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STABILIZED CALCIUM FATTY ACID BASE GREASE

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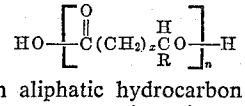
This invention relates to novel anhydrous calcium fatty acid greases. More particularly, this invention discloses a novel additive that stabilizes anhydrous calcium fatty acid greases.

Anhydrous calcium fatty acid greases require the presence of a stabilizer such as glycerol monostearate or calcium acetate to prevent separation of the components. This invention involves the discovery of a novel stabilizer for calcium fatty acid greases which has the additional advantage of increasing grease yields.

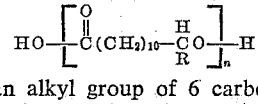
The anhydrous calcium base grease compositions of this invention comprise an oleaginous lubricating base as the major component, a calcium salt of a C_{12} to C_{24} fatty acid as the thickening agent and 0.5 to 3.0 weight percent estolide of a C_{12} to C_{24} hydroxy fatty acid. It is necessary to shock cool the estolide-containing calcium fatty acid greases of this invention from a temperature of 190 to about 100° F. in order for the estolide to act as a stabilizer.

The use of an estolide of a hydroxy fatty acid as a stabilizer for calcium fatty acid greases has the additional advantage that the preferred estolide concentration effects a substantial improvement in the yield of a calcium fatty acid base grease. Estolide concentrations falling between 1 and 2.5 weight percent of the total grease composition substantially harden the grease mixtures so that it is possible to obtain the desired grease grade with less soap concentration. The action of the estolides in calcium fatty acid base greases in this respect is similar to their action on sodium fatty acid base greases as disclosed in the commonly assigned copending application Serial No. 533,232, filed September 8, 1955, by J. R. Roach, J. F. Lyons and J. P. Dilworth.

The estolides which act as stabilizers for the anhydrous calcium fatty acid greases of this invention are intermolecular esters and polyesters of C_{10} to C_{24} hydroxy fatty acids having the following general formula



wherein R is an aliphatic hydrocarbon radical containing 1 to 21 carbon atoms, x is an integer having a value of 1 to 21 and n is an integer having a value of 2 to about 12. The average molecular weight of these estolides is in the range of 500 to 3500. The estolide of 12-hydroxy stearic acid, the most widely used and readily available hydroxy fatty acid, has the following general formula



wherein R is an alkyl group of 6 carbon atoms and n is an integer having a value of 2 to 12. The estolides are formed by heat treatment of 12-hydroxy stearic acid at temperatures between 200 and 300° F. and subsequent extraction of the estolides from the heat-treated hydroxy stearic acid with an aliphatic hydrocarbon solvent such as hexane. The preferred estolides of 12-hydroxy stearic acid have an average molecular weight between 800 and 3000, indicating that the estolide fraction comprises mainly trimers, tetramers, pentamers and hexamers.

The minimum estolide concentration required for stabilization of the anhydrous calcium fatty acid greases is 0.5 weight percent of the total grease composition. The upper concentration limit is placed at 3 weight percent of the total grease composition because higher concentrations of estolide result in decrease of the grease yield. The preferred estolide concentration for both stabilization and yield increase falls between 1.0 and 2.5 weight percent of the grease composition.

Grease stabilization and hardening are effected whether the estolide, in the prescribed amount, is added during the grease manufacture or to the finished grease. Regardless of whether the estolide is added with the charge, after dehydration or to the grease mixture on reheating to 320° F., stabilization and hardening are obtained as long as the estolide-containing grease mixture is shock cooled from 190 to about 100° F. When the estolide is added to a mixture of oil and calcium soap, which has separated because of the absence of stabilizer, stabilization is obtained by heating the estolide-containing mixture to about 300° F. with stirring to effect uniform distribution of the estolide throughout the grease mixture, cooling to about 200° F. without regard to the rate of cooling, and then shock cooling from about 190 to about 100° F.

If excess calcium hydroxide is present during the manufacture of the grease, the calcium salt of the estolide is present in the finished grease composition. The estolides and the calcium salts are equivalent in function in producing a stable product and in improving the yield.

A surprising feature of this invention is the necessity of shock cooling the grease from a temperature of about 190 to about 100° F. in order to produce a stable product. Shock cooling denotes cooling at an average rate above 2° F. per minute.

Cooling of the grease mixture from 190° F. can be effected in a number of ways. One procedure involves drawing the grease into shallow cooling pans. Another procedure involves passing the grease over a heat exchange surface in a thin film. The use of a shallow cooling pan is the most convenient procedure for obtaining the shock cooling necessary in this invention.

The remaining procedure for preparing the grease products of this invention is conventional. A recommended procedure involves mixing oleaginous lubricating base, fatty acid, lime and a small amount of water, saponifying the mixture at a temperature about 160 to 200° F. and dehydrating the saponified mixture at a temperature in the range of 270 to 320° F. The remainder of oleaginous lubricating base is added during stirred cooling of the grease to a temperature above 190° F. at which time the grease is drawn and shock cooled as described above.

The thickening agents of the grease compositions of this invention are calcium soaps of fatty acids containing 12 to 24 carbon atoms. Although the calcium soaps can be prepared from fats and fatty oils, the fatty acids per se are preferably employed. Calcium salts of hydroxy fatty acids are specifically excluded from the thickening agents contemplated in this invention. Examples of fatty acids that are used in this invention are stearic acid, myristic acid, palmitic acid, arachidic acid, behenic acid, lauric acid, oleic acid and mixtures thereof.

The concentration of the calcium soap varies within wide limits depending upon the grade of grease desired. In general, the soap concentration falls within the range of 5 to 30 percent of the total grease composition with

concentrations between 6 and 15 percent usually being employed.

The oleaginous lubricating base may be a conventional mineral lubricating oil, a synthetic lubricating oil prepared by cracking and polymerizing products of the Fischer-Tropsch process and the like or a synthetic oleaginous compound possessing lubricating characteristics and having an SUS viscosity within the lubricating oil viscosity range. The oleaginous base is usually a conventional mineral lubricating oil because of the cost factor, but a synthetic base material can be substituted in all or in part therefor.

The mineral lubricating oils can be a distillate or residual oil and can be derived from a paraffin base, naphthene base or mixed paraffin-naphthene base crude. These mineral lubricating oils are subjected to greater or lesser degrees of refining and solvent dewaxing, depending upon the use intended for the grease composition. Broadly speaking, the greases of this invention can be formulated with mineral lubricating oils having an SUS viscosity at 100° F. between 50 and 1000, but are usually prepared with base oils having an SUS viscosity at 100° F. between 50 and 300.

The synthetic lubricating bases are usually of the ester or ether type. High boiling esters of aliphatic dicarboxylic acids find particularly wide-spread use in greases adapted for extreme temperature lubrication, that is, lubrication at both high and low temperatures. Examples of the synthetic polyester lubricating bases are: di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, di-n-amyl sebacate, di-2-ethylhexyl adipate, and di-n-nonyl azelate. Polyalkylene ethers such as polyethylene glycol, polypropylene glycol, modified by etherification and esterification of the terminal hydroxy radicals, are also useful synthetic lubricating bases.

Additives to impart anti-oxidant and extreme pressure properties may be incorporated in the greases of the invention. Aromatic amine type inhibitors have been found particularly effective anti-oxidants; aromatic amines such as N,N,N',N'-tetramethyl 4,4'-diamino diphenyl methane, diphenyl amine and phenyl alphanaphthyl amine are preferred. Extreme pressure additives which may be incorporated in the greases are sulfurized fats, sulfurized oils, chlorinated organic compounds such as chloro-substituted waxes, chloro-substituted aromatic compounds and chlorinated olefin polymers and sulfo-chlorinated compounds such as sulfo-chlorinated olefin polymers and olefins derived from waxes.

The concentration of oleaginous lubricating bases varies between 60 and 94 percent of the total grease composition and usually falls between 85 and 90 percent of the composition.

The following examples demonstrate that the presence of estolides stabilizes calcium fatty acid greases and improves the yields thereof when present in the preferred amount. The necessity of shock cooling the grease from a temperature of 190° F. is also demonstrated in the following examples.

Example 1

An attempt was made to prepare anhydrous calcium stearate grease without the presence of a stabilizer in a paraffin base distillate oil having an SUS at 100° F. of about 330. This attempt was unsuccessful because the calcium soap separated from the oil on cooling regardless of the cooling procedure employed.

Example 2

Using the same oil, an attempt was made to prepare a stable calcium stearate grease employing as a stabilizer an estolide of 12-hydroxy stearic acid having an average molecular weight of about 2500. To this end 1430 grams of stearic acid, 131 grams of estolide, 222 grams of lime and 2.5 lbs. of water were added to 3.5 lbs. of the afore-identified paraffin base oil. After saponification at a temperature of 180 to 200° F. for 4 hours, the grease mixture was dehydrated at a temperature of 270 to 275° F. for 3 hours. The remainder of the paraffin base oil, namely 19.3 lbs., and 64 grams of diphenylamine were added as the mixture was slowly cooled at about 0.12° F. per minute to about 190° F. The mixture was allowed to cool statically from 190° F. to room temperature from midnight to 8:00 a. m. in the kettle. The mixture separated into soap and oil on standing.

Example 3

This example was a duplicate of Example 2 with the exception that the estolide-containing grease mixture was shock cooled. A reaction mixture was formed comprising 1430 grams of stearic acid, 131 grams of estolide, 222 grams of lime, 2.5 lbs. of water and 3.5 lbs. of paraffin base oil. The reaction mixture was saponified at a temperature of 180 to 200° F. for 4 hours and then dehydrated at a temperature of 270 to 275° F. for 3 hours. The remainder of the paraffin base oil, 19.3 lbs., and 64 grams of diphenylamine were added during the stirred cooling at a rate of 0.12° F. per minute to about 190° F. The mixture was drawn into shallow cooling pans having a depth of ¼ to ½ inch and shock cooled from 190° F. to room temperature. The average cooling rate was more than 2° F. per minute. The resulting grease was dark brown, stiff and glossy and became smooth and buttery-like on working. The product was a No. 3 grade grease having a worked penetration of 232. Its composition was as follows:

	Percent by wt.
Calcium stearate	12.4
Calcium soap of estolide	1.3
Excess calcium hydroxide	0.2
Base oil	85.6
Diphenylamine	0.5

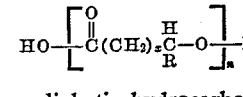
The foregoing examples prove that estolides are effective stabilizers for anhydrous calcium fatty acid greases. They also demonstrate the necessity of shock cooling the grease from a temperature about 190° F. to room temperature in order for the estolide to be an effective stabilizer.

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. A stable anhydrous calcium grease comprising an oleaginous lubricating base as the major component, a calcium salt of a C_{12} to C_{24} unsubstituted fatty acid as the thickening agent and 0.5 to 3 weight percent of a compound selected from the group consisting of an estolide of a hydroxy fatty acid containing 12 to 24 carbon atoms, a calcium salt of said estolide and a mixture thereof said estolide having an average molecular weight between 500 and 3500 said grease having been shock cooled from a temperature of 190° F. to about 100° F.

2. An anhydrous calcium base grease according to claim 1 in which said estolide has the following general formula



wherein R is an aliphatic hydrocarbon radical containing 1 to 21 carbon atoms, x is an integer having a value of 1 to 21 and n is an integer having a value of 2 to about 12.

3. An anhydrous calcium base grease according to claim 1 containing 1 to 2.5 weight percent estolide.

4. An anhydrous calcium base grease according to claim 1 in which the thickening agent is calcium stearate and the estolide is derived from 12-hydroxy stearic acid

and has an average molecular weight of between 800 and 3000.

5. A process for preparing a stable anhydrous calcium grease of a C_{12} to C_{24} unsubstituted fatty acid which comprises adding a compound selected from the group consisting of estolides, calcium salts thereof and mixtures thereof, said estolide being derived from a hydroxy fatty acid containing 12 to 24 carbon atoms and having an average molecular weight between 500 and 3500 to an anhydrous grease mixture, comprising an oleaginous lubricating base and the calcium soap of said C_{12} to C_{24} fatty acid as the thickening agent, heating the resulting grease mixture to a temperature of about 300° F., cooling said mixture to a temperature of about 190°

F. and shock cooling said mixture from a temperature of 190° F. to about 100° F.

6. A process according to claim 5 in which said shock cooling is effected by drawing said grease at a temperature of 190° F. into shallow cooling pans.

7. A process according to claim 5 in which the mixture is cooled from 190° F. to about 100° F. at an average rate above 2° F. per minute.

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