

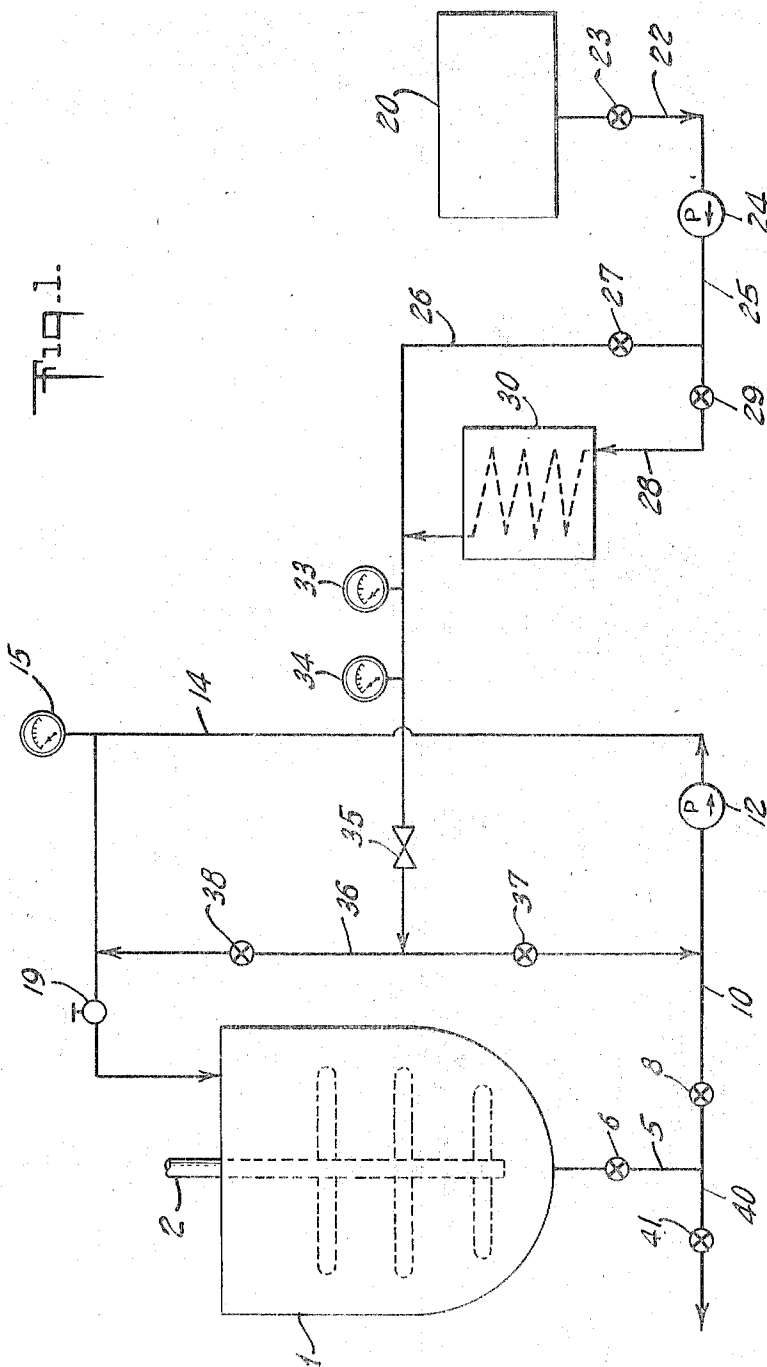
March 22, 1966

F. T. CROOKSHANK ET AL
METHOD OF GREASE MANUFACTURE

3,242,083

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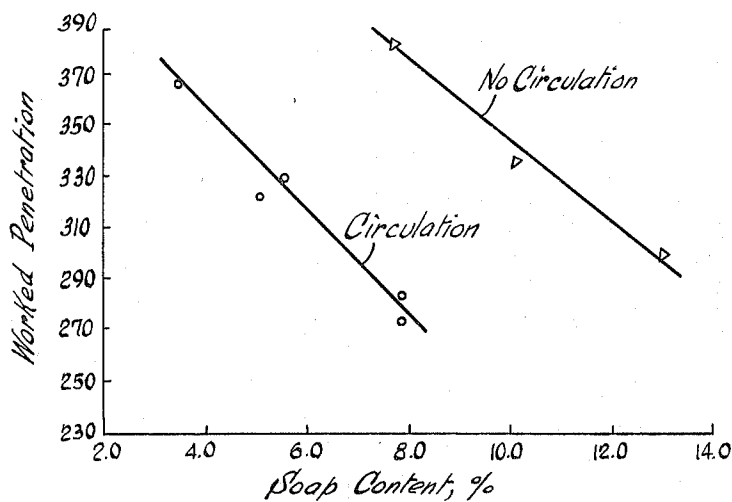
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Fig. 2.



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METHOD OF GREASE MANUFACTURE

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8 Claims. (Cl. 252—39)

This invention relates to improvements in the manufacture of lubricating greases. More particularly, it relates to an improved method for the manufacture of anhydrous calcium hydroxy fatty acid soap thickened greases.

Calcium hydroxy fatty acid soap thickened greases are very difficult to prepare in satisfactorily smooth form by the low temperature processes of the prior art, due to the tendency of these greases to form lumpy or grainy products. Very close control of the operating conditions is therefore required in the preparation of these greases. In addition, the low temperature methods of the prior art have the serious economic disadvantage of requiring very long manufacturing times, due primarily to the slow heating required in order to avoid local overheating and partial melting of the soap and the slow addition of oil required during the cooling step.

The present invention provides a means of consistently obtaining smooth grain-free and lump-free calcium hydroxy fatty acid soap thickened greases in substantially improved yields, amounting to a reduction in the soap content for a given grade of about 30 percent or more. By operating under the conditions comprising the preferred embodiment of the invention these advantages are obtained in combination with a large reduction in the manufacturing time required. The invention is employed with special advantage in the manufacture of greases containing paraffinic oils as the oil component, such greases being particularly difficult to prepare in satisfactorily smooth form.

The method of this invention involves essentially subjecting the grease mixture comprising calcium hydroxy fatty acid soap and lubricating oil in a relatively high oil-soap ratio to continuous shearing during the heating cycle following the saponification step, and very advantageously during the cooling cycle also. The shearing is suitably carried out by continuously recirculating the grease mixture through a recycle line containing a shear valve operated with a substantial pressure drop across the valve, such as from about 20 to 200 pounds per square inch, preferably from about 25 to about 125 pounds per square inch.

Circulation of the grease mixture through the shearing means is carried out for a minimum period of about 15 minutes while the mixture is at a temperature in the range from about 200° F. up to the maximum temperature on the heating cycle, and at a rate such that the weight of recirculated grease mixture during the heating in this temperature range is equal to at least about 5 times the total weight of grease mixture, i.e., a minimum of 5 complete batch turnovers. It is preferably carried out so as to give at least about 10 batch turnovers during the heating cycle and about 5 batch turnovers while the grease mixture is being heated from about 225° F. to about 275° F. Very advantageously, the recirculation with shearing may be carried out during other stages of the process also. In some cases, it may be desirable to carry out the grease making process with continuous recycle and shearing of the grease mixture during both the heating cycle including the saponification step and the cooling cycle.

The grease mixture before cooling preferably comprises

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lubricating oil and soap in a weight ratio of at least about 4:1, respectively, and most advantageously from about 5:1 to about 10:1, by weight, respectively, although higher oil-soap ratios may be employed in some cases, such as up to about 15:1 or higher, particularly in the preparation of greases containing less than about 5 percent by weight of soap. The grease mixture may be prepared by saponifying a saponifiable material in an amount of lubricating oil sufficient to give an oil-soap ratio in the desired range, or, as described hereinbelow, the saponification may be carried out in a smaller amount of oil and additional oil in an amount sufficient to provide the desired oil-soap ratio before cooling added after the saponification and substantial dehydration, preferably without any substantial cooling of the grease mixture.

The preferred embodiment of this invention comprises continuously recirculating the grease mixture through a recycle line on the grease making zone during the heating and cooling cycles with shearing of the recirculated stream of grease mixture during at least part of the heating cycle as described above, and with introduction of additional oil during the cooling and preferably during the heating cycle also into the recirculating stream of grease mixture, as described in copending application Serial No. 282,330 of L. F. Badgett, W. R. Hencke and F. T. Crookshank, filed of even date herewith.

FIG. 1 is a diagrammatic illustration of one form of apparatus suitable for making greases in accordance with the preferred embodiment of our invention.

FIG. 2 is a chart showing the yield improvements obtainable by the method of our invention over those obtained in preparations of calcium hydroxy fatty acid soap thickened grease by the conventional low temperature procedures.

Referring in more detail to FIG. 1, numeral 1 represents a jacketed grease kettle equipped with a stirrer 2 and adapted to be heated to temperatures up to at least about 350° F. In carrying out the grease preparation, the grease kettle is charged with saponifiable material, lubricating oil and a base such as calcium oxide, calcium hydroxide or calcium carbonate in approximately the stoichiometric amount required to react with the saponifiable material. If desired, a small excess of the calcium compound may be employed, such as to give a grease containing up to about 0.5 percent by weight of free alkalinity. The charge may also contain water, such as in a weight ratio with the calcium base up to about 3:1, respectively, although water is ordinarily not required. These materials may be introduced into the kettle in any desired order. The oil and saponifiable material are suitably employed in a weight ratio from about 1:1 up to about 6:1 respectively, preferably in about a ratio from about 2:1 to about 4:1. The kettle contents are heated with stirring until saponification and dehydration are substantially complete, as shown by the cessation of foaming, and then heated further to a higher temperature to complete the dehydration and to condition the soap.

The maximum temperature to which the great mixture is heated is ordinarily in the range from about 250° F. to just below the melting point of the soap. In grease preparations employing paraffinic oils as the oil component, the grease mixture is preferably heated at a maximum temperature at least 10° F. below the melting point of the soap, or at a maximum temperature of about 275° F. in the preparation of calcium 12-hydroxystearate thickened greases from paraffinic oils. The heating time in the range above about 250° F. until the beginning of the cooling cycle is ordinarily at least about 15 minutes, the total heating time following the saponification being at least about 30 minutes, and preferably at least about 1 hour.

During the heating cycle and before the grease mixture has been heated to the maximum temperature, recirculation of the grease mixture around kettle 1 is begun by turning valves 6 and 8 to the open position and starting pump 12. The grease mixture passes through line 5, containing valve 6, line 10 containing valve 8, pump 12, and line 14 containing pressure gauge 15 and shear valve 19, which is suitably a gate valve. Valve 19 is located a sufficient distance from kettle 1 to avoid spraying of the grease mixture into the kettle when the valve is operated under a back pressure, suitably a distance equal to at least about 12 times the diameter of pipe 14. Lines 5, 10 and 14 may be jacketed or otherwise provided with means for applying additional heating or cooling to the recirculating stream of grease mixture. The shear valve is suitably a gate valve, set in a partly closed position so as to give a pressure drop of about 20–200 pounds per square inch across the valve. Recirculation through the recycle line may be begun during or before the saponification step and carried out continuously throughout the grease making process, with valve 19 operated with a pressure drop throughout the process or in a wide open position during a portion of the process.

Circulation of the grease mixture through the recycle system during the heating cycle following the saponification step is carried out at a rate sufficient to give one batch turnover within about 22 minutes, such as in about 0.3–22 minutes, and preferably in about 0.4–15 minutes, based on the weight of the grease mixture during the heating cycle, or in about 0.25–15 minutes, and preferably 0.3–12 minutes, based upon the average weight of grease mixture during the heating cycle when the process is carried out with additional oil added during the heating cycle as described hereinbelow. Recycling during the cooling cycle is suitably carried out at a rate sufficient to provide a batch turnover in about 0.5–35 minutes, and preferably in about 1–20 minutes, based on the weight of the finished grease, or in about 0.4–27 minutes, and preferably about 0.5–17 minutes, based on the average weight of grease mixture during the cooling cycle.

Cooling of the grease mixture is carried out by cutting off the heat to the kettle and to the recycle line, if such additional heating is employed, and introducing lubricating oil from tank 20 into the recirculating stream of grease mixture. The added oil is at a temperature substantially below that of the grease mixture, such as at least about 100° F., and preferably at least about 150° F., below the temperature of the grease mixture at the beginning of the cooling step. The lubricating oil passes from tank 20 into line 36 by way of line 22 containing valve 23, pump 24, line 25 and line 26 containing valve 27, dial thermometer 33, pressure gauge 34 and valve 35. Valve 35 is preferably a one way valve, most suitably of a type designed to prevent gravity flow of oil through pump 24 when the pump is not operating, such as a diaphragm controlled reducing valve or a spring loaded check valve. In line 36, the oil may pass into the recirculating stream of grease mixture at the intake of pump 12 by passing through valve 37 into line 10, or into the grease mixture at the discharge side of pump 12 by passing through valve 38 into line 14. It is preferably passed into the grease mixture at the intake side of pump 12 in order to obtain increased mixing and shearing by the action of the pump. The oil may be introduced into the recirculating stream of grease mixture at a rate such that the ratio of the rate of flow of the grease mixture before the point of confluence to the rate of oil injection is from about 1:1, to about 400:1, preferably in a ratio from about 2:1 to about 150:1, and most advantageously in a ratio from about 3:1 to about 50:1, by weight, respectively. During the oil injection, valve 19 is preferably in a partly closed position, such as to give a pressure drop across the valve of about 20–200 pounds per square inch and preferably about 25–125 pounds per square inch.

The cold oil addition is preferably commenced at the

beginning of the cooling step, and may be carried out over the entire cooling period or during only a portion thereof. Additional cooling may be applied to the kettle, and also to the recirculating stream of grease mixture. The amount of lubricating oil added during the cooling may amount to from about 10 to as high as about 90 percent of the total oil contained in the grease. It will usually be from about 25 to about 75 percent of the total oil contained in the grease. When the oil addition is carried out during only a portion of the cooling step, it is advantageous in some cases to continue recirculation of the grease mixture with shearing down to the drawing temperature. The cooled grease mixture is finally drawn through line 40 containing valve 41.

In the grease preparation by the method comprising the particularly preferred embodiment of this invention, the saponification is carried out in the presence of lubricating oil in a ratio of less than 5:1, respectively, with the saponifiable material, and preheated oil is introduced into the recirculating stream of grease mixture during the heating step in an amount sufficient to give an oil-soap ratio of at least about 5:1, and preferably at least 6:1, respectively. The preheated oil is introduced into the recycle line by passing from tank 20 to heater 30 by way of line 22, pump 24, line 25 and line 28 containing valve 29. Heater 30 may be any suitable type of heater, such as a coil heater, as indicated in the diagram. From heater 30 the oil passes into line 26 and is introduced into the circulating stream of grease mixture at either the intake or the discharge side of pump 12 as described hereinabove in connection with the introduction of the oil during cooling. The temperature of the oil added in this manner is preferably substantially higher than that of the grease mixture, and may be up to or even slightly higher than the melting point of the soap in some cases. The rate at which this oil is introduced may suitably be such that the ratio of the rate of recirculation of the grease mixture to the rate of oil injection is within the ranges disclosed hereinabove in connection with the introduction of cold oil during the cooling cycle. The amount of oil added in this manner may be up to about 70 percent of the total oil employed in the grease. It is very advantageously from about 35 to about 65 percent of the total oil contained in the finished grease. A portion of this oil may be added through the kettle top, if necessary, to obtain a grease mixture which is sufficiently fluid to circulate.

The method of this invention produces greases of excellent texture and appearance and in good yields without the necessity of milling the cooled grease. However, in some cases an additional yield improvement is obtained by milling these greases in the usual manner and it may be desirable to carry out a milling step upon such greases, suitably in a colloid mill.

Greases of the so-called rheopectic type are very conveniently obtained by the method of this invention by subjecting the cooled greases at temperatures in the range from about 160° F. to about 240° F. and preferably in about the range 180° F. to 220° F., to stirring in the kettle for a period up to about one hour or longer until a fluid consistency is obtained, ordinarily requiring about 15–30 minutes. Greases prepared by our method soften to a pronounced degree under these conditions involving mild, nonturbulent shearing, and readily harden again upon moderate turbulent shearing of the order to which they are subjected in automotive bearings in service. This characteristic of our greases is apparently due to the longer and more perfectly shaped fibers formed by the recycling which are readily agglomerated by unidirectional mixing to form loose agglomerates which are redispersed at relatively low energy inputs, due to the smooth fiber form. By employing this further step in our process, fluid greases containing about 2–12 percent by weight of calcium hydroxy fatty acid soaps are obtained which harden to N.L.G.I. No. 0–2 grade con-

sistency upon shearing at rates below about 150,000 reciprocal seconds, and ordinarily upon shearing at rates below about 100,000 reciprocal seconds.

The greases which are prepared in accordance with this invention comprise a lubricating oil as the chief component and a minor amount, sufficient to thicken the lubricating oil to a grease consistency, of a calcium soap of a fatty acid material comprising at least about 35 percent by weight of a hydroxy fatty acid material. Preferably the soap comprises at least a major amount, and most suitably at least about 75 percent by weight of a calcium hydroxy fatty acid soap. The amount of calcium soap will ordinarily vary from about 3 percent by weight up to about 30 percent by weight of the composition, although somewhat smaller or larger amounts of soap may be employed in some cases. The method is employed with particular advantage in the preparation of greases thickened with about 5-15 percent by weight of calcium 12-hydroxystearate.

Suitable soap forming hydroxy fatty acid materials which may be employed in the production of these greases are essentially saturated hydroxy fatty acids containing at least 12 carbon atoms and one or more hydroxyl groups separated from the carboxyl groups by at least one carbon atom, and the glycerides and other esters of such acid. The acids preferably contain from about 16 to 22 carbon atoms and one or two hydroxy groups, such as mono- and dihydroxy-stearic, oleic, myristic and palmitic acids. Particularly suitable materials of this character are 12-hydroxystearic acid, the glyceride and the methyl ester thereof. Other acids of this character which may be employed include 9- and 10-hydroxystearic acids and 8-hydroxy palmitic acid. Such hydroxy fatty acid materials may be employed in the saponification in admixture with non-hydroxy saponifiable fatty acid materials, particularly saturated fatty acids containing about 16 to 24 carbon atoms per molecule, and the glycerides of such acids.

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 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 100 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 olefinic dicarboxylic acid diesters, such as di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, di-2-ethylhexyl azelate, di-iso-octyl adipate, etc. However, a lubricating oil which is substantially unreactive under the saponification conditions is preferably employed in the saponification mixture. Lubricating oils employed for this purpose are very suitably mineral oils having viscosities of at least about 300 seconds Saybolt Universal at 100° F., which may be mixtures of lighter and heavier oils.

Various additives of the usual types such as corrosion inhibitors, oxidation inhibitors, extreme pressure agents, anti-wear agents, etc., may be employed in these greases. Suitable oxidation inhibitors include particularly those of the amine type, such as, for example, diphenylamine, phenylalphanaphthyl amine and tetramethyl diamino diphenyl methane. Suitable extreme pressure additives include sulfurized fatty oils and lead soaps, which may be

employed either separately or in combination. Such compounds may be added to the grease mixture during cooling, preferably when the grease mixture is below about 200° F.

The following example is given for the purpose of further disclosing the invention.

EXAMPLE I

A lubricating grease comprising a mineral lubricating oil thickened with calcium 12-hydroxystearate was prepared by the method of this invention employing recirculation with shearing in the manner described below.

The following materials were employed in this preparation: The mineral oil employed was a refined paraffinic distillate oil having a Saybolt Universal viscosity at 100° F. of 346, with about 1 percent by weight of a heavy paraffinic residual oil having a Saybolt Universal viscosity at 210° F. of 658. The saponifiable material employed was a commercial 12-hydroxystearic acid having a neutralization number of 173, a saponification number of 187 and an iodine number of 6.

The equipment employed in the preparation of this grease was a 150 pound capacity steam heated laboratory kettle with auxiliary equipment for grease recirculation with shearing and with hot and cold oil injection into the recycle stream as shown in FIG. 1. The circulation equipment consisted of a 1 1/4 inch pipe connecting the kettle drawoff with a No. 2 Globe Rota Piston pump having a capacity of 1 gallon per 100 revolutions, or 18 gallons per minute, and a 3/4 inch pipe extending from the pump to the top of the kettle, containing a gate valve employed as a shear valve.

Following is a detailed description of the method employed in the grease preparation: The grease kettle was charged with 27 pounds of paraffinic distillate oil, 1.25 pounds of lime, 1.25 pounds of water and 9.0 pounds of 12-hydroxystearic acid. Heating of the kettle contents was begun with stirring and with circulation through the recycle line at a rate of about 130 pounds per minute with the shear valve in the wide open position. The kettle contents were heated gradually up to 225° F. in one hour, at which time the saponification and dehydration were substantially complete as shown by the cessation of foaming. The shear valve was then adjusted to give a pressure drop across the valve of 60 pounds per square inch, and circulation through the valve in this manner continued throughout the remainder of the process. During the heating, beginning when the grease mixture was at 225° F., an additional 45 pounds of the paraffinic distillate oil preheated to 283-296° F. were added at a rate of about 64 pounds per hour, which resulted in bringing the temperature of the grease mixture up to 266° F. in about 42 minutes. The preheated oil was introduced into the recirculating stream of grease mixture at the intake side of the circulation pump. The grease mixture was maintained at 269° F. for one hour and then cooled to 230° F. in 55 minutes with the addition of 37.3 pounds of distillate oil at ambient temperature at a rate of 60 pounds per hour in the same manner as the preheated oil. During the cooling and when the grease mixture was at a temperature of about 240° F., 0.53 pound of diphenylamine and 1.20 pounds of heavy residual oil were added. An additional 10 pounds of paraffinic distillate oil required for correction of the grease grade was added during the finishing. The total manufacturing time without the finishing step was 3 hours and 55 minutes.

The product obtained in the above manner was an N.L.G.I. No. 2 grade grease of excellent texture and appearance. The shear stability and other lubricating properties of this grease were fully equivalent to those greases containing substantially higher soap contents obtained by the conventional procedures. The following table shows results of inspection and service tests upon this grease in comparison with those obtained upon a

grease of the same composition prepared in the conventional manner without circulation or shearing of the grease mixture.

Table I

	Circulation Method	Conventional Manufacture
Soap Content, percent.....	7.3	13.1
ASTM Penetration at 77° F.:		
Unworked.....	249	295
Worked.....	282	296
ASTM Dropping Point, ° F.....	305	299
Shell Roll Test, Penetration change, percent.....	+2.2	-9.2

The above table shows the large yield advantage obtained by carrying out the preparation of the above grease by our process. The amount of soap saving obtained in the above preparation is representative of the results obtained in a large number of laboratory scale grease preparations, including greases of different grades, as shown by FIG. 2. Somewhat lower yields were obtained in plant scale manufacture of this grease employing lower batch turnover rates, a soap content of 9.3 percent being required to produce a grease of the same grade in a representative manufacture of a 10,000 pound batch employing a recycle rate giving a batch turnover in about 7 minutes.

The following table shows the effect of the soap concentration before cooling in our process upon the yield obtained. All of the greases of the table were of the same composition and prepared in substantially the same manner with recycle shearing from 270-275 to finish, except for the difference in the concentration of the soap slurry as shown in the table.

Table II

Oil to Soap Ratio.....	4.7:1	5.6:1	7.5:1
Soap Content, percent.....	8.7	7.5	5.9
ASTM Penetration:			
Unworked.....	274	315	292
Worked.....	317	326	326

EXAMPLE II

A calcium 12-hydroxystearate thickened grease was prepared in substantially the same manner as that described in Example I, with circulation shearing from 223° F. on the heating cycle to the end of the cooling cycle, employing an initial charge comprising oil and 12-hydroxystearic acid in a 4:1 weight ratio and adding additional oil during the heating to give an oil-soap ratio at the top temperature of about 7:1. The grease obtained in this manner was an N.L.G.I. No. 1 grade grease containing 5.8 percent of calcium 12-hydroxystearate.

The above grease was converted to a rheopectic grease by stirring in the kettle at a temperature from 198° F. to 210° F. for 30 minutes, until a fluid product was obtained. This product hardened readily to a grease consistency again upon only a small amount of shearing, the original consistency being restored by circulation shearing for only 5 minutes at a recycle rate of 130 pounds per minute with the shear valve set to give a pressure drop of 60 pounds per square inch. The following tabulation shows the effect of the stirring and of the shearing upon the consistency of this grease.

Original grease:

 ASTM penetration at 77° F.—

 Worked, 60 strokes 333.

After stirring:

 ASTM penetration at 77° F.—

 Unworked Too soft for pene.

 Worked, 60 strokes 375.

5 After circulation shearing:

 ASTM penetration at 77° F.—

 Unworked 304.

 Worked, 60 strokes 333.

10 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.

15 We claim:

1. In a process for preparing a calcium hydroxy fatty acid soap thickened grease comprising the steps of saponifying a fatty acid saponifiable material comprising at least about 35 percent by weight of hydroxy fatty acid material with a calcium base in the presence of at least a portion of the lubricating oil employed in the grease, heating the grease mixture thus obtained to a top temperature in the range from about 250° F. to 275° F., said top temperature being just below the melting point of the said soap and thereafter cooling the grease mixture with the addition of additional lubricating oil at a lower temperature than the grease mixture, the improvement which comprises shearing the grease mixture during the said heating step by recirculating the said grease mixture from a maintained body thereof through a shear valve operated with a pressure drop of about 20-200 pounds per square inch at a rate such that the weight of recirculated grease mixture equals the total average weight of grease mixture during the said heating step in from about 0.25 to about 15 minutes, for a minimum period of about 15 minutes and until the weight of recirculated grease mixture is equal to at least 5 times the total weight of grease mixture.

2. The process of claim 1 wherein the said valve is operated with a pressure drop of about 25-125 pounds per square inch.

3. The process of claim 1 wherein the grease mixture is recirculated at a rate such that the weight of recirculated grease mixture equals the total average weight of grease mixture during the said heating step in from about 0.3 to about 12 minutes.

4. The process of claim 1 wherein the said grease mixture during the said shearing comprises lubricating oil and soap in a weight ratio of at least about 3:1, respectively.

5. The process of claim 1 wherein the said grease mixture before cooling comprises lubricating oil and soap in a weight ratio from about 5:1 to about 10:1, respectively.

6. The process of claim 1 wherein the said lubricating oil is a paraffinic oil.

7. The process of claim 1 wherein the said saponifiable material is chosen from the class consisting of 12-hydroxystearic acid and esters thereof.

8. The process of claim 1 wherein a rheopectic grease is prepared by stirring the cooled product for about 15 to 60 minutes at a temperature in about the range 160-240° F.

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