water-insoluble and preferably different in the extent of their individual solubilities in lubricating oils.

The organo anions (or anions substantially hydrocarbonaceous in character) of the aluminum soaps of this invention are generally oleophilic (i. e., anions derived from acids which are oil-soluble); however, one organo anion has a greater solubility in lubricating oil than another organo anion. For purposes of simplification of the discussion of the characteristics of the organo anions of the complex basic aluminum soap, 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 basic complex aluminum soaps are prepared from acids substantially organic in character, at least one of which is relatively oil-soluble and another of which is relatively oil-insoluble. That is, the organo-acids of the relatively oleophilic anions are relatively oil-soluble, while the organo-acids of the relatively oleophobic anions are relatively oil-insoluble, i. e., less oil soluble as compared to the oleophilic organo-acids.

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 di-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 oleophilic anions) are soluble

in the base lubricating oil 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 the base lubricating oil. On the other hand, the aluminum soaps of the less soluble organo-anions (i. e., the relatively oleophobic anions) are soluble in the base 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 the aluminum soap containing the oleophobic anions will dissolve in the base lubricating oil to form a true solution. For example, in the aluminum benzoate stearate, the aluminum di-soap of the benzoate anion (i e., aluminum di-benzoate) is soluble in lubricating oil in an amount less than 1% at 400° F., while the aluminum di-soap of the stearate anion (i. e., aluminum di-stearate) is soluble in lubricating oil in an amount of at least 5% at 400° F.

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.

Suitable relatively oleophilic anions are anions of aliphatic (saturated and unsaturated), aromatic, aralkyl, and cycloaliphatic monocarboxylic acids, and organo-substituted acids of sulfur and/or phosphorus. The acids must be sufficiently hydrocarbonaceous in character to impart the desired oil solubility, depending upon the base oil employed, as noted hereinabove. Thus, the aliphatic (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 a total of about 16 carbon atoms. The relatively oleophilic anion may also be derived from phenols; that is, the oleophilic anion may be an alkyl phenol containing at least 4 carbon atoms in the alkyl group, preferably 16 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 acid anions 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.

Relatively oleophilic anions can be derived from dibasic acids, provided that the aluminum di-soaps of such anions have solubility characteristics as defined hereinabove. Such dibasic acids have highly branched hydrocarbonaceous groups. For example, when one of the methylene groups of adipic acid has an aliphatic group containing 16 carbon atoms attached thereto, the resulting anion is a relatively oleophilic anion for the purpose of this invention.

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, hexyl benzoic acid, octyl benzoic acid, dodecyl benzoic acid, phenyl butyric acid, phenyl hexanoic acid, phenyl decanoic acid, cetyl benzene sulfonic acid, a di-dodecyl benzene sulfonic acid, (e. g., a di-polypropylene benzene sulfonic acid), an alkane phosphonic acid having at least 24 carbon atoms in the alkane group, cetyl thiophosphoric acid, naphthenic acids, branched dibasic acids containing radicals of at least 14 carbons substituted on a methylene group of the dibasic acids (e. g., beta-tetradecyl adipic acid), etc. Of these, stearic acid, hydroxy stearic acids, naphthenic acids of molecular weight above about 250, and alkyl benzene sulfonic acids having at least 20 carbon atoms in the alkyl substituents are preferred.

The relatively oleophobic anions are substantially hydrocarbon in structure and may be selected from anions of aliphatic (saturated and unsaturated), aromatic, aralkyl, alkaryl and cycloaliphatic monocarboxylic acids. For the desired properties, aliphatic monocarboxylic acids having from 4 to 7 carbon atoms are employed. When aralkyl and alkaryl monocarboxylic acids are used, the alkyl groups contain no more than 3 carbon atoms in addition to the carboxyl carbon. Thus, alkaryl and aralkyl monocarboxylic acids contain a total of no more than 10 carbon atoms, preferably a total of 8 carbon atoms. Acids having two carboxyl groups can also be used; however, the monocarboxylic acids are especially preferred.

When the carboxylic acid contains two 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 oleophobic. The greater the number of carbon atoms in the dicarboxylic acid anion the less preferable is branching of the hydrocarbon portion; i. e., the higher the molecular weight the more the hydrocarbon portion should be confined to a straight chain between the carboxyl groups. However, side chains such as alkyl groups on the alkylene portion connecting the carboxyl groups are not objectionable provided the resulting anion is relatively oleophobic, as defined hereinabove. For example, when suberic or azelaic acids have alkyl substituents containing 3 or 4 carbon atoms, the aluminum di-soaps of such substituted suberic or azelaic acids are soluble in oil in amounts less than 1% at 400° F. Thus such anions are still relatively oleophobic for the purposes of this invention. On the other hand, if the azelaic or suberic acids should contain aliphatic substituents having 8 or more carbon atoms, the resulting anions would be too oil-soluble and not suitable as the relatively oleophobic anion in the complex aluminum soaps for the grease compositions according to the present invention.

When complex aluminum soaps are formed with organo anions which are not relatively oleophilic and relatively oleophobic as defined hereinabove, the resulting soaps do not yield the water-resistant, high-temperature greases of the present invention. Thus, a complex aluminum soap may be formed with an anion, the aluminum di-soap of which is water-soluble, in place of the oil-soluble relatively oleophobic anion of the present invention. However, when such a soap is dispersed in oil by devious means to form a grease, the grease lacks high melting point and resistance to emulsification at high temperatures, which properties are characteristic of the greases of the present invention. For example, aluminum nitrate was added to an aqueous solution containing a mixture of potassium adipate and potassium stearate, and the aluminum soaps separated therefrom. When this soap mixture was incorporated into a petroleum oil, the resulting grease had the characteristics of an ordinary aluminum stearate grease, not in the least similar to the water-resistant, high-temperature greases of the present invention.

Suitable oleophobic anions are derived from: benzoic acid, methyl benzoic acid, ethyl benzoic acid, toluic acid, phenyl acetic acid, phenyl propionic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, salicylic carboxymethylcellulose, polyacrylic aid, etc. Of these, the benzoic, azelaic and toluic acids are preferred.

Because of the increased effectiveness in obtaining a high melting, high water-resistant grease, it is preferred that the oleophilic anion of the aluminum soap of this invention be an anion of an aliphatic carboxylic acid (e. g., stearic acid), and that the oleophobic anion be an anion of an aromatic carboxylic acid (e. g., benzoic acid).

It is essential to the success of this invention that the more oil-soluble organo-anion (i. e., the relatively oleophilic group) and the less oil-soluble organo-anion (i. e., the relatively oleophobic group) be present in such pro-

portions to each other that the complex aluminum soap of this invention will have the desired dispersibility in the base oil to bring about the formation of a grease structure having high-melting, high water-resistant characteristics. The ratio of oleophobic to oleophilic anions in the average molecule of the soap has a preferred value from about 0.3 to 3; however, the ratio of oleophobic to oleophilic anions may have a value ranging from about 0.2 to about 5.

The ratio of oleophobic anion to the oleophilic anion (on an average molecule basis) can be altered so that the desired grease structure may be obtained in lubricating oils of varying solvency characteristics. That is, it is generally desirable when using a lubricating oil of high solvent capacity to employ a basic aluminum soap which is less oil-soluble than the basic aluminum soap preferred when the lubricating oil is of a low solvent capacity. For example, when using a petroleum lubricating oil which is almost devoid of aromatic hydrocarbons, it is usually desirable to use a basic aluminum soap of this invention wherein the oleophilic anion is considerably more oil-soluble than the oleophobic anion. On the other hand, when using a petroleum lubricating oil having considerable quantities of aromatic hydrocarbons present, it is desirable to use a basic aluminum soap of this invention wherein the oleophilic anion is not too highly oil-soluble. Stated in another manner, greases prepared from the aluminum soaps of this invention normally become more gelatinous as the aniline point of the oil and as the oleophobic-oleophilic anion ratio are lowered. Conversely, greases become more granular as these variables are raised.

A number of free hydroxyl groups present in the basic aluminum soap of this invention may vary from 1.0 to 1.5 hydroxyl groups for each aluminum atom in the soap. When there is substantially less than one free hydroxyl group for each aluminum atom in the soap, the resulting aluminum soap has a higher degree of acidity than that which is normally desired in greases. On the other hand, when there are as many as two hydroxyl groups per aluminum atom in the soap, the grease prepared therefrom is somewhat granular. Thus it is preferred that the basic aluminum soaps of this invention contain from about 1 to about 1.5 hydroxyl groups per aluminum cation.

Although aluminum has a valence of +3, it is not meant herein to limit the complex basic aluminum soap of this invention to one containing only three specific anions. In the over-all average, the three valence bonds may be directed to more than three specific anions. Thus, the average molecule in the soap may contain a plurality of relatively oleophilic anions or a plurality of oleophobic anions. For example, a complex basic aluminum soap having the oleophilic portion of the average molecule derived from a mixture of acids, such as stearic acid and hydroxy-stearic acid, is sometimes preferred.

Although it is preferred to use oleophobic anions derived from carboxylic acids because of the improved texture of the greases prepared therefrom, the relatively oleophobic anion may on the average be partly an anion of an inorganic acid of phosphorus, e. g., phosphoric acid, an inorganic acid of boron, e. g., boric acid, or in some cases an anion of an inorganic acid of silicon, e. g., silicic acid. For example, the oleophobic anion portion of the average molecule may contain, in part, a phosphate ($-PO_4$) anion. Furthermore, the relatively oleophobic anion may be derived from phenol; that is, the relatively oleophobic anion may be an alkyl phenol containing no more than 3 carbon atoms in the alkyl group.

Examples of complex basic aluminum soaps of this invention are: aluminum benzoate stearate, aluminum benzoate oleate, aluminum benzoate 12-hydroxy stearate, aluminum toluate stearate, aluminum benzoate naphthenate, aluminum benozate hydrogenated rosin, aluminum benzoate sulfonate, aluminum azelate stearate, aluminum phosphate benzoate stearate, aluminum benzoate hydroxy stearate, etc. Of these aluminum azelate stearate, aluminum toluate stearate, and aluminum benzoate stearate are preferred, the last being especially preferred.

The aluminum soaps of this invention can be prepared according to methods involving co-precipitation. For example, aqueous solutions of mixtures of the water-soluble soaps (e. g., sodium soaps) in the desired proportion of relatively oleophilic and relatively oleophobic anions are admixed with an aqueous solution of an aluminum salt (e. g., aluminum sulfate). The resulting precipitate of the basic aluminum complex soap is then preferably purified to remove the salts such as sodium sulfate. Basic aluminum complex soaps yielding greases of high water resistance, high melting point and excellent chemical and physical stability may also be prepared in situ according to the method described in Jones Patent No. 2,469,041, wherein a fatty acid (e. g., stearic acid), is added to a mineral oil solution of an aluminum alcoholate (e. g., aluminum butoxide), to form aluminum stearate.

While the true basic aluminum complex soaps of the present invention produce greases having high water resistance and high melting points as well as excellent texture, physical mixtures of aluminum soaps from the relatively oleophilic acids, e. g., stearic acid, with aluminum soaps of the relatively oleophobic acids, e. g., benzoic acid, do not yield satisfactory greases, even though such mixture of soaps is exposed to prolonged heating.

Suitable base oils include a wide variety of lubricating oils such as naphthenic base, paraffin base, and mixed base mineral oils, other hydrocarbon lubricants, e. g., lubricating oil derived from coal products and synthetic oils, e. g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers, dicarboxylic acid esters and liquid esters of acids of phosphorus. Synthetic oils of the alkylene-oxide type polymer which may be used include those exemplified by the alkylene oxide polymers (e. g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing alkylene oxides, e. g., propylene oxide, in the presence of water or alcohols, e. g., ethyl alcohol and esters of alkylene oxide type polymers, e. g., acetylated propylene oxide polymers prepared by acetylating propylene oxide polymers containing hydroxyl groups.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, (such as those described in Moser Patents 2,124,628 and 2,133,734), etc., with alcohol such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of dicarboxylic acid ester synthetic oils include di-butyl adipate, di-hexyl adipate, di-2-ethylhexyl sebacate, etc.

Synthetic oils of the type of liquid esters of acids of phosphorus include the esters of phosphoric acid, e. g., tricresyl phosphate, the esters of phosphonic acid, e. g., di-ethyl ester of decane phosphonic acid, etc. Other suitable phosphonic acid esters may be obtained by the process described in Jensen and Clayton application Serial No. 202,396, filed December 22, 1950, now Patent No. 2,683,168 which is a continuation-in-part of application Serial No. 86,856, filed April 11, 1949 (and now abandoned), according to which process hydrocarbons containing at least one aliphatic carbon atom are exposed simultaneously to the action of phosphorus trichloride and an oxygen-containing gas to produce hydrocarbon phosphonyl chlorides which may be converted to the desired esters, such as by reacting the alkyl phosphonyl chlorides with hydroxyl-containing compounds such as phenols and aliphatic alcohols or with olefin oxides such as propylene oxide or the like.

The complex basic soaps of this invention are admixed

with lubricating oils to thicken the oil to grease consistency, that is, in amounts sufficient to form a satisfactory grease. Such amounts as about 3% to 50% (based on the finished composition) may be used. However, about 10% to about 16% are the preferred amounts.

The examples presented hereinbelow will further illustrate the preparation of the complex basic aluminum soaps and the grease compositions of this invention.

Example 1.—The preparation of aluminum azelate stearate

A mixture of 13.5 parts by weight of commercial stearic acid (approximately 60% stearic acid and the remainder mainly palmitic acid), 10 parts by weight of azelaic acid and 9 parts by weight of sodium hydroxide was dissolved in 400 parts by weight of water at approximately 180° F. This solution was slowly added, with stirring, to a solution of 24.9 parts by weight of aluminum sulfate octadecahydrate in 300 parts by weight of water at this same temperature. The resulting reaction mixture was filtered. The white precipitate which was formed during the reaction was washed with water by adding the white precipitate to a large amount of water and then stirring vigorously. The precipitate was washed in this manner three separate times until only a faint positive sulfate ion test was attained in the filtrate from the third wash. The resulting mixed soap was then dried at a temperature ranging from 210° F. to 250° F., was powdered and passed through a No. 60 mesh sieve.

Example 2.—Preparation of aluminum toluate stearate

A mixture of 28.6 parts by weight of toluic acid containing a 2:1 mixture of the meta and para isomers, 27 parts by weight of commercial stearic acid, and 18 parts by weight of sodium hydroxide was dissolved in 400 parts by weight of water at about 180° F. This solution was slowly added, with stirring to 50 parts by weight of aluminum sulfate hydrate in 300 parts by weight of water at the same temperature. The resulting complex polyvalent metal soap was filtered, washed and dried as described in Example 1. On ashing, the soap left 13.9% Al_2O_3 (theoretical for basic aluminum toluate stearate is 13.6%).

Example 3.—Preparation of aluminum benzoate stearate

A mixture of 12.2 parts by weight of benzoic acid, 27.1 parts by weight of commercial stearic acid and 16.8 parts by weight of potassium hydroxide was dissolved in about 500 parts by weight of water at 150° F., forming a clear solution. To this solution was added 33.3 parts by weight of aluminum sulfate octadecahydrate dissolved in about 300 parts by weight of water. The resulting aluminum benzoate stearate was obtained by filtering, washing and drying the precipitate as above in Example 1. On ashing, the soap left 11.6% Al_2O_3 (theoretical for $AlC_{24}H_{39}O_5$=11.4%).

Example 4.—Preparation of aluminum benzoate 12-hydroxy stearate

A mixture of 28.8 parts by weight of sodium benzoate, 48 parts by weight of 12-hydroxy stearic acid and 13.6 parts by weight of sodium hydroxide was dissolved in about 500 parts by weight of water at 150° F., forming a clear solution. To this solution was added 68 parts by weight of aluminum nitrate dissolved in about 300 parts by weight of water. The resulting aluminum benzoate hydroxy stearate was obtained by filtering, washing and drying the precipitate as shown above in Example 1.

Example 5.—Preparation of aluminum benzoate naphthenate

A mixture of 14.4 parts by weight of sodium benzoate, 31 parts by weight of naphthenic acid (molecular weight=280; 90% saponifiables) and 8 parts by weight of sodium hydroxide was dissolved in about 500 parts by weight of water at 150° F., forming a clear solution. To this solution was added 37.5 parts by weight of aluminum nitrate in about 300 parts by weight of water. The resulting aluminum benzoate naphthenate was obtained by filtering, washing and drying the precipitate as shown above in Example 1.

Example 6.—Preparation of aluminum benzoate alkyl benzene sulfonate

A mixture of 14.4 parts by weight of sodium benzoate, 74.6 parts by weight of sodium alkyl benzene sulfonate (70% of which was a sodium didodecyl benzene) and 4.0 parts by weight of sodium hydroxide was dissolved in about 500 parts by weight of water at 150° F., forming a clear solution. To this solution was added 33.3 parts by weight of aluminum nitrate dissolved in about 300 parts by weight of water. The resulting aluminum benzoate alkyl benzene sulfonate was obtained by filtering, washing and drying the precipitate as shown above in Example 1. The resulting soap contained some oil in the form of unsulfonated alkyl benzenes, which caused the soap to be somewhat gummy. Because of this gumminess, it was necessary, when dispersing the soap in oil to form a grease, to use petroleum ether in assisting the dispersion. The petroleum ether was boiled off during the preparation of the grease.

Example 7.—Preparation of aluminum benzoate phosphate stearate

A mixture of 8.2 parts by weight of benzoic acid, 18.0 parts by weight of commercial stearic acid, 8.4 parts by weight of trisodium phosphate, and 13 parts by weight of potassium hydroxide was dissolved in about 500 parts by weight of water at 150° F., forming a clear solution. To this solution was added 40 parts by weight of aluminum nitrate dissolved in about 300 parts by weight of water. The resulting aluminum benzoate phosphate stearate was obtained by filtering, washing and drying the precipitate as above in Example 1.

Greases were prepared from the above complex polyvalent metal soaps as follows:

Example 8.—Preparation of a grease containing aluminum azelate stearate

A mixture of 42.5 parts by weight of a California solvent refined paraffinic base mineral oil having a viscosity of 464 SSU at 100° F., 7.5 parts by weight of aluminum azelate stearate of above Example 1, was heated with constant stirring to 430° F. The mixture stood until it had cooled to room temperature. It was then milled through a 200 mesh screen. The product was a soft unctuous grease which changed little in consistency or texture on heating to 300° F.

Example 9.—Preparation of aluminum toluate stearate grease

A mixture of 5 parts by weight of aluminum toluate stearate of above Example 2 and 45 parts by weight of a California solvent refined paraffinic base oil having a viscosity of 541 SSU at 100° F. was stirred in a beaker. The temperature was raised to 440° F. The grease was cooled to room temperature and was then milled by being pressed through a 200 mesh screen. The grease was soft and unctuous.

Example 10.—Preparation of aluminum benzoate stearate grease

A mixture of 12 parts by weight of aluminum benzoate stearate of above Example 3 and 108 parts by weight of a California solvent refined paraffinic base oil having a viscosity of 485 SSU at 100° F. was heated in a beaker. The mixture was heated to 450° F., was then allowed to stand until the temperature had reached that of room temperature and was milled by being pressed through a 200 mesh screen. The final grease was a light brown, translucent, unctuous soft grease having an ASTM dropping point of 400+° F. When a 5-gram sample

was immersed in boiling water for 1 hour, it remained fully intact without any disintegration.

Example 11.—Preparation of aluminum benzoate 12-hydroxy stearate grease

A mixture of 69 grams of the aluminum benzoate 12-hydroxy stearate of Example 4 and 424 parts by weight of a California solvent refined paraffinic base oil having a viscosity of 1014 SSU at 100° F. was heated in a beaker. The mixture was heated to 480° F., then allowed to stand until the temperature had reached that of room temperature, then milled by being pressed through a 200 mesh screen. The grease was soft and unctuous and had an ASTM dropping point of greater than 400° F.

Example 12.—Preparation of aluminum benzoate naphthenate grease

A mixture of 10 parts by weight of the aluminum benzoate naphthenate of Example 5 and 90 parts by weight of a California solvent refined paraffinic base oil having a viscosity of 464 SSU at 100° F. was heated in a beaker to a maximum temperature of 480° F., was then allowed to stand until the temperature had reached that of room temperature, was then milled by being pressed through a 200 mesh screen. The resulting grease was soft and unctuous and had an ASTM dropping point of greater than 400° F.

Example 13.—Preparation of aluminum benzoate alkyl benzene sulfonate grease

A mixture of 20 parts by weight of the aluminum benzoate alkyl benzene sulfonate of Example 6 and 18 parts by weight of a California solvent refined paraffinic base oil having a viscosity of 485 SSU at 100° F. was heated in a beaker to a maximum temperature of 350° F. The mixture was then allowed to stand until the temperature had reached that of room temperature, was then milled by being pressed through a 200 mesh screen. The resulting grease was very smooth and had an ASTM dropping point of greater than 400° F.

Example 14.—Preparation of aluminum benzoate phosphate stearate grease

A mixture of 6 parts by weight of the aluminum benzoate phosphate stearate of Example 7 and 34 parts by weight of a California solvent refined paraffinic base oil having a viscosity of 485 SSU at 100° F. was heated in a beaker to a maximum temperature of 440° F. The mixture was then allowed to stand until the temperature had reached that of room temperature and then milled by being pressed through a 200 mesh screen. The resulting grease was very smooth.

In the preparation of the greases the maximum heating temperature may be from about 20° to 100° F. above the temperature at which the soap begins to thicken the oil noticeably. Also, the method of cooling the grease composition may be varied; that is, the hot grease may be permitted to cool with or without stirring, or the hot grease may be drawn into shallow pans for more rapid cooling.

As noted hereinabove, the greases prepared in accordance with the methods of this invention have a remarkable resistance toward change over a wide temperature range. For example, the texture and the consistency of the aluminum benzoate stearate grease of above Example 10 vary only slightly between room temperature and 400° F. In determining quantitatively the homogeneity of texture and the phase changes occurring on heating the greases, the following method of analysis was devised:

A sample of grease (150 grams) is placed in a Buechner funnel containing an ordinary piece of filter paper. The Buechner funnel is inserted in a suction flask, heated in an oven at the desired temperature for 2 hours, then filtered with the aid of suction for 5 hours at the desired temperature. The weight of the oil sucked from the grease is recorded. A graphical plot of oil loss versus temperature then gives a picture of the soap-oil relationship over the entire useful range of the grease. Figure I presents curves showing the stability of the grease composition of this invention over a wide range of temperature as compared to presently used grease compositions. The greases were prepared by compounding the soap in a California solvent refined paraffinic base mineral lubricating oil blend at a temperature about 400° F. The resulting grease composition was then cooled to room temperature and milled.

The test results recorded in the curves of Figure I present a comparison of the grease compositions in such a manner that one can readily see which grease has the greatest stability to temperature. A lithium stearate grease (composed of 12% lithium stearate in a California solvent refined oil having a viscosity of 485 SSU at 100° F.) rapidly lost oil as the temperature was raised to 300° F. at which point there was a sudden decrease in oil loss due to gelation, with a minimum loss at about 350° F. As the temperature was raised further, the lithium stearate dissolved in the oil and both the oil and the soap passed through the filter paper as a solution.

An aluminum di-stearate grease (composed of 12% aluminum di-stearate in a California solvent refined paraffinic base oil having a viscosity of 485 SSU at 100° F.) began to gel at about 180° F. and to form a solution at about 200° F.

The aluminum benzoate stearate grease of Example 10 above, which is an example of the grease composition of this invention, was notably free from appreciable oil separation or phase change over the whole range of temperatures from 120° F. to 372° F.

It is extremely important that there be no excess of oil separation, gelation or soap dissolution of a grease composition as the temperature is increased because the efficiency of the grease is reduced thereby. A highly desirable feature of the grease composition of this invention is the remarkable ability of this grease composition to maintain only one phase during the normal practical temperature range.

The above comparison of the lithium stearate grease, the aluminum di-stearate grease and the aluminum benzoate stearate grease shows the remarkable stability and resistance of the basic aluminum complex soaps of this invention to changes over a wide range of temperatures.

The basic aluminum complex soap greases of the present invention have advantages over other high-melting, water-resistant greases in chemical as well as physical stability. As compared to presently used greases, the greases of the present invention have other specific advantages, including finer texture, good resistance toward oxidation, reduced tendency to "bleed" (i. e., the amount of oil separating from the grease is reduced), etc.

Although the grease composition of the present invention consists essentially of a lubricating oil and a complex basic aluminum soap containing an oleophilic anion group and an oleophobic anion group, other additives may be included in the grease composition, such as dyes, other grease modifiers, fillers, oxidation inhibitors, anti-corrodants (e. g., nonylamine), antithixotropic agents, e. g., aluminum and calcium alkyl benzene sulfonates, antigelators, stringiness agents, e. g., polybutenes, barium soaps and sodium soaps, e. g., sodium oleate, peptizing agents, etc.

While the present greases have good oxidation resistance, this property may be readily improved by the addition of various antioxidants such as di-alkyl selenides, e. g., di-lauryl selenide; di-thiocarbamates, e. g., zinc di-butyl di-thiocarbamate; thiazines, e. g., phenothiazine, etc. For example, when 0.5% of phenothiazine is added to a grease composition containing 11.5% of aluminum benzoate stearate, the oxygen pressure drop occurring in a Norman-Hoffmann oxidation test (Spec. An–G–5*a*) at 210° F. after 50 hours was 1.8%, while the same grease

composition without the phenothiazine had an oxygen pressure drop of 3.7%. A lithium stearate grease, on the other hand (containing 11% lithium stearate), had an oxygen pressure drop of 65% at 50 hours for the same test.

In addition to the base oils noted hereinabove, other synthetic base oils include oils derivable from silicon compounds, such as polysiloxane, e. g., phenyl methyl polysiloxane, and silicate esters, e. g., tetracresyl silicate.

Exceptionally high-melting, water-resistant greases are obtained by incorporating the basic complex aluminum soaps of this invention in polysiloxane synthetic base oils, such as dimethyl silicone, diethyl silicone, diethyl silicone trimer, and preferably the phenyl alkyl polysiloxanes described in U. S. Patent 2,410,346. Greases prepared according to the present invention by using polysiloxane synthetic base oil have the property of being soft and unctuous and resistant to oxidation at such high temperatures as approximately 500° F. The following Example 15 illustrates the preparation and the properties of such polysiloxane synthetic base oil greases.

Example 15

A mixture of 17.5 parts by weight of basic aluminum benzoate stearate, 32.5 parts by weight of a phenyl-methyl polysiloxane having a viscosity of 1060 SSU at 100° F. and a specific gravity of 1.11 at 25° C. (Dow-Corning Fluid 710) was heated to 490° F. and then cooled to room temperature. A sample of the resulting grease was placed directly on a hot plate at a temperature of approximately 500° F., at which temperature the grease remained soft and unctuous.

Greases prepared by incorporating basic complex aluminum soaps of this invention in polysiloxane synthetic oils maintain good texture and consistency from room temperature and below to approximately 500° F. without evidence of excess gelatin or bleeding. In contrast, some silicone greases (e. g., silicone grease containing lithium stearate) exhibit gelation or bleeding at lower temperatures; for example temperatures about 400° F.

The basic aluminum soaps of this invention are also used as a minor or major part of the thickener in greases to improve or to prevent rusting, etc. Thus, the present basic aluminum complex soaps can be beneficially incorporated with greases containing other thickening agents such as simple aluminum soaps, e. g., aluminum di-stearate, calcium soaps, e. g., calcium stearate, soda-base soaps, e. g., sodium oleate, lead soaps, e. g., lead naphthenate.

Besides being excellent thickening agents for greases, the present basic aluminum complex soaps are suitable as improving agents in lubricating oils, in pigment manufacture, in dusting powders, for imparting greater waterproofness in such materials as leather, textiles, wood and other fibrous or porous materials, etc.

We claim:

1. A grease composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to form a grease, a complex basic aluminum soap, said complex basic aluminum soap being an aluminum benzoate stearate wherein the benzoate anion-stearate anion ratio has a value from 0.2 to about 5.

2. A grease composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and from 10% to 16% of a complex basic aluminum soap, said complex basic aluminum soap being an aluminum benzoate stearate wherein the benzoate anion-stearate anion ratio has a value from 0.2 to about 5.

3. A grease composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to form a grease, a complex basic aluminum soap, said complex basic aluminum soap being an aluminum toluate stearate wherein the toluate anion-stearate anion ratio has a value from 0.2 to about 5.

4. A grease composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and from 10% to 16% of a complex basic aluminum soap, said complex basic aluminum soap being an aluminum toluate stearate wherein the toluate anion-stearate anion ratio has a value from 0.2 to about 5.

5. A grease composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and, in an amount sufficient to form a grease, a complex basic aluminum soap, said complex basic aluminum soap being an aluminum benozate 12-hydroxystearate, wherein the benzoate anion-12-hydroxystearate anion ratio has a value from 0.2 to about 5.

6. A grease composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and from 10% to 16% of a complex basic aluminum soap, said complete basic aluminum soap being an aluminum benzoate 12-hydroxystearate, wherein the benzoate anion-12-hydroxystearate anion ratio has a value from 0.2 to about 5.

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