Patented Dec. 1, 1942 2,303,558

UNITED STATES PATENT OFFICE

2,303,558

PREMIUM CUP GREASE OF IMPROVED HEAT AND TEXTURE STABILITY

Gus Kaufman and Robert S. Barnett, Beacon, N. Y., assignors, by mesne assignments, to The Texas Company, a corporation of Delaware

No Drawing. Application August 10, 1940, Serial No. 352,116

13 Claims. (Cl. 252—39)

This invention relates to lubricants and more particularly to anhydrous lime soap greases of wide adaptability and to methods of preparing anhydrous lime soap greases.

Ordinary 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 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 temperatures at or above their melting points, or even below their melting points, because of loss of stabilizing water. Such greases are unsuited 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 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.

It is an object of the present invention to provide a premium grade lime soap grease, having a wider field of use than ordinary cup grease, which has a substantially higher melting point of the order of 220° F. and above, which is heat stable and does not break down at temperatures even above the melting point up to 300° F. and above, and which has improved storage stability against texture changes, formation of hard crusts, etc.

A further object of the invention is to provide an improved lime soap grease of this character which is anhydrous, substantially free from glycerine, prepared from fatty acids of the character adapted to impart higher melting points and other improved characteristics to the product, and stabilized with high boiling, non-volatile organic stabilizers of such character or in such proportions and combinations as to impart superior storage and heat stability and other advantages, as more fully pointed out hereinbelow.

In our copending application Serial No. 261,772, filed March 14, 1939, now Patent No. 2,246,467, dated June 17, 1941, of which this application is a continuation-in-part, we disclose and claim an improved cup grease comprising a naphthene base lubricating oil, lime soap, lanolin, and an ester of a higher fatty acid and a polyhydric alcohol, such as glyceryl monostearate. It is an object of this invention to further improve the composition of said copending application.

The improvements in the composition of the present invention over the composition of the copending application have resulted from the recognition that a carefully controlled and critical proportion of high molecular weight free fatty acid in the lubricant materially affects its characteristics. Certain modifications have also been made in the proportions of the stabilizing agents.

The improved lubricant of this invention comprises a petroleum oil, lime soap, and, as stabilizing agents, mixtures of lanolin, esters of higher fatty acids and polyhydric alcohols, and free fatty acid. The petroleum oil, as more fully pointed out hereinafter, is not restricted to naphthene base oils, as in the prior application, but paraffin base oils or mixed base oils may be used.

In the manufacture of the lubricant or grease of this invention, fatty acids are employed for the production of lime soaps rather than fats or fatty oils, in order to avoid the liberation of glycerine which would be mainly non-volatile and retained in the product at the temperature 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 by the combination of stabilizers employed in accordance with our invention, we have found that a superior product having a higher melting point, increased heat stability, and 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	4 (max).
Titer, °C.	54.6	54–56

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 proportion 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 should 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%. However, 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.

The free acid in the composition may be incorporated by adding a deficiency of lime, as above disclosed, or the proportion of 0.4 to 0.8% of any of the above-enumerated fatty acids may be added to a composition containing neutral soap. This proportion of free fatty acid, in combination with the other stabilizers, lanolin and esters of higher fatty acids and polyhydric alcohols, has been found to materially improve the characteristics of the product as discussed more fully below.

By the term "free fatty acid" as appearing throughout the specification and claims unless otherwise stated is meant the amount of free fatty acid as determined by the following method of analysis: A 2–10 gram sample of the grease is weighed in a 250 ml. Erlemeyer flask, smearing the grease along the inside of the flask with a glass rod to facilitate disintegration. To this is then added 100 ml. of a neutral mixture of equal volumes of benzene and 98% isopropyl alcohol and some glass beads to further facilitate disintegration. The sample is then agitated or heated under a reflux condenser until disintegrated, cooled to room temperature, and the free acid promptly titrated with 0.1 N alcoholic potassium hydroxide using phenolphthalein as the indicator. It is preferable to effect a disintegration of the greases at room temperature wherever possible because lower free fatty acids of greater reactivity may be present and the higher temperature may accelerate their interaction with free alkali simultaneously present. Some greases are particularly difficult to disintegrate and on such greases it has been found helpful to add the benzene component alone, reflux for a few minutes and then add the isopropyl alcohol component and continue in the usual manner. The free acid is calculated in terms of oleic acid.

By the term "lanolin," it is to be understood that we contemplate the various purified and semi-purified greasy materials obtained from the washing of wool, including neutral degras and wool fat, and the commercially purified product sold under the name of lanolin. As examples of suitable types of lanolin that are commercially available we mention such products as Rowag No. 2, "A" Anhydrous Lanolin, and Anhydrous Lanolin U. S. P. Typical tests of "A" Anhydrous Lanolin are the following:

Neutralization number	1.48
Iodine number	45
Free fatty acid, per cent (A. S. T. M. method B)	0.74
Water	None

The third stabilizer to be used according to our 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, polyglycerines and polyglycols. Suitable esters of glycerine and glycols are the partial esters containing free hydroxy groups, but in the case of the polyglycerines and polyglycols, which are polyhydric alcohols containing ether linkages, both the partially esterified and the 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, New York, N. Y., as "Glyceryl Monostearate S," which has the following characteristics:

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

While it has heretofore been proposed to employ glyceryl monostearate in a proportion of 2–8% as a stabilizer for a lime soap grease, we have found that unusually superior results in the manufacture of a premium grade cup grease of the anhydrous and glycerine-free type are obtained by the use of somewhat smaller percentages of glyceryl monostearate of the order of 0.5–1.9% when used in combination with lanolin and free fatty acids as additional stabilizing agents. Lubricants which have been found

to be particularly effective have the following percentage composition:

	Per cent by weight
Lime soap	6–30
Ester stabilizer	0.5–1.9
Lanolin	1–3
Free fatty acids	0.4–0.8
Mineral lubricating oil	Balance

In the manufacture of greases of this type, the fatty acids and a portion of the mineral lubricating 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 added slowly with continued heating and agitation to effect the formation of lime soaps, the temperatures being maintained at about 160–180° F. until a smooth paste or liquid is obtained. Heating and agitation are then continued while raising the temperature gradually up to about 260–280° 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 lubricating oil employed. The remainder of the lubricating oil is added slowly in stepwise portions 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 levelling off or a rise of 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 lanolin 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 lubricating oil, keeping the proportion of stabilizers within the required range.

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 levelling off or rise of temperature, signifies that a novel change takes place, which, to the best of our knowledge, has never before been encountered in grease manufacture. In the ordinary grease manufacturing processes, continued stirring results in a thinning of the grease. We believe that the levelling off or rise of temperature, which represents an evolution of heat, is, perhaps, the result of a sudden 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.

It has also been noted that the free fatty acid content drops markedly when the grease passes from the soft stage to the stiff stage, possibly indicating that some of the neutralization of acid is not due to soap formation but to a binding or association of the free carboxyl groups in the formation of the characteristic structure of the grease. No matter what explanation is given to these phenomena, the resulting grease has a structure which is peculiarly resistant to objectionable hardening during storage. This is a very important advantage in that uniform, texture-stable products can be delivered to the consumer with the satisfaction that the products will retain the same uniform, texture-stable characteristics, irrespective of the time of use.

For the preparation of a No. 5 grade of grease, containing about 24% soap, the amounts of the ingredients may be as follows:

	Pounds
Snodotte acids	100
Hydrated lime (90.4%)	14.05
Water (with charge)	20
Mineral lubricating oil (paraffin base; S. A. E. 20 with charge	180
Added	134
Glycerol monostearate	8.35
Anhydrous lanolin	4.35

The full amount of Snodotte acids and 180 pounds of the lubricating oil are charged to a kettle with all of the lime and water, and heated with stirring at about 160–180° F. until a smooth paste or liquid is obtained. Heating and agitation are then continued while raising the temperature gradually up to about 260–280° F. to effect dehydration. The base becomes progressively clearer as water is removed, and finally is in a clear gel form upon complete or substantially complete dehydration. At this stage, heating is discontinued and 8.35 pounds of glyceryl monostearate cut into small pieces are slowly added. 134 pounds of the lubricating oil are then added slowly in stepwise portions, while the mass is stirred and allowed to cool slowly. In the range of about 220° F. to 190° F. the grease becomes progressively more opaque, adhesive and softer. At about 200° F. any suitable dye may be added, if desired. 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 short time. When there is no further increase in body upon continued stirring, a control penetration is run according to the usual A. S. T. M. method. If the composition is too soft, small amounts of Snodotte acids melted in oil are added to reduce the penetration to about 140. 4.35 pounds of lanolin are then added to give the product a more adhesive texture and glossy appearance. The product may then be drawn at about 160–170° F. as the No. 5 grade.

To prepare a No. 3 grade of grease, enough lanolin is added to the No. 5 grade at about 160–170° F. to bring the proportion up to about 2%. Lubricating oil is then added while maintaining the required proportion of stabilizers until a control penetration of about 230 is obtained.

A No. 1 grade may be prepared similarly by adding lubricating oil, while adjusting stabilizer content, until a control penetration of about 280 is obtained, and a 00 grade is prepared by further thinning down to a control penetration of about 340.

Other lubricating oils than the paraffin base oil of the example may be used, and the characteristic texture-stable grease structure discussed above is still obtained. For example, blends of paraffin base and naphthene base oils, and naphthene base oils alone, have been found to be suitable, although it is preferred to use the paraffin base oils alone. The use of a high viscosity

paraffin base lubricating oil, having a viscosity of about 700 seconds at 100° F. Saybolt Universal, results in an improved railway brake cylinder lubricant which is not only heat stable but which has a greatly reduced tendency to swell rubber packings. The hard grades of grease prepared from paraffin base lubricating oil have characteristics, for example, high melting points, which render them eminently suitable for use as water pump greases.

An important feature of novelty is the characteristic structure discussed above which is the result of the use of combinations of the stabilizers, free fatty acid, esters of fatty acids and polyhydric alcohols, and lanolin. The greases prepared in accordance with this invention, in addition to having a uniform, texture-stable structure, which is resistant to long periods of storage, are extremely resistant to high temperatures so that no separation of ingredients or formation of hard crusts occurs at temperatures materially above the ordinary operating temperatures of bearings, even though the greases have melted. Upon cooling from such temperatures the greases return to a buttery texture with no separation.

The term "anhydrous," as used herein, is intended to include composition 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, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. An anhydrous lime soap lubricant free from glycerine comprising mineral lubricating oil, calcium fatty acid soap, and a stabilizing mixture comprising about 0.4 to 0.8% free higher fatty acid, lanolin, 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 lubricant according to claim 1 in which the ester is glyceryl monostearate.

3. A lubricant according to claim 1 in which the calcium fatty acid soap is calcium soap of a mixture of saturated fatty acids from hydrogenated fatty oil.

4. An anhydrous lime soap lubricant free from glycerine comprising mineral lubricating oil, calcium fatty acid soap, about 0.4 to 0.8% free higher fatty acid, about 1–3% lanolin, and about 0.5 to 1.9% 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 lubricant according to claim 4 in which the ester is glyceryl monostearate.

6. A lubricant according to claim 4 in which the calcium fatty acid soap is calcium soap of a mixture of saturated fatty acids from hydrogenated fatty oil.

7. An anhydrous lime soap lubricant comprising mineral lubricating oil, about 6–30% calcium fatty acid soap, about 0.4 to 0.8% free higher fatty acid, about 1–3% lanolin, and about 0.5 to 1.9% 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.

8. A method of preparing an anhydrous lubricant which comprises heating a mixture of mineral lubricating oil, fatty acids, water, and a proportion of lime to yield about 0.4 to 0.8% free fatty acid, heating to drive off the water and form an anhydrous soap base with the mineral oil present, adding an ester of a higher fatty acid and a polyhydric alcohol of the class consisting of esters containing free hydroxyl groups and ether linkages, adding more mineral oil, cooling and agitating the mixture until the composition no longer stiffens upon continued stirring, and drawing the lubricant at a temperature below 200° F.

9. A method of preparing an anhydrous lubricant which comprises heating a mixture of mineral lubricating oil, fatty acids and a proportion of lime to yield an excess of fatty acid of from 0.4 to 0.8%, heating at a higher temperature to drive off any water to form an anhydrous soap base with the mineral oil present, adding an ester of a higher fatty acid and a polyhydric alcohol of the class consisting of esters containing free hydroxyl groups and ether linkages, adding more mineral oil, cooling and agitating the mixture until the mixture no longer stiffens upon continued agitation, and drawing the lubricant at a temperature below 200° F.

10. A method of preparing an anhydrous lubricant which comprises heating a mixture of mineral lubricating oil, fatty acids and a proportion of lime to yield an excess of fatty acid of from 0.4 to 0.8%, 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 of the class consisting of esters containing free hydroxyl groups and ether linkages, adding more mineral oil, cooling and agitating the mixture until the mixture no longer stiffens upon continued agitation, adding a small amount of lanolin, and drawing the lubricant at a temperature below 200° F.

11. The method of claim 10 in which the ester is glyceryl monostearate.

12. A method of preparing an anhydrous lubricant which comprises heating a mixture of mineral lubricating oil, fatty acids and a proportion of lime to yield an excess of fatty acids of from 0.4 to 0.8%, heating at a higher temperature to drive off any water present and to form an anhydrous soap base with the mineral oil present, adding an ester of a higher fatty acid and a polyhydric alcohol of the class consisting of esters containing free hydroxyl groups and ether linkages, adding more mineral oil, cooling and agitating until the mixture no longer stiffens upon continued agitation, adding a small amount of lanolin, thinning to the desired consistency with mineral oil, and drawing the lubricant at a temperature below 200° F.

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

GUS KAUFMAN.
ROBERT S. BARNETT.