May 27, 1952 G. C. BAILEY ET AL 2,598,154

PROCESS FOR MAKING GREASE

Filed Aug. 21, 1947 2 SHEETS—SHEET 1

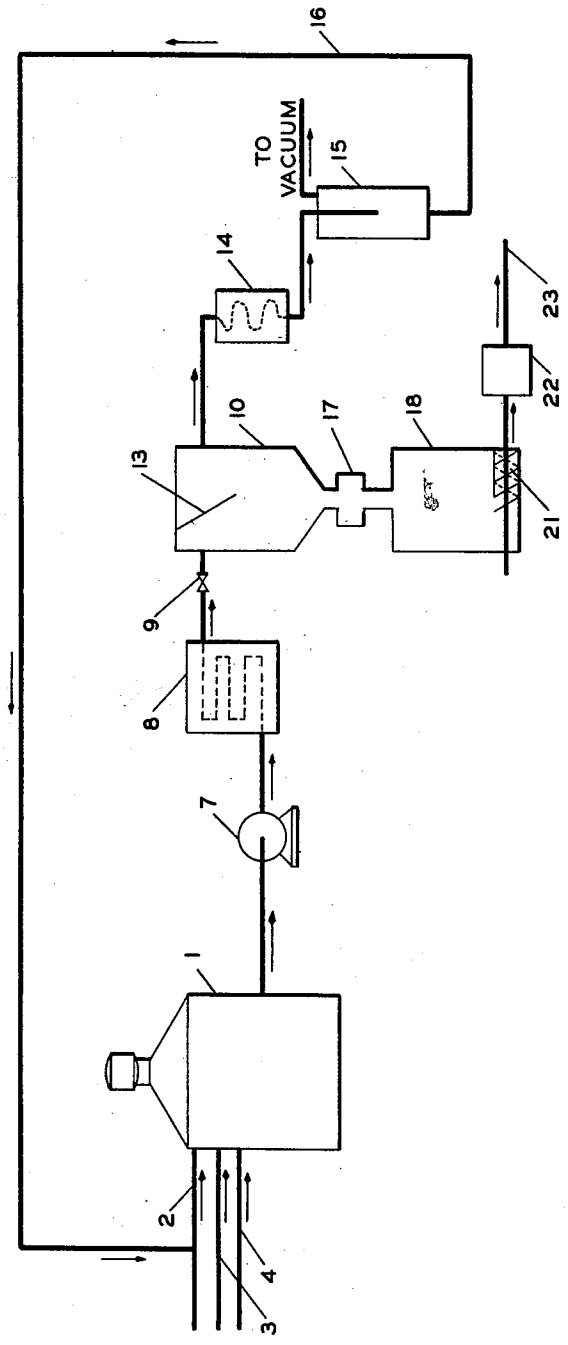


FIG. I

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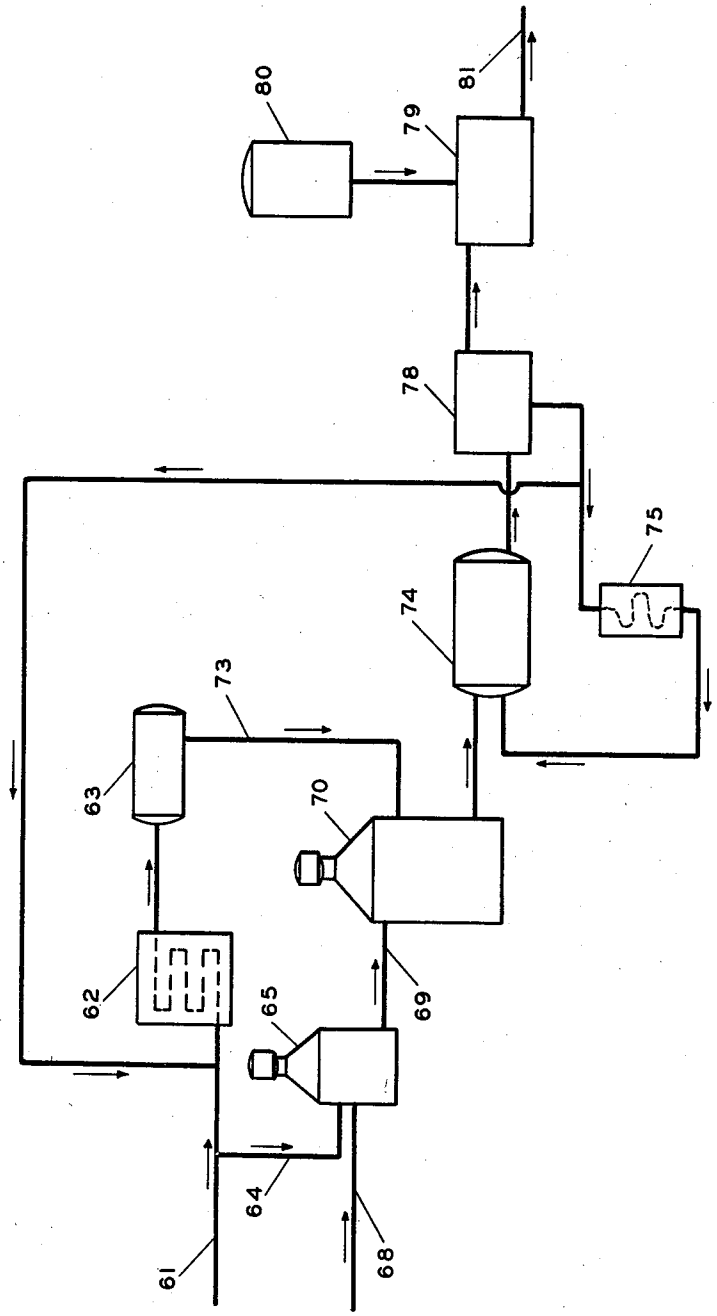


FIG. II

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PROCESS FOR MAKING GREASE

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9 Claims. (Cl. 252—41)

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This invention relates to an improved lubricant. In one of its more specific aspects it relates to a lubricating grease, and to methods of preparing such a grease, having a greater consistency and a higher resistance to bleeding when prepared by rapid cooling and severe working than by methods common in the art.

Grease making, according to the prior art, usually consists of heating, in a large kettle, a mixture of saponifiable oil and an aqueous solution of a metal hydroxide in the presence of a mineral oil. During this heating, which requires from 8 to 24 hours, a soap is formed, most of the water is boiled off, and the soap becomes dispersed in the mineral oil to form grease which is usually diluted and gradually cooled by the slow incorporation of more oil. During the heating and blending process, the kettle content must be continually stirred to maintain intimate contact of the saponifiable oil and the aqueous alkali to prevent scorching and secure a uniform product. During a considerable portion of this time the mixture is a stiff paste-like mass, the stirring of which consumes much power and requires the attention of a skilled grease maker. This method requires large floor space and expensive specialized equipment. The operation also lacks flexibility as small batches cannot conveniently nor cheaply be turned out in large kettles nor production changed from one type of grease to another in a short period of time. Use of large kettle equipment usually means that a large inventory of finished products is carried on hand.

There have been numerous continuous processes for making grease described in the patent literature, but most of the workers have been interested in using the continuous process for saponifying the fatty oil and therefore use a temperature of about 200° F. to about 300° F. for a period of from 8 to 24 hours. Although the literature pertaining to greases contains many references relating to their preparation and which references usually contain directions for cooling and milling (working) the directions which have been recorded refer to greases which on cooling, or on cooling and slight working, give a homogeneous grease-like structure. The statements concerning cooling are often contradictory and inexact, depending on the type of soap present, and are usually qualitative statements unaccompanied by any supporting evidence of the extent or the effect of cooling. The prior art is voluminous with directions describing substances to add to soap and oil mixtures to stabilize the otherwise incompatible mixtures. The substances most often used as stabilizers are water, glycerin, unsaponified fat, unsaponifiable portions of fat,

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free fatty acid, high molecular weight alcohol, wool fat, pitch, high molecular weight amides, glycols, and the like. The art is very careful to teach that certain combinations of soap and oils alone are very difficult if not impossible to secure and to maintain in stable combination, and that stabilizing substances must be present to prevent syneresis, which in extreme cases forms an oil-soaked granular mass of soap in liquid oil. The fact that this breakdown of the structure occurs for many combinations of soap when heated in oil and cooled rapidly, under the heating and cooling conditions disclosed in our procedure hereafter described, has been repeatedly demonstrated by us. Previous reports of improvements in grease properties by rapid cooling have been inexact as to what has been meant by rapid cooling. This has usually been stated as pouring out in pans to cool. The depth is usually stated as about 4 inches and the cooling medium is air at room temperature, although one reference specifies layers having a depth between ½ and ⅝ inch at room temperature. Chill rolls and scrapers have been reported but the cooling is not uniform nor rapid for the material considered as a whole.

One object of our invention is to provide a rapid and economic process for producing greases of improved qualities.

Another object of our invention is to provide a method for producing an improved grease utilizing any one of several metal soap bases or combinations of such bases.

Still another object of our invention is to provide a process for producing greases of improved qualities by the method of extremely rapid cooling and severe working.

A further object of our invention is to provide an improved method for producing a grease, with or without an additive designed to impart strength to the gel structure, which has increased consistency and resistance to bleeding.

Other objects and advantages of our invention will be apparent from the accompanying description and discussion.

Rapid cooling of a soap-oil mixture tends to encourage the formation of granular masses in liquid oil and especially so when such oil is substantially saturated with the soap at the elevated temperature. As the initial stage in producing a superior grease, we have found that it is desirable to encourage by rapid cooling the formation of a mass consisting of a hard gel which breaks into lumps or crumbles with or without the exudation of much free oil. This non-grease-like mass is then severely milled (worked) to bring it to a grease-like texture. The severe milling process produces a result which is un-

expected and contrary to that of the known art. Instead of producing a grease which continues to soften on extended working, it produces a grease which, during a process of severe working, usually increases in consistency and always tends to reach a degree of consistency that remains substantially constant. These greases thus produced have only a slight tendency to bleed. The reasons for these phenomena are unknown but appear to be in the inter-relation of the metal and the fatty acid used to form the soap and in the degree of mutual solubility of the oil and soap. By rapid cooling we mean that the mixture of soap and oil should be cooled to the desired temperature within a period of from about 1 to about 600 seconds, preferably between about 10 and about 300 seconds.

An important application of the above described process is the production of a grease from a mixture comprising a stiffening agent, such as a metal soap, and oil of such a nature that the soap does not dissolve when heated in an open vessel, even when heated to a temperature just below the thermal decomposition point of the ingredients, but stratifies into a lower layer of soap with a minor proportion of oil and an upper layer of oil containing a minor proportion of soap which separate phases cannot be homogenized by mild agitation. On cooling, a dense gel results from the lower layer and a soft gel from the upper layer. On milling the two portions together, a grease of excellent quality as to the low loss of consistency is produced, on extended working, which has only a slight tendency to bleed.

In heating the soap-oil mixture it is only necessary to heat it to a point at which the soap begins to ball up in the oil during the stirring. That balling will usually begin to occur in the vicinity of about 365° F. It is not however preferred to cool from that point because the mixture which is formed is relatively difficult to work. In the preferred method of our process we continue to heat, with stirring while adding soap to the soap-oil mixture, beyond the point at which balling of the soap takes place and until the entire mixture is substantially liquefied and preferably till the oil and soap are miscible. In this manner the oil may be substantially saturated at some temperature between 365° F. and the decomposition temperature. Cooling of the mixture may be started at or above the saturation temperature. Heating is carried out quite rapidly so as not to injure the ingredients of the mixture. The critical temperature, on heating, is that temperature at which thermal decomposition may occur. Precaution should be taken to avoid burning or scorching of the mixture. Our process may be utilized in either open or closed vessels.

We have found that in many cases two greases of identical composition which have been heated similarly, but one of which has been subjected to the customary method of slow cooling and the other to the method of rapid cooling used in our invention, show markedly different characteristics. The one cooled slowly will be softer, more homogeneous and will not have as great a resistance to change of consistency on extended working nor as great a resistance to bleeding.

We have further found that this invention is not limited to the improvement of greases of compositions now known such as a hydrocarbon oil with sodium stearate, lithium laurate, aluminum laurate, aluminum tristearate, aluminum distearate, or aluminum monostearate, but by its

application greases may be prepared which have hitherto not been possible. For example, all attempts to obtain a smooth grease by rapid cooling of solutions of anhydrous barium stearate in high viscosity index mineral oil have failed to make a smooth stable grease whereas by the method of rapid cooling of the heated mass to form a gel which synerizes, a good smooth grease was obtained by subsequent severe working. Similar results were obtained with calcium oleate, magnesium stearate and calcium stearate. Good results may be obtained with combinations of these soap bases and oils but we have found that greases made from combinations of soap bases do not ordinarily give a product which is as resistant to penetration as monosoap base greases.

It has been found advantageous to substantially match the metal and the fatty acid radical so as to make the best soap and grease. Sodium soaps have been found to produce the best grease when sodium hydroxide is combined with a fatty acid radical falling within the C_{16}–C_{20} range and preferably with a C_{18} acid radical. The best lithium greases are made when a fatty acid radical in the C_{10}–C_{14} range and preferably a C_{12} acid radical is used.

The stiffening agent used in this invention is generally a soap. Such a soap is a salt of a fatty acid. The fatty acid used in making the soap should be relatively pure. Another important factor in producing such greases is that the stiffening agent should generally be substantially neutral so that it contains substantially no free fatty acid. A grease produced from such a neutral stiffening agent or soap produced from a relatively pure fatty acid will, when combined with an oil as herein described, form a gel which in turn will form a grease having excellent characteristics when it has been worked to substantially constant consistency. By the term "relatively pure fatty acid radical" we mean one of substantially the same carbon content per molecule, e. g. C_{18}. If a mixture of fatty acids is used they should be so close together in structure as to be nearly the same. Thus in making a sodium soap it is desirable to use a fatty acid radical having 18 carbon atoms per molecule. This gives a much better grease than one prepared from a soap in which the fatty acid was a mixture of C_{14} to C_{22} fatty acids which had an average molecular weight equivalent to 18 carbon atoms per molecule. Fatty acid radicals differing by as much as two carbon atoms, for example C_{18} and C_{16}, or C_{18} and C_{20}, may be used together and produce very satisfactory soaps, for they fall within the exception pointed out above in that they are bordering or adjoining structures and will not alter the soap structure materially.

The temperature below which the grease must be cooled is that at which solidifying from a liquid to a gel, which is definite and possibly related to the crystalline or colliodal structure of the soap, occurs. We do not, however, limit the rapid cooling to any specified temperature. The limit constitutes only those conditions which will produce a hard gel from a solution substantially saturated under the conditions above described. This gel usually breaks or crumbles to an oil soaked mass on crushing and may be worked to a consistent grease by severe milling or working. The temperature at which gelling of most greases will generally begin to take place usually falls between about 330° F. and about 400° F. depending upon the type grease. The time of cooling,

as has been pointed out above, is short, usually within a period of between 10 and 300 seconds, and the milling is equivalent to several thousand strokes of an ASTM grease worker (Precision Scientific Motormatic model) as described in ASTM Test D-217-44T. By working severely we mean that the gel is worked an equivalent of from about 2,000 to about 100,000 strokes of an ASTM grease worker. The exact number of strokes to be used is that number which will give the greatest consistency to the finished grease.

In a preferred process of our invention, the soap is added to lubricating oil and heated rapidly with stirring. The soap passes through the stages of being merely suspended, then becoming sticky and agglomerated, then changing to a stringy, viscous mass and finally turning to a substantially homogeneous non-viscous liquid or dispersion. When this stage has been reached, usually between 390° F. and about 485° F., the mixture is cooled rapidly to form a hard gel which cracks, breaks, or crumbles and requires severe milling or working for a short time to produce a smooth grease. During this milling process many greases tend to reach a constant penetrability, which penetrability is substantially maintained for several hundred thousand strokes of the ASTM worker. Though we prefer that the gel formed be sufficiently hard that it may be cracked, broken or crumbled, gels which are to some degree softer may be severely worked with beneficial effect.

In one modification of our process, we use a soap-oil-diluent mixture, rapidly heat to a temperature between about 355° F. and about 540° F. and cool rapidly to about 285° F. As diagrammatically shown in Figure I of the drawing, diluent, soap and oil are delivered to mixing chamber **1** through lines **2**, **3** and **4** respectively. The materials are mixed and kept in suspension to form a substantially uniform suspension in the mixing chamber. The soap is any substantially pure fatty acid salt which is suitable for grease making. The oil is any lubricating oil suitable for grease making and which is substantially matched with said soap. The diluent is a low or medium boiling liquid which may or may not be miscible with the oil. Suitable diluents would be butane or other low or medium boiling hydrocarbons or hydrocarbon derivatives such as chlorinated hydrocarbons, ethers, esters, ketones, alcohols, alkyl halides, aldehydes, or amines. The ratio of diluent to soap-oil combination should be such that on suddenly reduced pressure and evaporation of the diluent, the latent heat of vaporization absorbed by the diluent shall produce the desired cooling effect described below. Mixing chamber **1** must be of sufficient strength to withstand the vapor pressure of the diluent at operating temperature. By metering pump **7**, the mixture is forced into the heating section **8** where the mixture is rapidly heated, during agitation, to a temperature between approximately 355° F. and 540° F. The mixture changes on heating from a suspension of soap in the oil-diluent mixture to substantially a liquid dispersion of soap in the oil-diluent mixture. This liquid is forced through an expansion valve **9** into expansion chamber **10** which is maintained at a pressure low enough to insure that substantially all the diluent is flash evaporated, with the result that the soap-oil residue is cooled below the gelling temperature of the soap. A satisfactory temperature to which sodium stearate may be cooled is to about 285° F. or below. The expansion chamber may be maintained at a pressure above, below, or at atmospheric pressure, depending on the boiling point of the diluent used. Baffle plate **13** prevents grease from entering the exhaust with the vaporized diluent. The vapors are led through cooler **14** where they may be cooled and collected in condensation chamber **15**. The diluent is recycled through line **16** to line **2**. The residue of soap and oil is passed through grease worker **17**, where it is worked severely, into storage **18**, from which it is removed by screw conveyer **21**, through filter **22** and delivered to a container filling machine (not shown) through line **23**.

Another modified embodiment of our invention is diagrammatically illustrated in Figure II of the drawing. Lubricating oil is passed through line **61** into heater **62** and thence into hot oil surge tank **63**. Lubricating oil is also passed from line **61** through line **64** into soap mixing tank **65** where it is mixed with soap which is supplied through line **68**. The cold soap-in-oil slurry from soap mixing tank **65** is discharged through line **69** into mixing tank **70** simultaneously with the discharge of the hot oil from surge tank **63** through line **73**. The hot oil is in such proportions relative to the soap-in-oil slurry that there is only a slight drop in temperature. The soap is readily dispersed in the hot oil to form a liquid mixture. The resulting soap-in-oil dispersion is discharged continuously into cooling tank **74**, which continuously receives cool oil from cooler **75**. The cooling tank contents are agitated to mix quickly the hot soap dispersion with the cool oil in the tank. The low temperature of cooling tank **74** is maintained by the inflow of cool oil from cooler **75**. The soap, on cooling below its gelling temperature, separates as lumps of soap gel. The gel-oil mixture is discharged to a separator **78** consisting of a centrifuge or a screen sieve and the gel is separated from the oil. The free oil is recycled through cooler **75** to cooling tank **74** while any excess oil in the recycle system is returned to line **61**. The gel lumps are charged to grease mill **79** where they are mixed with the desired amount of oil from compounding oil storage **80**. It is obvious that a modification may be made in this system whereby a desired amount of oil may be retained with the gel passing from separator **78** rather than adding it from storage **80** and oil from another source passed through cooler **75** to cooling tank **74**. The finished grease is discharged from grease mill **79** through line **81** to storage or packaging machine. The hardness of the finished grease can be increased by removing greater amounts of oil from the gel before milling while a softer grease may be prepared by adding greater amounts of oil before milling.

Three different oils were used in the production of the greases of our Examples I and II. The three oils are denoted as A, B, and C. having the following properties.

Table I

	A	B	C
Viscosity at 100° F. SUS	183.2	532.7	152.8
Viscosity at 210° F. SUS	44.6	63.03	44.24
VI	90.7	87.1	115.9
n_D^{20}	1.4748	1.4921	1.4699
Density 20/4	0.8690	0.8888	0.8403

Example I

A mixture comprising 80 weight per cent mineral oil A and 20 weight per cent sodium stearate were heated to between about 392° F. and about 485° F. One portion of the mixture was then allowed to cool slowly to room temperature within a period of about 5 to 10 hours. The second portion was cooled by pouring it into a pan in which the layer was about ¼ inch thick, and the pan was then set in cold water. This portion gelled in about 2 minutes. A portion of the slowly cooled portion was severly worked or milled in a grease worker as was the rapidly cooled grease. These greases were then tested with a penetrometer as described in ASTM Test D-217-44T, but modified so as to use a micropenetrator needle, plunger, and cup, as described by Kaufman, Finn and Harrington in Industrial and Engineering Chemistry, analytical edition 11, 108-110 (1939). Bleeding tests were made as described with Army-Navy Specification AN-G-3a section F-5c. Results of the tests recorded in the following table indicate that the rapidly cooled, severely worked grease, is much superior in "bleeding resistance" as compared to the other greases.

Table II

Cooling rate	Milling Strokes	Penetration	Penetration after 90,000 Additional Strokes	Bleeding Weight per cent
slow	none	42	313	13.8
Do	10,000	188	313	13.8
rapid	10,000	80	84	0.65

Example II

Several other greases were prepared using different soap bases in conjunction with different oils. Penetration tests were made as in Example I. The effect of producing a grease by our method is clearly indicated by data contained in the following table.

Table III

Soap	Soap Content Weight per cent	Oil	Cooling Rate	Milling Strokes	Penetration	Penetration after 90,000 Additional Strokes
Al-tri-stearate	20	A	Slow	none	50	202
Do	20	A	do	10,000	151	202
Do	20	A	Rapid	10,000	89	159
Li-laurate	20	B	do	10,000	138	106
Do	20	C	do	10,000	162	100

The data in Table III show that an aluminum stearate grease, which had been prepared by methods employing slow cooling, had penetrations of 50, 151, and 202 in unworked, after being worked 10,000 strokes, and after being worked 100,000 strokes, respectively. A grease similar in all respects except rapidly cooled had a penetration of only 89 at 10,000 strokes and 159 at 100,000 strokes. The unworked penetration of the rapidly cooled grease was not of significance as the product was a non-homogeneous mixture of soap and oil. Thus, through the working range of 10,000 to 100,000 strokes, the rapidly cooled grease had maintained a more satisfactory consistency than the slowly cooled grease.

Example III

Three other greases were prepared from soaps containing substantially no free acid, which were produced by substantially matching the metal and fatty acid radical as above described, and preparing the grease from a mixture of such soaps and a white mineral oil having characteristics similar to oil A described above. A fourth grease was prepared by combining two of these three greases and working. Penetration tests were made as in Examples I and II. Results of such tests are recorded in Table IV.

Table IV

Soap	Soap Content Weight per cent	Oil	Cooling Rate	Milling Strokes	Penetration	Penetration after 90,000 Additional Strokes
(A) Na-stearate	20	A	Rapid	10,000	67	73
(B) Li-laurate	20	A	do	10,000	83	81
(C) Na-stearate	10	A	do	10,000	240	255
Li-laurate	10					
(D) (A) plus (B) [1]				10,000	108	130

[1] 50% each in the mixture.

Example IV

Sodium stearate was added to lubricating oil A to make 20 weight per cent soap in the oil. This was diluted with octane in the ratio of one part soap-oil mixture to six parts of octane. The materials were mixed and passed, under pressure, through a heated section where the temperature was raised to about 410° F. The liquid was discharged through an evacuated container and the vaporized octane removed. The residue was a mixture of soap lumps and oil which on milling produced a grease of excellent quality. The hardness of the finished grease can be increased by removing a part of the oil before milling or the hardness decreased by the incorporation of more oil.

Example V

Sodium stearate was mixed with oil A and heated to about 465° F. The soap was dispersed in the oil to form a liquid mixture. This mixture was poured into oil A which was at about 250° F. The soap solidified to a transparent gel and floated in the oil, in lumps. The temperature after mixing the two oils together was about 285° F. The excess oil was drained off and the soap and a portion of the oil was worked severely to a grease which had a low loss of consistency on extended working and only a slight tendency to bleed.

It may be desired to include some additives to give a finished grease certain otherwise unobtainable desirable characteristics. These additives may be added at any time during the process, but we prefer to add them after the mixture has gelled and while the gel is being worked. In that manner the structure of the gel is not affected in its formation.

In the past when hard soap cakes or lumps have appeared in the soap-oil mixture after heating and during the cooling step it has been the practice to throw such mixtures away as it was believed they were not suitable for the making of finished greases.

By the method of our invention we utilize such mixtures as those which were previously believed worthless, and gain from them a hard, even-textured, superior grease.

For those skilled in the art it will be obvious that many alterations may be made in the process of manufacture without change in the principle and the scope of our invention.

We claim:

1. A process for manufacturing a grease from an oil and a metallic soap which comprises the steps of forming a mixture comprising a metallic soap with a hydrocarbon lubricating oil, heating said mixture with agitation to substantially disperse the soap in the oil, chilling suddenly to form a hard friable gel in some free oil, separating said gel from a portion of said free oil, and working said gel and remaining free oil to a state of substantially constant consistency.

2. A process for manufacturing a grease from an oil and a metallic soap which comprises the steps of forming a mixture comprising said metallic soap, containing substantially no free acid, with a hydrocarbon lubricating oil, heating to a temperature between about 365° F. and the decomposition temperature of said mixture while agitating said mixture during said heating, chilling said mixture to form a hard fracturable gel in some free oil within from about 10 seconds to about 300 seconds, separating said gel from a portion of said free oil, and working said gel and remaining free oil to a smooth grease texture.

3. The process of claim 2 wherein said lubricating oil is substantially saturated with said metallic soap at a temperature within the heating range specified.

4. A process for manufacturing a grease from an oil and a metallic soap which comprises the steps of forming a mixture comprising said metallic soap containing substantially no free acid, a hydrocarbon lubricating oil and a low boiling diluent, heating said mixture to a temperature between about 355° F. and about 540° F. while agitating said mixture during said heating, flash evaporating said diluent to form a hard fracturable gel residue in some free oil within from about 10 seconds to about 300 seconds, separating said gel from said free oil, and working said gel to a smooth grease texture.

5. The process of claim 4, wherein said gel is separated from only a portion of said oil.

6. A process for manufacturing a grease from an oil and a metallic soap which comprises the steps of forming a mixture comprising said metallic soap, containing substantially no free acid, and a hydrocarbon lubricating oil, heating said mixture to a temperature between about 365° F. and the decomposition temperature of said mixture by means of adding heated oil thereto while agitating, chilling said mixture to form a hard fracturable gel in some free oil within from about 10 seconds to about 300 seconds, separating said gel from said free oil, and working said gel to a state of substantially constant consistency.

7. A process for manufacturing a grease from an oil and a metallic soap which comprises the steps of forming a mixture comprising said metallic soap, containing substantially no free acid, and a hydrocarbon lubricating oil, heating said mixture to a temperature between about 365° F. and the decomposition temperature of said mixture by means of adding heated oil thereto while agitating, chilling said mixture to form a hard friable gel in some free oil within from about 10 seconds to about 300 seconds by means of suddenly mixing said mixture with a cold oil, separating said gel from a portion of said free oil, and working said gel and oil to a smooth grease texture.

8. A process for manufacturing an improved grease from an oil and a stiffening agent which stiffening agent is formed by the combination of lithium hydroxide and a fatty acid in the C_{10}–C_{14} range and in which stiffening agent free acid has been substantially neutralized, which process comprises the steps of forming a mixture of a hydrocarbon lubricating oil and said stiffening agent, mixing said mixture while heating to a temperature between 365° F. and the decomposition temperature of the ingredients so as to disperse the stiffening agent in the oil, chilling said mixture to form a hard friable gel in some free oil within from 1 second to about 600 seconds, and working said gel to a state of substantially constant consistency.

9. A process for manufacturing an improved grease from an oil and a stiffening agent which stiffening agent is formed by the combination of lithium hydroxide and a fatty acid in the C_{10}–C_{14} range and in which stiffening agent free acid has been substantially neutralized, which process comprises the steps of forming a mixture of a hydrocarbon lubricating oil and said stiffening agent, mixing said mixture while heating to a temperature between 365° F. and the decomposition temperature of the ingredients so as to disperse the stiffening agent in the oil, chilling said mixture to form a hard fracturable gel in some free oil within from 10 seconds to about 300 seconds, and working said gel to a smooth grease texture.

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