

UNITED STATES PATENT OFFICE

2,334,239

STABILIZED GREASE COMPOSITION

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No Drawing. Application December 30, 1941,
Serial No. 424,924

15 Claims. (Cl. 252-39)

This invention relates to stabilized grease compositions and more particularly to anhydrous lime soap greases and methods of preparing them.

Ordinarily, lime soap cup greases, as usually manufactured, are composed of mineral lubricating oil, lime soap prepared from fats, such as tallow or tallow oil, a portion of the glycerine liberated in the saponification of the fat remaining unvolatilized, and a small amount of water to bring about the proper texture and to stabilize the product against separation. In the manufacture of these greases, it is difficult to adjust the water content required for stabilization. The final products have poor heat stability, relatively low melting points of the order of 200° F. and below and break down into gelled soap lumps and free oil when heated to a temperature at, above, or even below their melting points because of loss of stabilizing water. Such greases are unsuitable for use in bearings which operate at elevated temperatures due to the fact that the greases break down in the bearings at about 150-175° F.

These ordinary cup greases also have poor storage stability, are susceptible to oxidation, become rancid, develop red to brownish colors on the surface and cause corrosion, pitting and even seizure of the bearings packed therewith. In view of these limitations, the field of use of such cup greases has been limited primarily to cups on shafting and the like where elevated temperatures much above 175° F. are not encountered and where the grease is used up rather rapidly, requiring frequent replenishment.

In our co-pending application, Serial No. 352,116, filed August 10, 1940, of which this application is a continuation-in-part, there is disclosed and claimed a stabilized anhydrous lime soap grease which consists of a lubricating oil, lime soap and a stabilizing mixture of lanolin, and an ester of a higher fatty acid and a polyhydric alcohol, such as glyceryl monostearate. In addition to these components of the stabilizing mixture, there is also disclosed and claimed the use of critical amounts of high molecular weight free fatty acids.

According to the present invention, a stabilized grease composition may be obtained by incorporating in a lime soap grease a stabilizing mixture consisting of castor oil and esters of higher fatty acids and polyhydric alcohols. This stabilizing mixture may be modified as in the case of the co-pending application by the use of additional critical amounts of high molecular weight free fatty acids.

In the manufacture of the stabilized grease

compositions of this invention, fatty acids are used in the preparation of the lime soap rather than fats or fatty oils in order to avoid the liberation of glycerine which would normally be retained in the product at temperatures of manufacture. While the soap in the grease may be prepared from the customary fatty acids such as stearic, palmitic, tallow fatty acids, etc., and a fairly good product obtained, it has been found that a superior product having a higher melting point, increased heat stability, better texture, consistency and resistance to oxidation is obtained by the use of saturated fatty acids of higher molecular weight. These fatty acids may be split from hydrogenated oils or fats, particularly marine or fish oil. Preferably, the fatty acids should contain in excess of 40% of saturated acids higher in molecular weight than stearic acid. As an example, commercially available fatty acids known as "Snodotte acids," having the following composition, have been found to be eminently suitable:

	Per cent by weight
Myristic (C ₁₄)	9
Palmitic (C ₁₆)	22
Stearic (C ₁₈)	27
Arachidic (C ₂₀)	22
Behenic (C ₂₂)	20

Typical tests on a commercially available Snodotte acid and specifications which the acids should meet are as follows:

	Example	Specifications
Saponification No.	197	195-205
Neutralization No.	193	190-195
Iodine No.	1	14
Titer, °C.	54.6	54-56

1 Maximum.

Another suitable commercially available product is that known as Hydrofol acids which are also saturated fatty acids split from hydrogenated fats of this character.

In the manufacture of the greases of this invention, the proportion of soap may vary within quite wide limits, depending upon the grade or consistency of the grease desired. The proportions of soap, for example, may vary from about 6 to 30% or more, giving greases of the ordinary range of consistency. The amount of lime employed to form soaps by reacting with the fatty acids may be slightly less than the chemically equivalent amount so that the resulting grease contains a small excess of fatty acid of the order

of 0.4 to 0.8%. Proportions of free acid of the order of 1% or more should be avoided since such proportions result in a product which has a lower melting point. The use of an excess of lime of the order of 0.5% and over, on the basis of the finished grease, results in a granular product having little grease structure which is subject to oil separation and which is otherwise generally unsuitable. If free fatty acid is desired in the grease composition, it may be obtained by adding a deficiency of lime as indicated above, or the proportion of 0.4 to 0.8% of any of the high molecular weight fatty acids may be added to the composition containing neutral soap.

The castor oil component of the stabilizing mixture has been found to be very effective in depressing the "yield," raising the melting point of the finished grease, and in imparting an added resistance to discoloration and crust formation on the surface of the grease in the presence of excessive atmospheric humidity. An added advantage in the use of castor oil is its ability to prevent the swelling of rubber surfaces which are usually found in many types of lubrication systems. Typical tests of a castor oil which may be used according to the present invention are the following:

Saponification No.....	181.2
OH value (sealed tube method).....	164
Iodine No.....	88.6
Free fatty acid, per cent (as oleic acid)....	4.8
Flash, °F.....	535
Fire, °F.....	615
Visc./210° F., S. U.....	100

The other component of the stabilizer used in this invention is an ester of a higher fatty acid and a polyhydric alcohol. The polyhydric alcohol may be, for example, glycerine, glycol, or their polymerization products, polyglycerine and polyglycol. Suitable esters of glycerines and glycols are the partial esters containing free hydroxyl groups but in the case of the polyglycols and polyglycerines, which are polyhydric alcohols containing ether linkages, both the partially and completely esterified compounds may be used. Examples of compounds which have been found to be suitable are glyceryl monostearate, triethylene glycol monostearate and triethylene glycol distearate, the last mentioned being an example of a completely esterified product containing ether linkages.

From the standpoint of effectiveness, availability and cost, glyceryl monostearate is preferred. A commercially available glyceryl monostearate which we have used to advantage is a product now sold by Glyco Products Company of New York, New York, as "Glyceryl Monostearate S" which has the following characteristics:

Free fatty acid, per cent (as oleic acid)....	3.6
OH value (sealed tube method).....	344

In the manufacture of lime soap greases according to the present invention, the fatty acids and a portion of the mineral oil are charged to a kettle and heated with stirring to melt the acids. The lime in a slurry with a small amount of water is then slowly added with continued heating and agitation to effect the formation of the lime soap, the temperatures being maintained at about 160° F. to 180° F. until a smooth paste or liquid is obtained. Heating and agitation are then continued while raising the tem-

perature gradually up to about 260° F. to 280° F. to effect dehydration. The base becomes progressively clearer as water is removed and finally is in a clear gel form upon complete dehydration.

At this stage the heat is cut off and the glyceryl monostearate is added either in the form of small pieces or in solution in an equal proportion of the mineral oil employed. The remainder of the mineral oil is added slowly in small increments while the mass is stirred and allowed to cool slowly. In the range of about 220° F. to 190° F. the grease tends to become progressively more opaque, adhesive and softer. In the range of about 190° F. to 150° F. the grease starts to pick up body upon continued stirring and builds up to a very heavy, stiff body in a comparatively short period of time. This increase in body is accompanied by a leveling off or a rise in temperature. When there is no further increase in body upon continued stirring, the product is tested for hardness and, if necessary, the hardness is adjusted by the addition of fatty acids melted in a small amount of oil which promotes greater stiffness or "yield." The required proportion of castor oil is then added to give the product a more adhesive texture and glossy appearance. It is preferred to prepare the above product as a heavy grease and the lighter grades may be prepared by thinning the heavy grease with additional mineral oil.

The fact that the grease in the range of about 190° F. to 150° F. builds up to a very heavy body upon continued stirring with an accompanying leveling off or rise in temperature signifies that a novel change takes place. In the ordinary grease manufacturing processes, continued stirring results in a thinning of the grease. It is believed that the leveling off or rise of temperature which represents an evolution of heat is perhaps the result of a sudden crystallization or gelation and may be analogous to the evolution of heat during the crystallization of certain inorganic substances.

In view of the loss of energy from the system, the grease is left in a more stable structural state so that subsequent texture changes during storage are minimized. No matter what explanation is given to these phenomena, they result in grease of a structure that is peculiarly resistant to objectionable hardening during storage.

It has been found that the optimum results described previously which result from the addition of the stabilizing mixture of the present invention to a lime soap grease may be obtained by the addition of the various components within the following range of proportions. These percentage ranges are based upon an analysis of the finished grease composition.

	Per cent by weight
Ester stabilizer	0.5-1.9
Castor oil	1-3
Free fatty acids	0.4-0.8

As an example of the preparation of one type of grease composition falling within the scope of the present invention, namely, an air brake cylinder lubricant, the following example is presented:

A mixture of 25 pounds of Snodotte acids, 30.1 pounds of a mineral lubricating oil of an S. A. E. 40 grade, 16.9 pounds of a mineral lubricating oil of an S. A. E. 20 grade, 1620 grams of lime, and 7 pounds of water, was charged to a kettle and heated while stirring at about 200° F. until a smooth paste or liquid was obtained. The heating and agitation were then continued while rais-

ing the temperature gradually up to about 260° F. to 280° F. to effect dehydration. The paste became progressively clear as water was removed and finally was in a clear gel form upon complete or substantially complete dehydration. At this stage the heating was discontinued and a solution of 6.25 pounds of glyceryl monostearate in a mineral lubricating oil was added. Thereafter, 184.7 pounds of a blend of mineral lubricating oils in the proportion of 63% lubricating oil of an S. A. E. 40 grade and 37% lubricating oil of an S. A. E. 20 grade were slowly added in graduated portions while the mass was being stirred and allowed to cool slowly. In the range of about 220° F. to 200° F. the grease became progressively more opaque, adhesive, and softer. In the range of about 200° F. to 170° F. the grease started to pick up body upon continued stirring and built up to a stiff body in a short time. At approximately 170° F. a control penetration was run according to the usual A. S. T. M. method. The reaction mass was then adjusted by the addition of small increments of mineral oil blend to obtain a penetration of approximately 225 at 77° F. 1494 grams of castor oil were then added to depress the yield and give the product a more adhesive texture and a glossy appearance. The product was then drawn at about 140° F. as the finished grease composition which contained 13.0% soap, 1.3% glyceryl monostearate, 1.9% castor oil, and 83.5% mineral oil.

The term "anhydrous" as used herein is intended to include compositions which may contain traces up to 0.15% of water as determined by the ordinary methods of analysis.

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

We claim:

1. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, an amount of lime soap of high molecular weight fatty acids sufficient to impart to said mineral oil the consistency of a grease, and a minor proportion of a stabilizing mixture consisting of castor oil and an ester of a higher fatty acid and a polyhydric alcohol, said ester being of the group consisting of partial esters and esters containing ether linkages.

2. A stabilized grease composition according to claim 1 in which the ester is glyceryl monostearate.

3. A stabilized grease composition according to claim 1 in which the fatty acid constituent of the lime soap is a mixture of saturated fatty acids from a hydrogenated fatty oil.

4. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, an amount of lime soap of high molecular weight fatty acids sufficient to impart to said mineral oil the consistency of a grease, and a minor proportion of a stabilizing mixture consisting of free higher fatty acid, castor oil, and an ester of a higher fatty acid and a polyhydric alcohol, said ester being of the group consisting of partial esters and esters containing ether linkages.

5. A stabilized grease composition according to claim 4 in which the ester is glyceryl monostearate.

6. A stabilized grease composition according to claim 4 in which the fatty acid constituent of

the lime soap is a mixture of saturated fatty acids from a hydrogenated fatty oil.

7. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, 6-30% lime soap, about 1-3% castor oil, and about 0.5-1.9% esters of a higher fatty acid and a polyhydric alcohol, said esters being of the group consisting of partial esters and esters containing ether linkages.

8. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, an amount of lime soap sufficient to impart to said mineral oil the consistency of a grease, about 0.4-0.8% free higher fatty acid, about 1-3% castor oil, and about 0.5-1.9% esters of a higher fatty acid and a polyhydric alcohol, said esters being of the group consisting of partial esters and esters containing ether linkages.

9. A stabilized grease composition according to claim 8 in which the ester is glyceryl monostearate.

10. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, about 6-30% lime soap, about 0.4-0.8% free higher fatty acid, about 1-3% castor oil, and about 0.5-1.9% esters of a higher fatty acid and a polyhydric alcohol, said esters being of the group consisting of partial esters and esters containing ether linkages.

11. A method of preparing a stabilized grease composition which comprises heating a mixture of mineral oil, high molecular weight fatty acids, and a proportion of lime to yield an excess of fatty acid of from 0.4-0.8%, the amounts of high molecular weight fatty acids and lime used being sufficient to impart to said mineral oil the consistency of a grease, heating at a higher temperature to drive off any water and to form an anhydrous soap base with the mineral oil present, adding an ester of a higher fatty acid and a polyhydric alcohol, adding more mineral oil, cooling and agitating the mixture until the mixture no longer stiffens under continued agitation, adding a small amount of castor oil, and drawing the lubricant at a temperature below 200° F.

12. The method of claim 11 in which the ester is glyceryl monostearate.

13. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, about 6-30% lime soap, and a minor proportion of a stabilizing mixture consisting of castor oil and an ester of a higher fatty acid and a polyhydric alcohol, said ester being of the group consisting of partial esters and esters containing ether linkages.

14. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, about 6-30% lime soap, and a minor proportion of a stabilizing mixture consisting of free higher fatty acid, castor oil, and a polyhydric alcohol, said ester being of the group consisting of partial esters and esters containing ether linkages.

15. A stabilized grease composition comprising a homogeneous mixture of a mineral oil, an amount of lime soap of high molecular weight fatty acids sufficient to impart to said mineral oil the consistency of grease, and a minor proportion of a stabilizing mixture consisting of 0.4-0.8% free higher fatty acid, castor oil, and an ester of a higher fatty acid and a polyhydric alcohol, said ester being of the group consisting of partial esters and esters containing ether linkages.

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