Patented Aug. 19, 1952

2,607,735

UNITED STATES PATENT OFFICE

2,607,735

ALKALINE EARTH METAL SOAP GREASES

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No Drawing. Application March 12, 1949, Serial No. 81,206

11 Claims. (Cl. 252—40.5)

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The present invention relates to alkaline earth metal soap greases and particularly to new types of lubricating greases having superior high temperature properties. The invention relates also to a process for making superior calcium base greases and other alkaline earth metal greases such as barium and strontium and involves as one aspect, the combination of particular types of alkaline earth metal soaps, especially calcium soaps, with other materials of low molecular weight to form the grease structure.

In the prior art, the alkaline earth metal soaps have been used to thicken oils to grease consistency and in particular lime base greases have been used for many years and for many purposes. For relatively low operating temperatures, they have highly desirable structural characteristics, being smooth and homogeneous and quite free from oil separation. The lime soap greases particularly have the serious disadvantage for some purposes however, that they require a certain small minimum water content for stability. When this water is removed the grease breaks down. This characteristic renders the lime base greases unsatisfactory for service conditions where the water is eliminated due to high operating temperatures, or other causes. The other alkaline earth base greases such as barium and strontium soap greases behave somewhat similarly.

The present invention has an object the preparation of alkaline earth metal greases having improved stability at higher temperatures. Because of their widespread use, the invention deals primarily with lime base greases, but it is not limited thereto. By the expression "lime base" greases, it is intended to include not only greases which are thickened with pure lime soaps, but also those mixed base greases which contain substantial quantities of the calcium soaps of fatty acids and which may also contain minor proportions of soda soaps, and the like.

The present invention is based, in one aspect, upon the discovery that calcium and other alkaline earth metal soap greases may be substantially improved by the use of saturated or substantially saturated hydroxy fatty acids, such as the mono and di-hydroxy acids of 12 to about 24 carbon atoms in lieu of the normal fatty acids commonly employed. The invention involves as another aspect, the further discovery that greases of this type may have their high temperature properties substantially improved by adding to the soaps of the substantially saturated hydroxy acids certain low molecular weight salts of the same metal such as the acetate, propionate, etc. The salts of certain inorganic compounds may be used in some cases, e. g. those of boric acid and its derivatives.

It has already been suggested in the prior art

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that certain hydroxy acids may be used advantageously in the preparation of some types of lubricating greases, particularly aluminum base greases and certain types of soda base greases. Thus, in the patents to Fiero, No. 2,283,602, and Frazer No. 2,445,935, it is suggested that 12-hydroxy stearic acid or the equivalent hydrogenated ricinoleic acid may be substituted for ordinary saturated fatty acids in making the soap ingredients of aluminum and soda base greases, respectively. The outstanding and unexpected properties of the hydroxy forms of substantially saturated fatty acids in calcium and other alkaline earth metal base greases apparently have not been realized, however.

The prior art also contains a number of suggestions for the use of various low molecular weight salts in combination with the usual soaps employed as thickening agents. Thus, in the patents to McLennan Nos. 2,417,328–33 for example, it is suggested that certain complex salts may be formed by combining the metal derivatives of high molecular weight and low molecular weight aliphatic carboxylic acids. Also, in the patent to Carmichael, No. 2,197,263, it is suggested that lime base greases and mixed soda-lime greases may be made more stable at high temperatures by adding acetic acid to the usual fatty acids prior to saponification so as to incorporate calcium acetate into the grease.

The present invention involves definite improvements over the prior art suggestions referred to above particularly in the discovery of the unexpected properties of the hydroxy fatty acid salts of calcium and the other alkaline earth metals. Whereas a conventional lime soap grease becomes unstable at temperatures around the boiling point of water, for example above about 200° F., according to the present invention, the melting point and the useful lubricating range of lime soap greases may be raised about 70° to 100° F. or more by the direct substitution of a hydroxy fatty acid for the normal fatty acid. Also, the high temperature range of this material may be raised as much as an additional 200° F. or so by adding certain of the low molecular weight materials referred to above. The peculiar properties of the hydroxy acid soaps of alkaline earth metals are not fully understood. It is believed, however, that in conventional calcium soap greases, the water affects the soap favorably to establish a fibrous structure which breaks down when the water is taken away, as by evaporation. Apparently the hydroxyl radicals of hydroxy acids perform the same function and remain effective at temperatures where water would disappear. The invention, therefore, has two aspects, namely, the remarkable improvement in high temperature properties resulting from the outright substitution of hydroxy, fatty acids, for conventional fatty acids and the further and often very substantial improvement resulting from the addition of low molecular weight materials to the hydroxy acid soaps.

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

Example I

	Percent by weight
Mineral oil of 300 S. U. S. viscosity at 100° F.	84.4
12-hydroxy stearic acid	13.0
Hydrated lime	2.1
Phenyl alpha naphthylamine	[1]0.5
Water—a trace.	

[1] Optional.

The above composition was prepared in the conventional manner by cooking the soap forming ingredients in part of the mineral oil to a temperature between 200° and 300° F. to form the soap. The balance of the oil was added and the mixture stirred with continued heating until a homogeneous product was obtained. After cooling, a smooth grease resulted which had a worked penetration at 77° F. of 220 mm./10 and an A. S. T. M. dropping point of 288° F. After storage in an oven for one hour at 225° F., the grease was smooth and homogeneous and it retained these properties even after one hour storage at 260° F. This grease was subjected to the high speed spindle test in a ball bearing operating at 10,000 R. P. M. at a temperature of 250° F. and it operated successfully for 942 hours.

By comparison, a conventional lime base grease containing 80.5% of the same mineral oil, 15.3% animal fat, 2.1% hydrated lime and 2.1% water, showed an initial worked penetration of 235 mm./10 at 77° F. with an A. S. T. M. dropping point of 210° F. After storage in an oven for one hour at 225° F., the soap separated from the oil. This grease was entirely unsuitable for use at temperatures above 210° F. and probably could be used for extended periods only at considerably lower temperatures, e. g. 150° F.

Example II

Another composition was prepared from the following ingredients:

	Percent by weight
Mineral oil of 330 S. U. S. at 100° F. (viscosity index 40)	78.2
Mono hydroxy stearic acid	11.0
Calcium hydroxide	1.5
Calcium acetate	5.3
Candelilla wax	4.0

This grease was prepared as in Example I being heated, however, to about 400° F., and was found to have a melting point above 480° F. It should be noted that in this instance the calcium acetate as such was added directly to the composition, but acetic acid may be used, being converted to the acetate by using a correspondingly increased quantity of calcium hydroxide.

As shown in the following data, certain low molecular weight materials, e. g., calcium acetate, raise the dropping point very materially. Others, such as boric acid, do not so materially raise the melting point but appear nevertheless to be valuable ingredients in further stabilizing the greases at higher operating temperatures.

Examples III, IV and V

Formula—Per cent by weight	Ex. III	Ex. IV	Ex. V
S. A. E. 20 Base Oil (300 S. U. S. at 100° F.; 40 V. I.)	76% by wt.	77.5% by wt.	81.2% by wt.
12-Mono-hydroxy stearic acid	11	----------	12
9-10-di-hydroxy stearic acid	----------	11	----------
Acetic Acid	4	4	----------
Boric Acid	----------	----------	2.5
Lime	4	3.5	3.8
Candelilla wax	4	4	----------
Phenyl alpha naphthylamine	1	----------	0.5

The above compositions of Examples III, IV and V were all prepared in the same general manner by forming the soap in part of the lubricating oil, adding the remainder later. The following comparative data were obtained:

	Ex. III	Ex. IV	Ex. V
Per cent Alkali or acid	neutral	0.3 acid	0.12 alk.
Worked Penetration	278	240	295
Penetration after working at 2,500 sec.—1 shear:			
3,000 strokes	308	----------	----------
10,000 strokes	----------	----------	320
A. S. T. M. Dropping Point, ° F.	480+	299	281
Bleeding—Per cent oil loss at 225° F.—after 100 hrs.[1]	3.7	----------	10.8
Viscosity in stokes at 100 sec.—1 shear:			
77° F.	170	----------	120
200° F.	30	----------	38
225° F.	27	----------	35
250° F.	17	----------	40
275° F.	7	----------	4.2
300° F.	7	----------	----------
Water Resistance at 150° F.—No. of ccs. of water absorbed before shedding begins[2]	25	----------	8

[1] 185 gms. of grease in a 3" galv. cone (28 mesh).

[2] 100 gms. of grease are mixed with 20 ccs. of water for 300 strokes in an A. S. T. M. grease worker at the test temp. Further 20 cc. portions of water are added and worked into the grease until water is shed or the grease becomes emulsified and fluidized.

The candelilla wax of Examples III and IV is useful as a plasticizing or dispersing agent and is recommended where a smooth grease of high structure stability is desired. In other cases, its use is not always essential but it is a highly desirable ingredient. Other non-paraffinic waxes may be used such as montan wax, ceresin, carnauba wax and the like.

The following examples illustrate compositions of strontium and various soap greases, using hydroxy acids. They are similarly improved over non-hydroxy acid greases.

	Ex. VI	Ex. VII
Formula: Per cent by weight:		
12-Hydroxy Stearic Acid	16.5	18.00
Barium Hydroxide ($Ba(OH)_2.8H_2O$)	----------	9.35
Strontium Hydroxide ($Sr(OH)_2.8H_2O$)	7.85	----------
Mineral Oil (V/100: 320 S. U. S. V. I.: 40)	75.15	72.15
Phenyl Alpha Naphthylamine	0.5	0.5
Inspections:		
Worked Penetration	290	340
A. S. T. M. Dropping Pt. (° F.)	279	308
Texture of Grease at 250° F.	([1])	([1])
Texture of Grease at 300° F.	([2])	([1])

[1] Smooth grease: No separation.

[2] Separates.

The foregoing data show that by merely replacing conventional fatty acids, such as stearic acid, with a corresponding mono-hydroxy acid, the high temperature range for calcium base greases may be raised about 100° F. or from 150°–175° F. to about 250°–275° F. The data show also that various types of low molecular weight materials may be combined very advantageously with the soaps of the mono and/or di-hydroxy acids. Example V, using a calcium borate (formed upon neutralization of the boric acid with calcium hydroxide), is of particular interest because of the very low cost of boric acid and the high quality of the composition obtained. For service, under conditions where an extremely high temperature is not encountered, the calcium or other alkaline earth metal borate grease has very satisfactory properties. Its percentage of oil loss (about 10%) was somewhat high at 225° F. and it lost viscosity rapidly at higher temperatures. Nevertheless, this material appears to be quite satisfactory for lubrication at temperatures up to about 250° F. Spindle tests at this temperature and at 10,000 R. P. M. showed a useful life of 1000 hours which is remarkable for a lime base grease.

It should be emphasized that a grease stable at temperatures above 225° F. apparently can not be prepared from ordinary calcium stearate and the corresponding borate. The soaps of hydroxy acids, on the other hand, seem to combine very well with the salts of boric acid to form a grease stable at reasonably high temperatures, i. e. temperatures ranging around 225° to 250° F.

While the foregoing examples have referred specifically to the mono and di-hydroxy stearic acids soaps, the corresponding saturated or substantially saturated hydroxy acids of shorter or longer chain length are equally useful. The unsaturated hydroxy acids, such as those prepared from castor oil (ricinoleic acid) do not show such superiority over the corresponding normal fatty acids. Thus, the mono or di-hydroxy lauric, myristic, palmitic, behenic, and other saturated acids of about 12 to 24 carbon atoms may be employed and may be mixed in various proportions, as will be apparent to those skilled in the art. The usual quantities of soap, from about 5% to as much as 30%, may be used, preferably about 8 to 20% based on the weight of the total composition depending upon the consistency of the grease desired. Lubricating oils are preferably the mineral base oils of about 50 to 1,000 S. U. S. viscosity at 100° F., but synthetic oils such as the esters of dibasic acids, the polyglycols, and the like, may be used alone or in combination with mineral oils. If the latter are used, the soaps should be preformed, preferably in a mineral oil slurry to avoid hydrolysis of the esters which would occur upon saponification of the fatty acids.

While phenyl alpha naphthylamine is a desirable ingredient as an oxidation inhibitor, other oxidation inhibitors may be used if desired, and for many purposes such inhibitors may be omitted entirely. Conventional tackiness agents, extreme pressure compounds, viscosity index improvers, corrosion inhibitors, and the like, may be included, as will be obvious to those skilled in the art.

The low molecular weight material is preferably a salt of an acid which acid has a molecular weight below about 160, and preferably below 120. The proportions of such material may be varied within rather wide limits but ordinarily will be between 1% and 10% by weight, based on the total composition. Proportions of 2% to about 6% are normally preferred.

The use of a vegetable or non-paraffin wax, such as carnauba or candelilla wax, or the like, as a plasticizing agent, is preferred where the calcium salts of low organic acids such as calcium acetate are employed. Such waxes may be optional in compositions which include inorganic salts such as calcium chloride or calcium borate. The proportions of such plasticizers are usually between about 1 and 8%, preferably 2 to 6% by weight.

What is claimed is:

1. A substantially anhydrous calcium base lubricating grease composition which is stable at temperatures above the boiling point of water consisting essentially of a lubricating oil of 50 to 1000 S. S. U. at 100° F. containing as a thickener 5 to 30% by weight of a calcium soap of acid selected from the group which consists of at least one of the mono and di-hydroxy substantially saturated fatty acids of 12 to 24 carbon atoms, and 1 to 10% of the calcium salt of a low molecular weight acid, the acid radical of said calcium salt having a molecular weight below 160 and having the property of forming a complex with said soap to raise the melting point of said grease.

2. The composition of claim 1 in which the low molecular weight calcium salt is calcium borate.

3. The composition of claim 1 in which the low molecular weight calcium salt is calcium acetate.

4. The composition of claim 1 which contains 2 to 6% of a low molecular weight calcium salt of an acid with a molecular weight below about 160.

5. A substantially anhydrous calcium base lubricating grease consisting essentially of about 81.5% mineral base lubricating oil, about 14% of the calcium soap of 12-mono-hydroxy stearic acid, and about 4.5% of calcium borate.

6. A substantially anhydrous alkaline earth metal base grease consisting essentially of lubricating oil and a thickener composed of a major proportion of an alkaline earth metal soap of substantially saturated hydroxy fatty acid of 12 to 24 carbon atoms a minor amount of a salt of the same metal having an acid radical molecular weight below about 160 and having the property of forming a complex with said soap to raise the melting point of said grease, and 0 to 8% of a non-paraffinic wax of vegetable origin.

7. Composition as in claim 6 containing 1 to 8% by weight of candelilla wax.

8. Composition as in claim 1 including 2 to about 6% of candelilla wax.

9. Composition as in claim 6 wherein the quantity of hydroxy acid soap is between 8 and 20%, based on the weight of the total composition, and the quantity of low molecular weight salt is between 2 and 6%.

10. Composition as in claim 6, wherein the alkaline earth metal is strontium.

11. Composition as in claim 6 wherein the alkaline earth metal is barium.

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