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3,068,175

PROCESS FOR PREPARING COMPLEX CALCIUM SALT-CALCIUM SOAP GREASE

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No Drawing. Filed Aug. 24, 1959, Ser. No. 835,445
8 Claims. (Cl. 252—39)

This invention relates to an improved method for the preparation of calcium salt-calcium soap thickened greases containing high proportions of calcium salts.

It has been found, as disclosed and claimed in co-owned, copending applications Serial No. 835,443 of J. R. Roach and T. B. Jordan and Serial No. 835,444 of W. S. Pelton and N. R. Odell, both filed of even date herewith, that calcium salt-calcium soap thickened greases of very exceptional extreme pressure properties and other desirable lubricating properties are obtained by employing high proportions of calcium salts of low molecular weight fatty acids and carrying out a complexing step upon the grease mixture within a low temperature transition range below 400° F. This method produces much higher extreme pressure properties than are obtained with complex calcium salt-calcium soap thickened greases of the prior art, including such greases containing high proportions of calcium salts obtained by carrying out the preparation with complexing within a high temperature transition range above about 400° F. However, this low temperature method produces greases in lower yields than the high temperature method, and it also has the disadvantage of requiring a longer treating time in order to obtain the desired effect.

The present invention involves the discovery that very substantially improved yields and other advantages are obtained in the grease preparation described in the above-mentioned applications by carrying out the heat treating step upon a relatively concentrated slurry, containing from about 25 percent to about 75 percent, and preferably from about 40 percent to about 60 percent, of the total oil contained in the finished grease, and adding the remainder of the oil after the salt-soap complex is formed. In order to obtain improved yields by this method, it is necessary that the slurry contain at least about 25 percent by weight, and most advantageously at least about 30 percent by weight, of the calcium soap and calcium salt mixture. A still further improvement in both yield and quality of the grease produced is obtained by shearing the grease mixture during the complexing step, and very advantageously during the subsequent steps of the process also.

The preferred procedure in accordance with this invention comprises employing in the grease mixture a small amount of an estolide of a high molecular weight hydroxy fatty acid, as disclosed in the copending application Serial No. 700,984, of J. R. Roach and T. B. Jordan. Suitable materials of this character are obtained by the interesterification of C₁₀ to C₂₄ hydroxy fatty acids and have average molecular weights in the range from about 500 to about 2500. By employing these estolides in amounts from about 0.1 to about 2.5 percent by weight, based on the weight of the finished grease, a further very substantial improvement in the grease yield is obtained.

The greases with which this invention is concerned comprise a lubricating oil as the chief component thickened to a grease consistency with a calcium lower fatty acid salt and calcium higher fatty acid soap in a mol ratio between about 6:1 and about 20:1, respectively, and preferably from about 7:1 to about 15:1, respectively. The calcium salt is present in an amount between about 13 percent and about 24 percent of the weight of the grease, and preferably in an amount between about 14 percent

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and about 22 percent of the weight of the grease. The calcium soap is present in an amount of about 4–10 percent by weight, preferably in an amount of about 4–8 percent by weight of the grease. The grease may be substantially neutral, or it may contain either a small amount of free acid or free alkali. It is preferably slightly alkaline with about 0.1–1.5 percent by weight of free alkali, calculated as calcium hydroxide. Greases obtained in accordance with the preferred procedure wherein a small amount of estolide is employed in the grease mixture, may contain about 0.1–2.5 percent by weight of estolide or calcium salt thereof.

The lubricating oils forming the major constituent of these greases may be any oils of lubricating characteristics which are suitable for use in lubricating greases generally. Such oils include particularly the conventional mineral lubricating oils having Saybolt Universal viscosities in the range from about 75 seconds at 100° F. to about 225 seconds at 210° F., which may be either naphthenic or paraffinic oils or blends thereof. The preferred mineral oils are those having Saybolt Universal viscosities in the range from about 300 seconds at 100° F. to about 10 seconds at 210° F., which may be blends of lighter and heavier oils in the lubricating oil viscosity range.

Synthetic lubricating oils, which may be preferred for obtaining greases having special properties required for certain types of lubricating service, include oils prepared by cracking and polymerizing products of the Fischer-Tropsch process and the like, as well as other synthetic oleaginous compounds such as diesters, polyesters, polyethers, etc., having viscosities within the lubricating oil viscosity range. Examples of suitable diesters include the aliphatic dicarboxylic acid diesters, such as di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, di-2-ethylhexyl azelate, di-iso-octyl adipate, etc. A particularly suitable class of synthetic polyesters are those described in U.S. 2,628,974, obtained by reacting an aliphatic dicarboxylic acid with a glycol and a monofunctional aliphatic alcohol or acid. Examples of polyethers include particularly polyalkylene glycols such as polyethylene glycol and polypropylene glycol. The sulfur analogs of these diesters, polyesters and polyalkylene ethers are also suitable for use in the grease compositions of this invention. Examples of suitable compounds of this type include di-2-ethylhexylthiosebacate, di-n-octylthioadipate, polyethylenethioglycol and the reaction product of adipic acid, thioglycol and 2-ethylhexyl mercaptan.

The calcium soap component of the grease is obtained by the saponification of a high molecular weight substantially saturated fatty acid containing 10–22 carbon atoms. By substantially saturated is meant such acids having iodine numbers below about 40, and preferably below about 20. The acids may be either unsubstituted or hydroxy substituted acids, or mixtures thereof. Examples of suitable high molecular weight fatty acid materials which may be employed in the saponification include stearic acid, palmitic acid, myristic acid, lauric acid, 12-hydroxystearic acid, 9-hydroxystearic acid, 9,10-dihydroxystearic acid, 8-hydroxypalmitic acid and the monoesters and glycerides of such acids. The preferred saponifiable materials contain a major proportion of unsubstituted fatty acid materials. Very advantageously, a mixture of acids of the character described containing a major proportion of unsubstituted fatty acids having from 12 to 16 carbon atoms per molecule, or the esters of such acids, is employed.

The calcium salt component of these greases is derived from low molecular weight saturated fatty acids containing 1–3 carbon atoms. The calcium salt can thus be calcium formate, calcium acetate, calcium propionate, or mixtures thereof. In further description of the invention, calcium acetate will be used to illustrate the calcium salt

component of these greases, although it will be understood that calcium salts of formic and propionic acids may be substituted therefor.

In accordance with this invention, a heat treating step is carried out upon a slurry comprising about 25-75 percent of the lubricating oil contained in the finished grease and at least about 25 percent by weight of a mixture of a calcium salt of a low molecular weight fatty acid and a calcium soap of a high molecular weight fatty acid of the types described above in a mol ratio of about 6:1 to 20:1, respectively. Under the preferred conditions, a slurry is employed comprising about 40-60 percent of the oil in the finished grease and containing at least about 30 percent by weight of the calcium salt-calcium soap mixture wherein the calcium salt and calcium soap are in a mol ratio of about 7:1 to 15:1, respectively.

The heat treating step is carried out at an elevated temperature above about 250° F. but below 400° F. until at least substantial thickening has occurred. The length of time required varies with the temperature, and may range from a few minutes at the higher temperatures to several hours at lower temperatures within the disclosed range. The heating is preferably carried out at a temperature of at least about 275° F., in order to obviate excessively long heating times, and not in excess of about 375° F. in order to avoid local overheating of the grease mixture to temperatures within the high temperature transition range. When a preformed calcium salt is used, or when the slurry contains less than about 30 percent by weight of the calcium salt and calcium soap, the heat treating step is preferably carried out at a temperature of at least about 290° F.

The remainder of the lubricating oil contained in the grease is added at any time after the complex is formed, as shown by a substantial thickening of the grease mixture which is in excess of the separate thickening effects of the calcium salt and calcium soap. Very advantageously, at least a portion of this oil, preferably equivalent to at least about 10 percent of the total oil in the grease, is added before the cooling and while the grease mixture is maintained at an elevated temperature, preferably above about 300° F. The remainder of the oil may be added during the cooling or during the finishing. The grease may be cooled by any convenient means and finished in the usual manner, preferably with milling.

The preferred method of this invention comprises shearing the grease mixture during the complexing step, most advantageously by the method which comprises continually withdrawing a minor recycle stream of the grease mixture from a maintained agitated body thereof and passing the recycle stream through a shearing means, as described by J. P. Dilworth, T. B. Jordan and B. L. Bengé in U.S. 2,886,525. A particularly suitable shearing device is a shear valve, such as a gate valve, through which the grease mixture is passed with a substantial pressure drop, preferably in about the range 25-200 p.s.i. Very advantageously, recirculation of the grease mixture through the shear valve is continued during the cooling process also, and in this case a grease may be obtained which does not require milling or other shearing during finishing.

The grease mixture may be obtained in any convenient manner, such as by neutralizing a mixture of high and low molecular weight fatty acid materials with a suitable basically reacting calcium compound, by employing preformed calcium salts and calcium soaps, or by a combination of these methods. The preferred method comprises forming at least the calcium soap in situ in a portion of the lubricating oil contained in the grease, which is a mineral oil or other oil substantially non-reactive under the saponification conditions, and introducing the calcium salt into the mixture before dehydration of the saponification mass, either by adding preformed calcium salt or by forming it in situ. When the calcium salt is formed in situ it is preferably added after at least the ma-

jor part of the saponification has occurred, in order to obtain a smooth product. The calcium salt may be formed from a low molecular weight fatty acid or ester thereof or from an acid salt as described in the above-mentioned application of J. R. Roach and T. B. Jordan.

The estolides which are employed in accordance with the preferred embodiment of this invention may be added to the grease mixture at any time before cooling. They are preferably added before the heating step, suitably to the initial charge in the grease kettle.

The following examples are given for the purpose of more fully disclosing the invention.

EXAMPLE I

A grease comprising calcium acetate and calcium soap in a 7.5:1 mol ratio was prepared in accordance with this invention by the method comprising heating a concentrated slurry of calcium salt and calcium soap at a temperature within the low temperature transition range and adding the remainder of the lubricating oil after the complexing step. The lubricating oil employed was a blend in a 2:3 ratio by weight respectively of a refined paraffinic distillate oil having a Saybolt Universal viscosity of about 185 at 100° F. and a refined residuum from a mixed base crude having a Saybolt Universal viscosity of about 156 at 210° F. The calcium soap was obtained by saponifying commercial coconut oil fatty acids, having a saponification number of 253 and an iodine number of 12.2.

The following is a detailed description of the method of preparation employed: A grease kettle was charged with 20.5 pounds of mineral lubricating oil, 4.64 pounds of coconut oil fatty acids, 0.3 pound of an estolide of 12 hydroxystearic acid having an average molecular weight of 1600, and 7.3 pounds of lime, and the mixture heated with stirring. When the temperature of the mixture had reached 130° F., 9.3 pounds of glacial acetic acid were added and the heating continued until the temperature of the mass had reached 318° F., which required 130 minutes. The temperature was maintained at about 318° F. for 120 minutes and the mixture then cooled to 200° F. at a rate of about 0.5° F. per minute while adding an additional 30.8 pounds of mineral lubricating oil. Phenylalphanaphthylamine (0.35 pound) was then added and the grease finished by milling in a Manton-Gaulin homogenizer at 7000 p.s.i.g.

A grease of satisfactory texture and appearance was obtained in the above manner and in a very substantially improved yield as compared with a grease of the same composition obtained by carrying out the heat treating step upon a more dilute slurry, as shown by the following table. Grease No. 1 of the table was prepared in substantially the same manner except that the entire amount of lubricating oil was added to the grease mixture before the heat treating step.

Table I

Grease No.	1	2
Composition, percent:		
Ca salt	17.5	17.5
Ca soap	7.1	7.2
Excess Ca(OH) ₂	1.0	1.0
Ca soap of estolide	0.5	0.5
Phenylalphanaphthylamine	0.5	0.5
Lubricating oil	Remainder	Remainder
Preparation:		
Oil in slurry, percent of total	100	40
Maximum temperature, ° F.	318	318
Tests:		
ASTM Penetration at 77° F.—		
Unworked	233	202
Worked, 60 strokes	346	319
Dropping point, ° F.	+500	+500
Timken Test, O.K. load, lbs.	65	65

As shown by the data given in the above table, a substantial yield advantage, represented by 27 points in ASTM worked penetration, was obtained by carrying out the grease preparation employing a concentrated slurry

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in the complexing step and thereafter diluting the grease mixture with additional lubricating oil. Aside from the difference in yield, the lubricating properties of the two greases were substantially the same.

EXAMPLE II

As an example of the preferred method of this invention, a grease of the following composition in percent by weight was prepared by carrying out the heat treating step upon a concentrated slurry and shearing the slurry during the process:

Ca salt	14.8
Ca soap	5.9
Excess $\text{Ca}(\text{OH})_2$	0.2
Ca soap of estolide	0.5
Phenylalphanaphthylamine	0.5
Lubricating oil	Remainder

The lubricating oil employed was the same as that described in Example I. The saponifiable material employed for forming the calcium soap was a commercial coconut oil, having a neutralization number of 8.6, a saponification number of 258, an iodine number of 9.8 and a titer, ° C. of 22.8.

The grease preparation was carried out in a 150 pound jacketed steam heated open kettle equipped with a stirrer and a recycle line for recycling the grease mixture from the bottom to the top of the kettle, comprising a ¾ inch diameter pipe containing a Globe Rota-piston pump and a ¾ inch gate valve. The method in detail was as follows: The kettle was charged with 49.3 pounds of mineral oil, 0.60 pound of the estolide described in Example I and 7.02 pounds of coconut oil, and circulation through the recycle line commenced at a rate of about 10 gallons per minute while 10.4 pounds of lime were added. The mixture was then heated to 180° F. in about 20 minutes and 13.7 pounds of glacial acetic acid were added. The mixture was heated further to about 325° F. in about 40 minutes with continued recirculation through the recycle line. Shearing of the grease mixture during the circulation by adjusting the shear valve to give a pressure drop of 60–100 p.s.i. was then started and continued throughout the remainder of the process. The mixture was held at 325–335° F. for about 25 minutes and thereafter 14.5 pounds of additional lubricating oil were added gradually while the temperature was maintained at above 300° F. The mixture was then cooled to 200° F. by the addition of 30.7 pounds additional lubricating oil, and 0.60 pound of phenylalphanaphthylamine then added.

A clear buttery grease of good texture and appearance was obtained as described above having an ASTM penetration at 77° F. unworked 243, worked, 60 strokes, 337, and an ASTM dropping point above 500° F. It carried an O.K. load of 60 pounds in the Timken test.

EXAMPLE III

As an additional example of the preferred method of this invention, a grease was prepared substantially as described in Example II except that preformed calcium acetate was employed. The other materials and equipment employed were as described in Example II. The process comprised essentially the following steps: The kettle was charged with a mixture of preformed calcium acetate, lime and estolide in a portion of the lubricating oil employed in the grease, the charge heated to 130° F. and coconut oil added. The mixture was then heated to 300–320° F., and maintained at that temperature until the control penetration was in the N.L.G.I. No. 1 grade range, while circulating the mixture through the recycle line with a pressure drop of 60–90 p.s.i. across the valve. The remainder of the lubricating oil was then added gradually while the temperature of the mixture was held above 300° F., and the grease mixture cooled with continued recycling through the valve. The grease was drawn at 200° F. and finished by milling.

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A smooth grease having excellent lubricating properties was obtained in good yield by the above method. The following table shows a comparison of the yield obtained in this preparation in comparison with that obtained in a typical preparation carried out in substantially the same way except that all of the lubricating oil was added to the grease mixture before the heating step.

Table II

Composition, Percent:		
Ca salt	19.4	14.8
Ca soap	8.1	6.2
Excess $\text{Ca}(\text{OH})_2$	1.0	0.8
Ca soap of estolide	0.5	0.4
Glycerin ¹	1.0	0.8
Phenylalphanaphthylamine	0.5	0.4
Lubricating oil	Remainder	Remainder
Preparation:		
Oil in slurry, percent of total	100	60
Maximum temperature, ° F.	310	320
ASTM penetration at 77° F:		
Unworked	171	208
Worked, 60 strokes	322	316

¹ Calculated from glycerin content of fatty oil.

As shown by the above table, a large increase in yield of the salt-soap complex thickened grease was obtained by employing a concentrated slurry together with shearing of the grease mixture during the complexing and cooling steps, represented by a reduction of 6.5 percent in the amount of salt-soap complex thickener required compared with the amount required to produce a grease of the same worked penetration when all of the lubricating oil was added to the grease mixture before the complexing step.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In the preparation of an extreme pressure calcium base grease comprising essentially a lubricating oil as the chief component, about 13–24 percent by weight of a calcium salt of a low molecular weight fatty acid and about 4–10 percent by weight of a calcium fatty acid soap, by the method which comprises forming a mixture in a 7:1–20:1 mol ratio respectively of a calcium salt of a saturated C_{1-3} fatty acid and a calcium soap of a high molecular weight fatty acid by saponifying a mixture of an aliphatic monocarboxylic acid containing 1–3 carbon atoms and a higher aliphatic monocarboxylic acid material chosen from the class consisting of substantially saturated unsubstituted and hydroxy substituted C_{12-18} fatty acids, mixtures thereof and their esters, with a basic reacting calcium compound in a portion of the lubricating oil contained in the finished grease, carrying out a heat treating step upon the said mixture at an elevated temperature above about 250° F. but below 400° F. until at least substantial thickening has occurred, and thereafter cooling the said mixture and adding additional lubricating oil, the improvement which comprises carrying out the said heat treating step upon the said mixture containing about 25–75 percent of the total lubricating oil contained in the finished grease and comprising about 25 percent to about 67 percent by weight of the said calcium salt and calcium soap, while shearing the said mixture by continuously withdrawing a minor stream from a maintained body of the said mixture, passing the said stream through a shear valve with a pressure drop of about 25–200 pounds per square inch and returning the said stream to the said maintained body of mixture.

2. The method according to claim 1 wherein the said calcium salt is calcium acetate.

3. The method according to claim 1 wherein the said heat treating step is carried out at a temperature below about 375° F.

4. The method according to claim 1 wherein the said heat treating step is carried out at about 290-375° F.

5. The method according to claim 1 wherein an estolide of a hydroxy fatty acid containing 10-22 carbon atoms is added to the said grease mixture before completion of the said saponification. 5

6. The method according to claim 1 wherein the said shearing is carried out during the cooling also.

7. The method according to claim 1 wherein the said mixture contains 40-60 percent of the total oil contained in the finished grease. 10

8. The method according to claim 1 wherein at least about 10 percent of the total lubricating oil contained in the finished grease is added after the said heat treating

step and while the temperature of the grease mixture is maintained above about 300° F.

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