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PREPARATION OF SOAP-SALT COMPLEXES UTILIZING PREFORMED ACID SALT

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This invention relates to grease compositions and more particularly relates to lubricating grease compositions containing complex soap-salt thickeners. Still more particularly, this invention relates to a method of preparing such greases wherein a preformed acid salt is employed as the salt-forming portion of the thickener and to grease compositions so formed. The method of this invention is especially useful in the preparation of lubricating grease compositions containing complex soap-salt thickeners in which there is a high ratio of salt to soap on a mole basis.

Soap-salt complexes are well known in the art for thickening lubricating oils to produce lubricating grease compositions. These complex thickeners have been employed for high temperature greases and consist of combinations of metal salts of low molecular weight carboxylic acids with metal soaps of high molecular weight fatty acids. Normally the soaps and salts have been employed in proportions in the range of about 0.5 to 3 moles of salt per mole of soap. Because the thickening effect of the salt is rather low, it has been generally considered desirable to maintain the mole ratio of salt to soap below about 3 since above a mole ratio of about 3 the total requirement of soap-salt thickener needed to make greases of satisfactory penetration characteristics was found to be quite high.

However, recently it has been found that by drastically increasing the salt content and with it the metal content of soap-salt complexes, entirely new properties may be built into these complexes which greatly increase their value as grease thickeners. More specifically, it has been found that complexes of metal salts of low molecular weight carboxylic acids with metal soaps of high molecular weight carboxylic acids which contain at least 7 moles and up to as much as 40 moles or more, preferably about 8 to 25 moles, of the low molecular weight acid per mole of the high molecular weight acid have outstanding load-carrying, dispersant, and various other beneficial characteristics in addition to thickening properties comparable to soap-salt complexes containing substantially lower proportions of low molecular weight carboxylic acids. These particular thickeners and their utilization in lubricating grease compositions are described in detail in the co-pending Morway and Kolfenbach application Serial No. 387,527, filed October 21, 1953.

Because of the difficulties encountered in handling large quantities of the low molecular weight acids and in particular acetic acid in the manufacture of these lubricating grease compositions which contain a complex soap-salt thickener having a high salt to soap ratio, it was recognized in the aforementioned patent application that it would be desirable to employ a preformed metal salt of the low molecular weight acid, such as calcium acetate, in the grease-making procedure in lieu of the direct use in the grease-making procedure of the low molecular weight acid itself. However, it was found that unsatisfactory greases were formed if the preformed metal salt constituted more than about 80% of the final salt portion

of the complex soap-salt thickener. Thus it was not possible to completely eliminate the difficulties such as acid solidification, storage, pumping, etc, encountered with handling the low molecular weight acids such as acetic acid.

It has now been found in the case where acetic acid is employed as the low molecular weight carboxylic acid that by employing an acid salt of calcium, barium, or strontium instead of the neutral acetate, it is possible to produce excellent greases without the necessity of employing any free acetic acid in the grease-making procedure. Although it will be clearly understood that these preformed acid salts may be employed in greases containing complexes having a salt to soap ratio below about 3, the method of this invention is especially useful in and is particularly directed to the preparation of lubricating grease compositions containing complex soap-salt thickeners in which there is a high ratio of salt to soap on a mole basis. More particularly, the present invention is directed to lubricating grease compositions containing a complex soap-salt thickener wherein the ratio of salt to soap on a mole basis is at least 7 and up to as much as 40 or more and preferably about 8 to 25.

The preformed acid salts of this invention are generally considered as having the following formula

$$M(C_2H_3O_2)_2 \cdot (C_2H_4O_2)_n$$

where M is an alkaline earth metal selected from the group consisting of calcium, barium, and strontium, and n is an integer of 1 to 3. The acid salt is employed in the grease-making procedure in accordance with this invention in lieu of acetic acid and is used in combination with a high molecular weight carboxylic acid to form a complex soap-salt thickener. The complex is formed by neutralizing the free acid portion of the acid salt and the high molecular weight carboxylic acid with a basic reacting compound of a metal which is preferably the same metal as that of the acid salt. The neutralization reaction is preferably carried out in at least a portion of the lubricating oil which is to be thickened to a grease consistency by the complex soap-salt thickener. The mixture of the lubricating oil and neutralized acid salt and high molecular weight carboxylic acid is heated to an elevated temperature, preferably in the range of about 450° to 550° F. or higher, to dehydrate the product and to promote formation of the complex. The amount of the complex in the final lubricating grease composition may be in the range of about 5 to 30% by weight based on the total composition.

The acid salts may be conveniently prepared by reacting a hydroxide or carbonate of calcium, barium, or strontium with approximately the stoichiometric proportions of acetic acid required to produce an acid salt having the aforementioned formula. Thus, for example in the case of calcium, about 1 mole of calcium hydroxide (or calcium carbonate) may be reacted with about 3 moles of acetic acid to form an acid salt having the formula

$$Ca(C_2H_3O_2)_2 \cdot C_2H_4O_2$$

Also, by way of example in the case of barium, about one mole of barium carbonate or barium hydroxide may be reacted with about 5 moles of acetic acid to form an acid salt having the formula

$$Ba(C_2H_3O_2)_2 \cdot (C_2H_4O_2)_3$$

The acid salts so formed are free-flowing powders or granules which may be simply and inexpensively stored and handled. When the metal hydroxide is employed, the powdered acid salt contains all of the water of reaction. The reaction itself may be conveniently conducted at atmospheric conditions of temperature and pres-

sure and is preferably carried out with intimate mixing of the reactants. The time required for completion of the reaction is short and in view of the excess acid present is almost instantaneous. The acid salt may also be conveniently prepared by adding the appropriate number of moles of the neutral acetate salt to acetic acid. For example, about 1 mole of neutral calcium acetate would be added to about 1 mole of acetic acid to form an acid salt having the formula

$$Ca(C_2H_3O_2)_2 \cdot C_2H_4O_2$$

The high molecular weight carboxylic acids useful for the purposes of the present invention are those having about 12 to 30 carbon atoms and preferably those having about 16 to 22 carbon atoms per molecule. These acids may be derived from saturated or unsaturated naturally occurring or synthetic fatty materials. The fatty acids normally used in the manufacture of conventional greases, particularly the more saturated acids, are preferred. Examples of such acids include stearic, hydroxy stearic, such as 12-hydroxy stearic, di-hydroxy stearic, poly-hydroxy stearic and other saturated hydroxy fatty acids, arachidic, hydrogenated fish oil and tallow acids, etc. However, unsaturated acids, such as oleic, ricinoleic and similar acids may likewise be used. It will be understood, of course, that the naturally occurring or synthetic fatty materials mentioned above may be directly employed in the grease-making process to form soaps of high molecular weight carboxylic acids by treatment thereof with the basic metal reacting compound in the grease making process.

The lubricating oil employed to produce lubricating grease compositions in the method of this invention may be mineral as well as synthetic lubricating oils. These synthetic oils include synthetic lubricating oils having a viscosity of at least 30 SSU at 100° F. such as esters of monobasic acids (e. g. ester of C_8 Oxo alcohol with C_8 Oxo acid, ester of C_{13} Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e. g. di-2-ethyl hexyl sebacate, di-nonyl adipate, etc.), esters of glycols (e. g. C_{13} Oxo acid diester of tetraethylene glycol, etc.), complex esters (e. g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, complex ester formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl hexanol, complex ester formed by reacting together one mole of azelaic acid, one mole of tetraethylene glycol, one mole of C_8 Oxo alcohol, and one mole of C_8 Oxo acid), esters of phosphoric acid (e. g. the ester formed by contacting three moles of the mono methyl ether of ethylene glycol with one mole of phosphorus oxychloride, etc.), halocarbon oils (e. g. the polymer of chlorotrifluoroethylene containing twelve recurring units of chlorotrifluoroethylene), alkyl silicates (e. g. methyl polysiloxanes, ethyl polysiloxanes, methyl-phenyl polysiloxanes ethyl-phenyl polysiloxanes, etc.), sulfite esters (e. g. ester formed by reacting one mole of sulfur oxychloride with two moles of the methyl ether of ethylene glycol, etc.), carbonates (e. g. the carbonate formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptals (e. g. the mercaptal formed by reacting 2-ethyl hexyl mercaptan with formaldehyde), formals (e. g. the formal formed by reacting C_{13} Oxo alcohol with formaldehyde), polyglycol type synthetic oils (e. g. the compounds formed by condensing butyl alcohol with fourteen units of propylene oxide, etc.), or mixtures of any of the above in any proportions. Quite generally the mineral or synthetic oil should have a viscosity within the range of about 35 to 200 SSU at 210° F. and flash points of about 350° to 600° F. Lubricating oils having a viscosity index of 100 or higher may be employed. However, oils of lower viscosity index such as below 60 VI give better yields. Complex salt-soap proportions of about 5 to 30 wt.% and preferably about 10 to 20 wt. per cent pased on the total grease composition may be employed in preparing grease compositions in accordance wtih the method of this invention.

The preferred grease-making procedure of this invention comprises the formation initially of a mixture of the acid salt, the high molecular weight carboxylic acid, and a basic reacting compound, such as the hydroxide, of a metal which is preferably the same as the metal in the acid salt in a portion or all of the lubricating oil which is to be utilized in the grease composition. Preferably at least one-third of the total lubricating oil is utilized in the preparation of this initial mixture. The free acid portion of the acid salt and the high molecular weight carboxylic acid are neutralized by the basic reacting compound. A sufficient amount of the basic reacting compound is employed to accomplish this neutralization. It will be understood that the term "free acid portion of the acid salt" as used herein refers to the right hand portion of the aforementioned formula, namely the

$$(C_2H_4O_2)_n$$

group. The high molecular weight carboxylic acids and the acid salt may be coneutralized by adding the basic reacting compound to the oil mixture containing both the acid salt and the high molecular weight carboxylic acid, or the carboxylic acids may be neutralized in a stepwise procedure. If the stepwise procedure is employed the high molecular weight acid may be added to the oil mixture containing the basic reacting compound first, followed by the addition of the acid salt. Thereafter the lubricating oil containing the neutralized materials is heated to an elevated temperature preferably in the range of about 450° to 550° F. or higher to dehydrate the product and to promote formation of the complex. Generally a period of heating in the range of about 10 to 30 minutes will be suitable to effect the formation of the complex. Thereafter the composition is cooled and the remainder of the lubricating oil is added in the case where only a portion of the lubricating oil was initially employed. It will be understood, however, that, if desired, the acid salt and the high molecular weight carboxylic acid may be neutralized together in a separate step and then added to the lubricating oil after which the mixture is heated to an elevated temperature in the range of about 450° to 550° F. to promote formation of the complex. It will be further understood that other conventional thickeners, anti-oxidants, corrosion inhibitors, tackiness agents, load-carrying compounds, viscosity index improvers, oiliness agents and the like may be added prior, during or after the heating step as will be apparent to those skilled in the art.

The following example is presented to more specifically set forth this invention, but it will be understood that it is not intended that the example limit the present invention in any way.

EXAMPLE

Four greases, 1, 2, 3, and 4, were prepared from the materials listed below. Greases 1, 2 and 3 were prepared by initially mixing the ingredients, with the exception of the phenyl alpha-naphthylamine, in the proportions indicated in a conventional grease mixer and heating the mixture to about 500° F. In the case of greases 1 and 2, the free acetic acid was added after the mixture of the other components had reached a temperature of about 135° F., whereupon heating was continued to 500° F. Thereafter greases 1, 2 and 3 were cooled to about 250° F. while agitated. Then the phenyl alpha naphthylamine was added and the greases were further cooled to about 200° F., homogenized and packaged.

Grease 4 was prepared by adding in order to the lubricating oil which was contained in a conventional grease kettle, the lime, the Hydrofol acid, the hydrogenated castor oil and the acid calcium acetate. The addi-

tion of these ingredients required about 0.5 hour. The mixture was then heated over about a 3 hour period to a temperature of about 500° F. The grease mixture was then transferred to a water-jacketed cooling kettle. This transfer took about 0.5 hour during which time the grease had cooled to about 400° F. The grease was then further cooled in the cooling kettle to about 250° F. over a period of time of about 2.5 hours at which point the phenyl alpha naphthylamine was added. The grease was then further cooled to about 200° F., homogenized and packaged.

Formulation

Ingredients	Wt. Percent			
Grease	1	2	3	4
Hydrofol Acid 51 [1]	2.00	2.0	2.0	2.0
Hydrogenated Castor Oil	2.00	2.0	2.0	2.0
Glacial Acetic Acid	8.00	4.0		
Hydrated Lime	6.00	3.3	0.6	3.0
Neutral Calcium Acetate		5.3	10.7	
Acid Calcium Acetate				[2] 11.0
Phenyl-α-Naphthylamine	0.50	0.5	0.5	0.5
Naphthenic-Type Mineral Oil Distillate Having a Viscosity of 55 SSU at 210° F	81.50	82.9	84.2	81.5

[1] Hydrogenated fish oil acids corresponding to commercial stearic acid in degree of saturation.
[2] 8.0% glacial acetic acid+3.0% hydrated lime giving an acid salt of the formula $Ca(C_2H_3O_2)_2.C_2H_4O_2$.

Properties

Appearance and Structure	Excellent	Excellent	Unsatisfactory [1]	Excellent, Smooth Uniform
Dropping Point, ° F	500+	500+		500+
Penetrations, 77° F. mm./10:				
Unworked 60 Strokes	220	210		210
Worked 60 Strokes	238	230		240
Worked 75,000 Strokes	308	315		
Worked 100,000 Strokes				272
Norma Hoffman Oxidation Hours to 5 p. s. i. drop in Oxygen pressure (210° F.)	245	254		260
Spindle Test, 1,000 R. P. M., 250° F	985	1,125		1,150

[1] Incomplete dispersion of the salt resulting in soft semi-fluid grainy grease.

It will be noted that greases 1 and 2 which were prepared by employing a substantial proportion of glacial acetic acid in combination with neutral calcium acetate were excellent greases. However, when a grease (grease 3) was prepared without the utilization of any glacial acetic acid by employing solely neutral calcium acetate, an unsatisfactory grease was produced. It will be noted, however, that grease 4 which was prepared in accordance with this invention by employing solely the acid salt of calcium acetate was an excellent grease and did not require the utilization of any glacial acetic acid in its preparation.

What is claimed is:

1. An improved method for preparing a lubricating grease composition containing a grease-thickening proportion of a complex soap-salt thickener which comprises preforming an acid salt having the formula

$$M(C_2H_3O_2)_2.(C_2H_4O_2)_n$$

where M is an alkaline earth metal selected from the group consisting of calcium, barium and strontium and n is an integer of 1 to 3, forming a mixture comprising a major proportion of a lubricating oil, a minor proportion of said acid salt, a minor proportion of a high molecular weight carboxylic acid and a basic reacting compound of a metal in an amount sufficient to neutralize said high molecular weight carboxylic acid and the free acid of said acid salt, heating the resultant mixture at an elevated temperature until a soap-salt complex is formed and then cooling to obtain said lubricating grease composition, the proportions of said salt and said soap in said complex being about 0.5 to 40 mols of salt per mol of soap.

2. Method according to claim 1 wherein the proportion of said complex soap-salt thickener in said grease composition is in the range of about 5 to 30% by weight based on the total composition.

3. Method according to claim 2 wherein the proportions of salt and soap in said thickener are in the ratio of about 7–40 moles of salt per mole of soap.

4. Method according to claim 1 wherein said heating step is carried out in the range of about 450° to 500° F.

5. In a method of preparing a lubricating grease composition containing in the range of about 5 to 30% by weight of a complex soap-salt thickener, the proportions of salt and soap in said thickener being in the ratio of about 7–40 moles of salt per mole of soap, wherein said grease composition is formed by neutralization of high molecular weight carboxylic acids with a basic reacting compound of an alkaline earth metal in admixture with a major proportion of a lubricating oil by subsequent heating of the mixture at an elevated temperature in the range of about 450 to 550° F. and then cooling to obtain said lubricating grease composition, the improvement which comprises incorporating into said grease composition a preformed acid salt having the formula

$$M(C_2H_3O_2)_2\cdot(C_2H_4O_2)_n$$

where M is an alkaline earth metal selected from the group consisting of calcium, barium and strontium and n is an integer of 1 to 3 as the salt forming portion of said complex soap-salt thickener.

6. An improved method for preparing a calcium base grease composition containing a complex soap-salt thickener which comprises preforming an acid salt of calcium acetate, said salt having the formula

$$Ca(C_2H_3O_2)_2\cdot C_2H_4O_2$$

forming a mixture comprising a major proportion of a mineral lubricating oil, a minor proportion of said acid salt, a minor proportion of a carboxylic acid having in the range of 18 to 22 carbon atoms per molecule and sufficient calcium hydroxide to neutralize the free acid of said acid salt and said carboxylic acid, and heating the resultant mixture at a temperature in the range of about 450 to 550° F. until a soap-salt complex is formed, and then cooling to obtain said grease composition, the proportion of said complex in said grease composition being in the range of about 10 to 20% by weight and the proportions of said salt and said soap in said complex being in the ratio of about 8–25 moles of salt per mole of soap.

7. Method according to claim 6 wherein said carboxylic acid comprises hydrogenated fish oil acids.

8. A lubricating grease composition comprising a major proportion of a lubricating oil and in the range of about 5 to 30% by weight, based on the total composition of a complex soap-salt thickener, said thickener having been formed by the neutralization of a high molecular weight carboxylic acid and an acid salt having the formula

$$M(C_2H_3O_2)_2\cdot(C_2H_4O_2)_n$$

where M is an alkaline earth metal selected from the group consisting of calcium, barium and strontium and n is an integer of 1 to 3, with a basic reacting compound of said metal, said composition having been heated to an elevated temperature to form said complex and cooling the composition to obtain said lubricating grease composition, the mol ratio of salt to soap in said thickener being within the range of about 0.5 to 40.

9. Composition according to claim 8 wherein the mole ratio of salt to soap in said thickener is in the range of about 0.5 to 3.

10. Composition according to claim 8 wherein the mole ratio of salt to soap in said thickener is in the range of about 7 to 40.

11. A lubricating grease composition comprising a

major proportion of a mineral lubricating oil and in the range of about 10 to 20% by weight, based on the total composition, of a complex soap-salt thickener, said thickener having been formed by the neutralization of an acid salt having the formula

$$Ca(C_2H_3O_2)_2 \cdot C_2H_4O_2$$

and a carboxylic acid having in the range of 18 to 22 carbon atoms, per molecule with calcium hydroxide, the mole ratio of salt to soap in said thickener being in the

range of about 8 to 25, said composition having been heated at a temperature in the range of about 450° to 550° F. for an extended period of time to form said complex and then cooling to obtain said lubricating grease composition.

References Cited in the file of this patent

Boner: Lubricating Greases. Pub. 1954 by Reinhold Publishing Corp., chapter 16, section 11, page 621, New York, N. Y.