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METHOD OF GREASE MANUFACTURE

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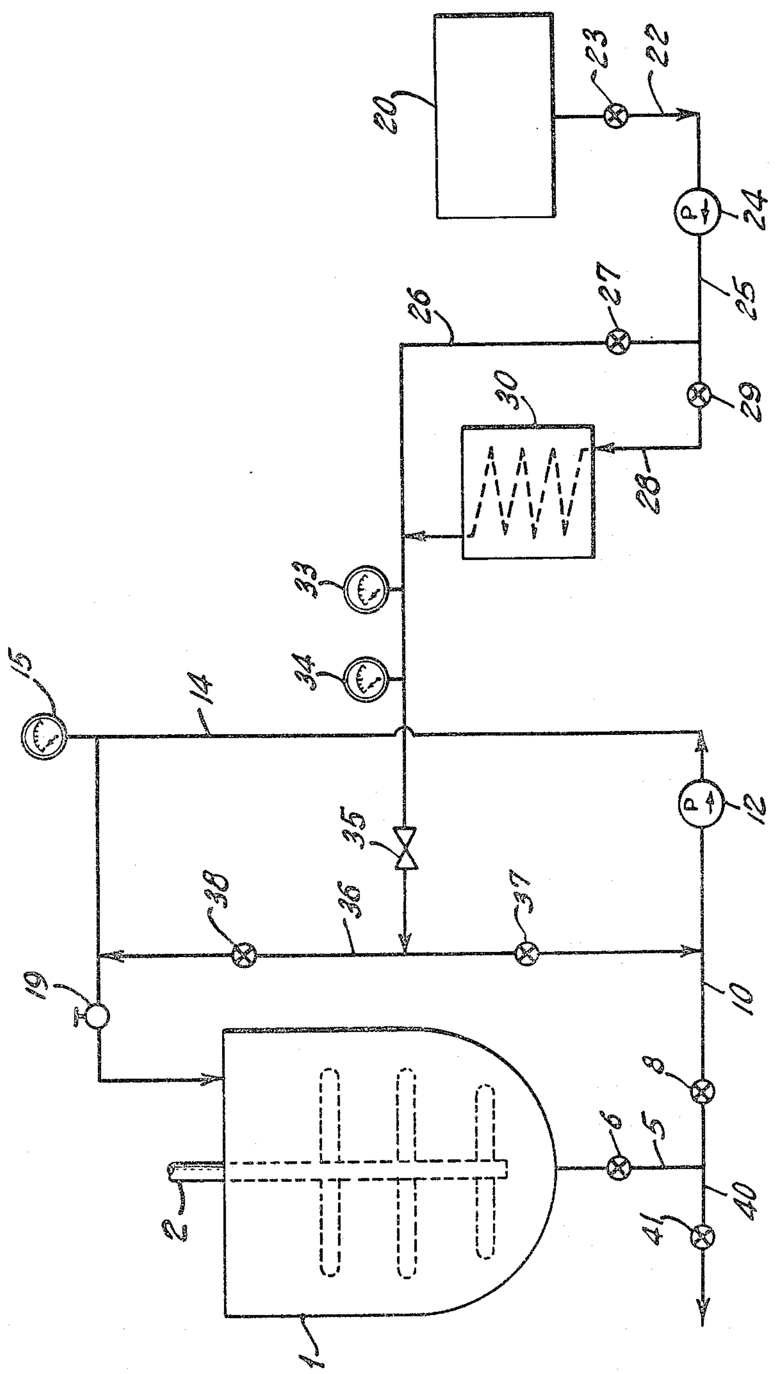

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METHOD OF GREASE MANUFACTURE

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This invention relates to an improved low temperature method for the preparation of soap thickened greases. It relates particularly to an improved low temperature method for the preparation of greases thickened with lithium or calcium soaps of hydroxy fatty acids.

Copending application Serial No. 282,330, filed of even date herewith by L. F. Badgett, W. R. Hencke and F. T. Crookshank, discloses and claims an improved low temperature method of grease manufacture which involves continuously recirculating the grease mixture from a grease making zone through a recycle line with injection of additional oil at a lower temperature into the recirculating stream of grease mixture during the cooling cycle, and preferably with injection of preheated oil during the heating cycle also. By this method, large reductions in the manufacturing times as well as increased yields are obtained.

We have found, in accordance with the present invention, that additional advantages are unexpectedly obtained in carrying out the preparation of soap thickened greases by the above procedure by employing a low temperature holding step following the saponification step in place of or in addition to a holding step at the top temperature, as conventionally employed in low temperature grease preparations. The low temperature holding step is carried out following the saponification and substantial dehydration by holding the grease mixture for a minimum period of about 15 minutes, and preferably for at least about 30 minutes, within the temperature range from about 200° F. to about 240° F. with continuous recirculation through a recycle line. In some cases, particularly in the preparation of greases which are difficult to prepare in satisfactorily smooth form, such as lithium and calcium hydroxy fatty acid soap thickened greases, the grease mixture is preferably subjected to continuous shearing during the low temperature holding step, suitably by means of a shear valve in the recycle line operated with at least a substantial pressure drop across the valve.

By carrying out the preparation of soap thickened greases by the recycle procedure of Badgett et al. with a low temperature holding step as described above, improved yields and product quality are obtained without substantially increasing the manufacturing time, and in some cases even with reduced manufacturing times. The method of this invention is employed with special advantage in the preparation of calcium and lithium hydroxy fatty acid soap thickened greases and particularly in the preparation of such greases containing paraffinic oils as the oil component.

While the reason for the effect of the low temperature holding step in the recycle procedure is not entirely understood, it is known that the recycling has a marked effect upon the soap fiber development, resulting in longer and more dispersed fibers, and it is thought that the effect of the low temperature holding step is due to decreasing the rate of fiber growth which permits an increased effect of the recycling upon the character of the fibers. In the case of greases which tend to form rough or grainy products, shearing during this step prevents the formation of aggregates which are difficult or impossible to redisperse at later stages in the grease making process.

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The figure is a diagrammatic illustration of a particularly suitable apparatus for making greases in accordance with this invention.

Referring in more detail to the figure, numeral 1 represents a jacketed grease kettle equipped with stirrer 2 and adapted to be heated to elevated temperatures above about 350° F. In carrying out the grease preparation, the grease kettle is charged with saponifiable material, lubricating oil and metal base in approximately the stoichiometric amount required to react with the saponifiable material. Water may be added to the charge also, suitably in an amount equal to from about 0.5 to about 10 times the weight of the metal base, although this is usually not required in the preparation of calcium hydroxy fatty acid soap thickened greases and the preparation of lithium hydroxy fatty acid soap thickened greases may be carried out without added water when employing recycling at high recycle rates. The lubricating oil and saponifiable material may be employed in a weight ratio between about 1:2 to about 6:1, respectively, and preferably in a weight ratio from about 1:1 to about 5:1, respectively. The kettle contents are heated in the kettle with stirring until the saponification is complete and the mixture substantially dehydrated and then further heated with recirculation of the resulting grease mixture. Recirculation from the bottom to the top of 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, line 14 containing pressure gauge 15 and shear valve 19, which is suitably a gate valve, and is returned at the top of kettle 1 as shown in the diagram. The circulation is ordinarily begun following the saponification and substantial dehydration and continued throughout the remainder of the process. However, it may be carried out during the saponification also, if desired, to obtain increased mixing of the reactants.

Following the saponification and substantial dehydration, the grease mixture is heated to a temperature in the range from about 200° F. to about 240° F., and maintained at a temperature in this range from about 15 minutes to about 1 hour. The preferred temperature range varies somewhat for different greases, depending principally upon the character of the soap thickener, a temperature range for this step of about 200–235° F. being generally optimum for calcium soap thickened greases and a temperature range of about 220–240° F. being generally optimum for lithium soap thickened greases. Recirculation of the grease mixture through the recycle line in the manner described above is carried out continuously during this holding period at a rate such that the weight of recirculated grease mixture equals the total weight of grease mixture, i.e. one batch turnover, in from about 0.25 to about 15 minutes, preferably in from about 0.25 to about 10 minutes, and ordinarily in from about 0.25 to about 5 minutes.

Recirculation of the grease mixture during the low temperature holding step is very advantageously carried out in some cases with valve 19 in a partly closed position, so as to give a pressure drop of about 10 to 200 pounds per square inch across the valve, and preferably with a pressure drop of about 25 to 125 pounds per square inch across the valve. The preferred procedure comprises shearing in this manner during the holding step carried out for a sufficient period and with recycle rates providing at least 5 batch turnovers, and preferably at least 10 batch turnovers during this heating period. Recirculation with shearing of the grease mixture in this manner may also be carried out at later stages of the grease making process if desired.

Following the low temperature holding step, the grease mixture is heated to a temperature in the range from just below the melting point of the soap to about 75° F. below the melting point of the soap with continued recirculation of the grease mixture. The heating may be accomplished rapidly by introducing preheated oil into the recirculating stream of grease mixture. The oil added in this manner passes from tank **20** to heater **30** by way of line **22** containing valve **23**, pump **24**, line **25** and line **28** containing valve **29**. Heater **30** may be a heater of any suitable type such as a coil heater as indicated in the diagram. From heater **30** the oil passes into 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. From line **26** the oil passes into line **36** and may be introduced into the recirculating stream of grease mixture at the intake side of pump **12** by passing through valve **37** into line **10**, or at the discharge side of pump **12** by passing through valve **38** into line **14**. It is preferably introduced at the intake of pump **12** in order to obtain increased mixing by the action of the pump, except where a light oil is employed which may cause vapor locking of the pump. The oil added in this manner is ordinarily at a temperature substantially higher than that of the grease mixture and may be up to or even slightly higher than the melting point of the soap. This 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. The amount of oil added in this manner may be from about 5 percent up to about 70 percent of the total oil contained in the finished grease. In the preparation of lithium hydroxy fatty acid soap thickened greases it is preferably not above about 50 percent, and most suitably from about 10 to about 30 percent by weight of the total oil employed in the grease.

Circulation of the grease mixture through the recycle system during the heating cycle following the low temperature holding 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 0.25–10 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 step as described hereinbelow. The use of a low temperature holding step in accordance with this invention is particularly advantageous as a means of obtaining the desired yields and product quality in the process carried out with relatively low recycle rates during the heating step, such as those requiring at least about 5 minutes for a batch turnover. 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.

In some cases, it is desirable to employ a high temperature holding step in addition to the low temperature holding step described above. Such a step is carried out by maintaining the grease mixture at a temperature in the range from just below the melting point of the soap down to about 75° F. below the melting point of the soap for a period from about 15 minutes to 1 hour, or longer if desired. It is preferably carried out at a temperature in the range from just below the melting point of the soap down to about 50° F below the melting point of the soap. The total heating time from the end of the saponification step to the beginning of the cooling step will ordinarily be in the range from about ½ hour to about 4 hours, and under the preferred conditions, in the range from about 1 to 3 hours.

Cooling of the grease mixture is carried out with the introduction of lubricating oil at a relatively low temperature, 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, into the recirculating stream of grease mixture. The lubricating oil passes from tank **20** into line **36** by way of line **22**, pump **24**, line **25** and line **26**, bypassing heater **30**. In line **36**, the lubricating oil may pass through valve **37** into the stream of grease mixture at the inlet side of pump **12** or through valve **38** into the stream in the discharge side of pump **12** as described above in connection with the introduction of preheated oil. The 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 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. The rate of oil addition 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 injection of preheated oil during the heating cycle. 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. Additives may be added to the grease mixture when it has been cooled to a suitably low temperature, ordinarily at below about 250° F. The grease mixture is finally drawn from the kettle through line **40** containing valve **41**.

The metal base employed in the saponification may be a hydroxide or other suitable compound of any of the metals ordinarily employed as the metal component of soaps in grease making, such as sodium, lithium, potassium, calcium, barium, magnesium, zinc, cobalt, manganese, aluminum, lead, etc. as well as mixtures of two or more metals. It is preferably a metal oxide, hydroxide or carbonate. The greases which are most advantageously prepared by the method of this invention are those wherein the soap thickener is an alkali metal or alkaline earth metal soap, or a mitxure of two or more soaps of this class.

Saponifiable materials which may be employed in the grease preparation comprise higher fatty acids and hydroxy substituted fatty acids containing from about 12 to 32 carbon atoms per molecule and the glycerides and other esters of such acids. The preferred materials are fatty acids and hydroxy fatty acids containing about 14 to 22 carbon atoms per molecule, their glycerides and other esters, and mixtures of such materials.

The oleaginous liquids employed in these greases may be any oils of lubricating characteristics suitable for use in grease making generally, including the conventional mineral oils, synthetic oils obtained by various refining processes, such as cracking and polymerization, and other synthetic oleaginous compounds, such as high molecular weight ethers and esters. The dicarboxylic acid esters, such as di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, di-2-ethylhexyl azelate, di-iso-octyl adipate, etc., are a particularly suitable class of synthetic oils and may be employed as the sole oleaginous component of the grease or in combination with other synthetic oils or mineral oils. The oil employed in the initial charge is preferably one which is substantially inert under the saponification conditions, such as a mineral oil. Suitable mineral oils for use in these greases are those having viscosities in the range from about 100 to about 2,000 seconds Saybolt Universal at 100° F. and may be either naphthenic or paraffinic in type or blends of the two.

The following example is illustrative of grease preparations carried out in accordance with the preferred embodiment of this invention.

EXAMPLE I

A lubricating grease comprising a mineral lubricating oil thickened with calcium 12-hydroxystearate was prepared by the method of this invention as 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 seconds, with about 1 percent by weight of a heavy paraffinic residual oil having a Saybolt Universal viscosity at 210° F. of 658 seconds. 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 comprised a 150 pound capacity steam heated kettle with auxiliary equipment for grease circulation with hot and cold oil injection into the recycle stream as shown in FIG. 1. The grease circulation equipment consisted of 1¼ inch pipe connecting the kettle drawoff with a No. 2 Globe Rota Piston pump having a capacity of 18 gallons per minute, and a ¾ 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 kettle was charged with 27 pounds of paraffinic distillate oil, 1.25 pounds of lime and 9.0 pounds of 12-hydroxystearic acid. Heating and stirring of the kettle contents was begun and at the same time recirculation of the kettle contents through the recycle line was begun at a rate of about 120 pounds per minute with the shear valve in the wide open position. After about 15 minutes, the temperature of the reaction mass had reached 180° F. and saponification had started. After an additional 15 minutes with continued heating the temperature of the mass had reached 218° F. and dehydration was substantially complete as shown by the cessation of foaming. The heating was then continued at a slower rate sufficient to maintain the reaction mass at 225–232° F. for ½ hour. Thereafter, the steam pressure was increased and the temperature brought up to 264° F. in about 23 minutes while 45 pounds of the paraffinic distillate oil preheated to 265–276° F. were added at a rate of about 120 pounds per hour into the recirculation line at the intake side of the pump. When the temperature of the mixture had reached 240° F., the shear valve was adjusted to give a pressure drop across the valve of 60 pounds per square inch and recirculation with shearing in this manner continued during the remainder of this process, amounting to a total time of about 1 hour and 50 minutes. When the temperature of the grease mixture was 270° F., the heat was cut off and cooling commenced with the addition of 23 pounds of distillate oil at ambient temperature at a rate of 120 pounds per hour during the cooling down to 234° F., which required about 12 minutes. During further cooling of the grease mixture to 179° F., 0.53 pound of diphenylamine, 1.06 pounds of the heavy residual oil and an additional 15 pounds of paraffinic distillate oil required for correction of the grease grade were added. The grease was drawn at 179° F.

A smooth grease of good yield and appearance was obtained as described above. The following table shows the effect of the low temperature holding period in this preparation.

Table I

Grease No.	1	2	3
Holding step:			
Temp., ° F.		270–275	220–230
Time, hrs.	None	0.5	0.5
Total mfg. time, hrs.	1.58	2.0	2.12
Product:			
Appearance	[1]	[1]	Smooth
Soap content, percent	9.00	9.00	7.9
ASTM pene.: Worked	292	301	273

[1] Soap particles.

The grease preparations shown in the above table were all carried out in substantially the same manner except for the differences in the holding step shown in the table. As shown by these results, relatively poor yields and unsatisfactory products were obtained by the process carried out in very short manufacturing times with no holding period or only a ½ hour holding period at top temperature. However, smooth products and good yields were obtained by employing a ½ hour low temperature holding step. By carrying out the preparation without a low temperature holding step but with a one hour holding period in the top temperature range, yields substantially equivalent to those shown above for Grease No. 3 were obtained but the appearance of the grease was less satisfactory, in addition to the disadvantage of the longer manufacturing time required. The advantage obtained by employing a low temperature holding step in the preparation of this grease containing a naphthenic oil as the oil component is ordinarily much less than that shown above for the grease comprising a paraffinic oil. However at least a substantial advantage in yield or product quality is ordinarily obtained by means of the low temperature holding step even in the preparation of greases from naphthenic oils, particularly in the process employing relatively low recycle rates as discussed hereinabove, and the preparation of calcium base greases comprising naphthenic oils is accordingly included within the purview of this invention.

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. The process of preparing soap thickened greases which comprises providing a reaction mixture consisting essentially of a saponifiable material, a metal base in an amount corresponding approximately to the stoichiometric amount required to react with the said saponifiable material, a lubricating oil which is substantially unreactive under the saponification conditions in an amount equal to about 0.5 to about 6 times the weight of the said saponifiable material, heating the said mixture up to about 200° F. over a period of time sufficient to obtain substantially complete saponification, further heating the grease mixture up to a maximum temperature in the range from just below the melting point of the soap to about 75° F. below the melting point of the said soap, and cooling with the addition of additional lubricating oil at a lower temperature than the grease mixture, said grease mixture being heated in the temperature range from 200° F. to the said maximum temperature from about ½ hour to 4 hours, including about 15 minutes to 1 hour at a temperature in the range from 200° F. to about 240° F. after the saponification step, said grease mixture being maintained in a grease making zone during the said grease making process with recirculation through a recycle line at a rate such that the weight of recirculated grease mixture is equal to the total weight of grease mixture in about 0.25 to about 15 minutes during heating in the range from 200° F. to 240° F., and with shearing of the grease mixture in the said recycle line during at least a substantial portion of the grease making process following the saponi-

fication step, said shearing being carried out by passing the recirculating mixture in said recycle line through a shear valve with a pressure drop across said valve of about 10–200 pounds per square inch.

2. The process of claim 1 wherein the said cooling is carried out by introducing additional oil at a substantially lower temperature into the recirculating stream of grease mixture.

3. The process of claim 1 wherein additional oil at a substantially higher temperature than the grease mixture is introduced into the recirculating stream of grease mixture during the heating from about 240° F. to the maximum temperature employed.

4. The process of claim 1 wherein the grease mixture is maintained at a temperature from just below the melting point of the soap to about 75° F. below the melting point of the soap for a period from about 15 minutes to about 1 hour.

5. The process of claim 1 wherein the recirculating stream of grease mixture is subjected to shearing during the cooling step by passing it through a shear valve with a pressure drop of about 10–200 pounds per square inch across the valve.

6. The process of claim 1 wherein the grease mixture is subjected to shearing during the heating cycle by passing the recirculating stream of grease mixture through a shear valve with a pressure drop across the valve of about 25–125 pounds per square inch.

7. The process of claim 1 wherein the said grease mixture is subjected to shearing during the cooling cycle and at least a portion of the heating cycle by passing it through a shear valve with a pressure drop across the valve of about 25–125 pounds per square inch.

8. The process of claim 1 wherein the said soap is a calcium-hydroxy fatty acid soap.

9. The process of claim 1 wherein the said soap is a lithium-hydroxy fatty acid soap.

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

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