Patented Feb. 12, 1946

2,394,907

UNITED STATES PATENT OFFICE

2,394,907

LUBRICANTS

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No Drawing. Application October 24, 1942, Serial No. 463,180

5 Claims. (Cl. 252—41)

This invention relates to novel lubricating greases and methods of manufacturing same, and it also relates to novel intermediate products useful for other purposes.

Heretofore soda base greases have been made by cooking up a fat or fatty acid in a mineral oil, and reacting the mixture with aqueous alkali while heating to 100° C. or higher until saponification is completed, which is followed generally by additional cooking to cause evaporation of the resultant water or glycerine; this process requires a large amount of time and is not as foolproof as might be desired. Various efforts have been made to improve one or another phase of this grease manufacturing process, but none has proved entirely satisfactory, either because the new step is too expensive or too time-consuming, or it is not subject to sufficiently accurate control for the preparation of lubricating greases having a uniform grease structure, which, as is well-known, is a very sensitive and elusive characteristic.

The primary object of the present invention is to solve the problems of the prior art by providing a method which is quick, economical, simple in its operation, efficient, and conducive to uniform results. These and other objects and advantages of the invention will appear more fully from the following description.

The invention comprises suspending an alkali such as caustic soda, in flake or other suitable form, or other saponifying agents as will be discussed later, in a non-reactive liquid medium, for example a portion of mineral oil and mechanically comminuting said alkali while dispersed in the oil until a predominant portion of the particles of alkali is at least as low as 5μ, in size, and then using the resultant very active alkali-oil dispersion for saponifying, i. e. substantially neutralizing, a fat or fatty acid, adding sufficient oil to make a grease of the required texture, and using enough heat to effect complete saponification. This saponification may be carried out in various ways.

In making the alkali-oil dispersion it is best to put the oil (or other non-reactive liquid medium) in a ball-mill or other suitable mill, and then add anhydrous caustic soda in flake, stick or other form and proceed with the milling until the alkali has been reduced to the desired degree of fineness so that it will stay in suspension in the oil. This mechanical comminution of the alkali produces particles of an extremely fine state of subdivision, such as mostly less than 5μ, and preferably less than 1μ in diameter. In fact, microsopic examination indicates that a number of particles in the resultant dispersion have dimensions approaching that of colloids. The time required in a ball-mill will, of course, depend upon a number of factors, such as the type, diameter and speed of rotation of the mill as well as the number and size of the balls (which may be of steel, stainless steel, flint pebbles or other suitable material) and the amount and viscosity of the alkali-oil charge. Normally, however, a milling time ranging from about 2 hours to about 18 hours is sufficient. With a ball-mill or pebble mill the best loading is practically half full of balls and liquid just covering the balls. This gives the most efficient grinding action.

If desired, the mechanical comminution of the alkali particles in the oil may be effected by passing the crude suspension through a colloid mill, one or more times, depending upon the original size of the alkali particles, the rotation speed of the colloid mill, the aperture setting of the discs or other adjusting means of the colloid mill, as well as the proportion and viscosity of the mineral oil vehicle. Chaser mills, pan mills, rod mills, mulling mills, disc mills and others could be used. The alkali to be used in preparing the alkali dispersion may be the ordinary alkali of commerce which usually contains less than 2% of water, and may be substantially anhydrous.

When the particles of alkali such as anhydrous caustic soda are thus finely divided in the presence of the mineral oil serving both as a fluid suspending medium or vehicle as well as protecting the alkali from contact with moisture of the air, etc., the resultant dispersion is uniform both in quality and in concentration of alkali in the oil, and is substantially stable against settling, particularly if a small amount of a protective agent is added prior or subsequently to milling, preferably prior to milling; and this is a great advantage from a practical and commercial point of view as it enables the production of lubricating greases of uniform quality and makes that possible with relatively simple fool-proof operations. If desired, instead of using the alkali-oil dispersion directly in the form in which it issues from the ball-mill, or the colloid mill if such is used, the procedure may be modified as for instance by first subjecting the suspension of alkali flakes in oil to ball-milling to effect a substantial reduction in alkali particle size, and then further reducing the alkali particle size by passing the first crude dispersion through a colloid mill with relatively fine setting of the discs, or other adjusting means.

As still another modification of the invention, the dispersion resulting from the passage of the flake alkali-oil suspension through either a ball-mill or a colloid mill may be fractionated in order to separately recover the ultra fine particles.

This may be accomplished by diluting the crude dispersion (coming from the ball-mill or colloid mill), with a substantial amount, e. g., 10% to 500% by volume, of an inert volatile diluent such as petroleum, naphtha, or a liquefied gaseous hydrocarbon such as pentane, butane, or propane, in the presence of which diluent only the ultra fine particles will stay in suspension and the less fine particles will settle out or can be separated readily by centrifuging, and the volatile diluent may then be removed by distillation in order to recover the concentrate of ultra fine colloidal alkali particles in the original oil-dispersing medium. Furthermore, if the very fine suspension is to be separated out, the preparation of the total suspension could be made initially in an inert volatile diluent as mentioned, leaving out the oil.

In using the above described alkali-oil dispersions for the preparation of lubricating greases, it is preferred to cause a saponification of the fatty material, such as a fat or fatty acid, directly in situ and this is preferably accomplished by first dissolving the fat or fatty acid in the proper amount of the desired type of mineral oil and then adding the alkali-oil dispersion thereto with agitation to obtain prompt and efficient mixing, and heating the resultant mixture to a saponification temperature which may range from room temperature, in the case of the most active materials, to slightly elevated temperatures, such as 140° F., 180° F., 210° F., or so. The saponification reaction yields glycerol with fats and water with fatty acids. The amount of water so formed is relatively so small that its removal is not required and therefore high temperatures to get rid of water are not required. Due to the great reactivity of the fine dispersion of the alkali in oil, saponification temperatures very much lower than used heretofore may be used satisfactorily. The resultant grease may, of course, be subjected to further cooking in order to evaporate moisture or to distill off glycerine resulting from the saponification reaction. The mineral oil to be used in carrying out the present invention, insofar as the alkali-oil dispersion is concerned, may be any type of refined mineral lubricating oil having a Saybolt viscosity at 100° F. between the approximate limits of 100 seconds and 5000 seconds, and preferably between the somewhat narrower range of 100 seconds and 900 seconds. It is to be understood that these are the common practical limits for the petroleum products to be used as the alkali carrying media, but lighter fractions such as fuel oil, naphthas and more volatile products may be used. The oil may be obtained from any of the commonly available crudes such as paraffinic, naphthenic or mixed base crude petroleum oils, and the oil used may have been recovered from crude petroleum by any of the commonly used refining methods, such as distillation, fractionation, solvent extraction, etc., and may have been subjected to various refining treatments, such as acid treating, clay treating, as well as treatment with various chemicals, such as aluminum chloride, etc. The additional quantity of oil to be used for dissolving the fats or fatty acid, may be any of the above types of oil and may have any desired viscosity or boiling range as commonly used for the preparation of lubricating greases.

The fatty material to be subjected to saponification may be any of the commonly available fats, such as mutton tallow, beef stearin and the like, or various fatty acids, such as stearic acid, oleic acid or other high molecular weight fatty acids, such as fatty acids derived from fatty oils, such as cottonseed oil and the like, or synthetic fatty acids obtained by the oxidation of high molecular weight or substantially saturated hydrocarbons, such as paraffin wax, or naphthenic acids, etc., or mixtures of these or other equivalent acids, including the whole range of fatty acids, for example stearic, butyric and acetic and mixtures of such acids.

The process of the present invention may be carried out by batch operation or continuously, to which it is adapted very satisfactorily by continuously mixing together a solution of saponifiable material in oil and active mechanically-comminuted alkali-oil dispersion, both of which may have been preheated if, and to such extent as, necessary for saponification in situ, with or without further continuous heating as by passage of the mixture through a heated pipe coil for a sufficient time to insure completion of the saponification reaction.

In preparing lubricating greases as above described, as an optional addition agent a small amount of materials such as sodium stearate, sodium oleate, stearic acid, oleic acid, or other similar soaps or fatty acids, etc., may be added to the alkali-oil mixture to give additional protective action during passage through the colloid mill or during the ball-milling operation, said protective action being against coagulation or agglomeration of the finely divided alkali.

Although in the above discussion caustic soda is the only alkali specifically mentioned, it should be understood that other alkalies may be used; for instance, lithium hydroxide and caustic potash may be used, or mixtures of these several alkali. Lithium hydroxide gives a water resistant grease which resists high temperatures. The amount of lithium soap required to give a good grease is relatively small. Furthermore although the invention is considered especially applicable to the alkali soap greases, calcium hydroxide, magnesium hydroxide, barium hydroxide, lead oxide (PbO), nickel oxide, cobalt oxide, manganese oxide (MnO), and others can also be used for grease manufacture according to this invention. The concentration of the alkali-oil suspension to be subjected to the mechanical combination may range between the approximate limits of 10% and 50% by weight, or preferably between the narrower limits of about 20% to 40% by weight, depending upon other factors such as the viscosity of the mineral oil vehicle, the mechanical power available, etc.

Lubricating greases made according to the present invention are generally short fibered in texture and excellent and uniform in quality. The yield obtained varies to a substantial extent with the type of saponifiable material used; for instance, with the same dispersion of caustic soda in oil, stearic acid gave a high yield, oleic acid a low yield, and mutton tallow an intermediate yield (a high yield means a low soap content for a grease of any particular penetration). Microscopic examination of the grease made with the stearic acid just referred to, showed that this grease contained a major proportion of very small soap crystals, whereas the similar grease made with oleic acid (which gave a low yield) contained a major proportion of relatively large agglomerates of soap crystals, and a similar grease made from mutton tallow contained a large number of both fine soap crystals and large agglomerates of soap crystals.

It has also been found that if the short fibered grease produced as above described is put through a colloid mill, the texture is changed with the resulting formation of a fiber grease. It should also be noted that some greases made according to this invention may be heated up to temperatures as high as 300° F. without making any apparent change in the grease structure but heating above 300° F. effects a substantial amount of recrystallization.

Although one obvious advantage of this invention is the reactivity of the alkali suspension and consequent rapid saponification even at room or relatively low temperatures, another important advantage is that the final product contains no soap-coated alkali particles as sometimes occurs when larger particles of alkali are used. A further advantage is the substantial absence of water in the alkali suspension, and therefore excessive heating is not required after saponification.

Having thus described the invention, some experimental data are now given for the sake of illustration but without the intention of limiting the invention to the specific examples used.

Example 1

10 parts by weight of stearic acid were dissolved at about 120° F. in 90 parts by weight of a mineral oil having the following inspection:

Viscosity (Saybolt) __seconds at 100° F.__	498
Viscosity (Saybolt) __seconds at 210° F.__	55.8
Viscosity index	47
A. P. I. gravity	23.2
Flash __°F.__	400
Robinson color	9¾
Neutralization No.	0.50
Pour point	−15° F.

35 parts by weight of anhydrous flake caustic soda were dispersed in 65 parts by weight of the same mineral oil at about 70° F. by ball-milling 18 hours in a one gallon capacity porcelain ball-mill having flint pebbles about 1.5 inches (about 4 cm.) diameter, the mill being about ⅓ filled with the balls. A total of 800 gms. of the alkali-oil suspension was used. The resultant caustic-oil dispersion was added to the acid-oil solution and the mixture heated to about 140° F. at which temperature saponification proceeded virtually instantaneously, the viscosity had very substantially increased and the saponification was complete. The manufacture of the grease was complete.

Examples 2 and 3

The procedure used in Example 1 was repeated with two different oils, using an oil having a 500 seconds viscosity but a 95 viscosity index in Example 2, and a steam refined cylinder stock having a viscosity of about 190 seconds at 210° F. in Example 3. The temperatures to which these mixtures were heated were 176° F. for Examples 2 and 3.

Tests on the greases made in Examples 1, 2 and 3 showed the following results:

Example No.	Oil	Unworked pen.	Worked pen.	Alkalinity, per cent
1	500 visc. 40 V. I.	108 at 86° F.	208 at 80° F.	1.30 acid.
2	500 visc. 95 V. I.	167 at 76° F.	238 at 80° F.	0.42 acid.
3	190 S. R. stock	165 at 76° F.	214 at 78° F.	0.35 acid.

Example 4

A 10% solution was made, at room temperature, of oleic acid in an acid and clay-treated Colombian distillate having a viscosity of about 500 seconds Saybolt at 100° F. and a viscosity index of 40, and some of the same caustic-oil dispersion made in Example 1 was added to the oleic acid solution and the mixture was heated to about 140° F. until saponification was complete. The resulting grease was a very satisfactory product, although the yield obtained was considerably lower than that obtained in the Examples 1, 2 and 3.

Examples 5 and 6

Similar greases were made by dissolving mutton tallow in mineral oil at 120° F. and adding some of the sodium hydroxide dispersion made in Example 1, the reaction being completed at a temperature of 140° to 180° F. Different proportions of mutton tallow and different oils were used as indicated in the following table which also shows the penetration data on the resulting greases, as well as the percent alkali therein.

Example No.	Formula	Unworked pen.	Worked pen.	Per cent alkali
5	10% mutton tallow soaps in 900 viscosity oil (acid and clay-treated Colombian distillate).	194 at 75° F.	305 at 78° F.	0.22
6	20% mutton tallow soaps in 500 viscosity oil (acid and clay treated Colombian distillate).	88 at 75° F.	213 at 79° F.	0.5

The resulting greases were very smooth and short fibered. Photo-micrographic examination shows that the structure of grease #5 (made with a 10% tallow in the refined Colombian oil) might be considered as a composite or mixture of a grease having the extremely fine particles as obtained in Examples 1, 2 and 3 with stearic acid, and a grease having larger soap particles or agglomerates as produced in Example 4 with oleic acid.

Example 7

Greases prepared in a manner similar to that described above in Examples 1–6 were passed through a colloid mill, and in all cases fiber greases were obtained, the length of texture decreasing with increasing V. I. of the oil and increasing with the degree of unsaturation of the soap.

Example 8

Using 10% of cottonseed fatty acids, saponifying in situ with the caustic-oil dispersion used in Example 1, and passing the resulting grease through a colloid mill produced a very fibrous grease.

Example 9

In order to study the effect of further heating, some of the greases prepared as above described were heated in a grease kettle with stirring, samples being examined microscopically during the heating period. By using 10% of sodium stearate in a 500 viscosity pale oil, it was found that there was no appreciable change up to 300° F. When this grease was allowed to cool, the consistency showed a marked decrease as compared with before heating, a microscopic examination indicating that the crystals had grown both in length and in cross-section, thus the reheating to a temperature of 300° F. brought about a partial recrystallization of the soap. Thus it may be stated that heating the grease to 300° F. does not produce any large effect on the texture and consistency of the grease.

It is not intended that this invention be limited to any of the examples which have been mentioned merely for the sake of illustration but only by the appended claims in which it is intended to claim all novelty inherent in the invention, as well as equivalents falling within the scope and spirit of the invention.

We claim:

1. The process of making greases which comprises dissolving a saponifiable compound in a portion of mineral oil, dispersing a saponifying agent in a non-reactive liquid vehicle, mechanically comminuting said saponifying agent while dispersed in said vehicle until the particle size of said saponifying agent is predominantly at least as low as 5μ, and mixing said solution of saponifiable compound and said saponifying agent dispersion to produce a saponification reaction.

2. The process of making greases which comprises dissolving a saponifiable compound in a portion of mineral oil, dispersing an alkali in a non-reactive liquid vehicle, mechanically milling said alkali while dispersed in said vehicle until the particle size of said alkali is predominantly at least as low as 5μ, and mixing said solution of saponifiable compound and said alkali dispersion to produce a saponification reaction.

3. Process according to claim 2 in which the mechanical comminution of the alkali is effected by colloid milling.

4. Process according to claim 2 in which the alkali dispersion is made by ball-milling and the resultant grease is put through a colloid mill to make a fiber grease.

5. The process of making lubricating greases which comprises dissolving a high molecular weight fatty acid in a mineral oil, suspending flake caustic soda in a mineral oil to obtain a mixture containing 20–40% by weight of caustic, mechanically milling this suspension until the caustic particle size is at least as small as 1μ, adding the resulting dispersion to the oil solution of the fatty acid, heating the mixture to a temperature of 140° to 180° F. until the saponification is complete.

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