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GREASES PREPARED BY ALKALI FUSION OF FATTY MATERIALS

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The present invention relates to new and improved lubricating greases and to a new process of preparing the same. More particularly, the invention pertains to a method of manufacturing new and improved lubricating greases of high dropping point and soft consistency over a wide temperature range and to greases produced by this method.

In its broadest aspect, the invention provides for the production of greases in which the thickening agent is a mixture of fatty acid soap obtained by saponification and of the product obtained by heating glycerine at high temperature in the presence of alkali. High temperature greases of excellent quality may be produced in this manner.

Prior to the present invention, soap-thickened greases of desirable hardness characteristics and high melting or dropping point, i. e., greases melting above about 400° F. and having a smooth soft consistency over a wide temperature range, i. e., between about 200° and 400° F., have been known. These greases have been prepared by the saponification of rapeseed oil with an excess of alkali while heating to a temperature between 480° and 520° F. in a lubricating oil vehicle containing a small amount of sodium sulfonate as described in U. S. Patent No. 2,265,791.

The desirable combination of excellent qualities of these greases was believed to be due largely to the use of the C_{22} long-chain acids such as erucic acid as the source of the soap. Rapeseed oil and the Brassidic family are the only known commercial sources for these materials. Erucic acid is present in fish oil but cannot be readily separated therefrom. Actually it has not been possible heretofore to prepare soap-thickened greases having similar properties from other glyceride-type fats or oils nor from the corresponding fatty acids as such. Even attempts of preparing similar greases by saponifying synthetic composites approximating rapeseed oil have failed.

More specifically, prior to the present invention no process was known by which such glycerides as tallow, other fats rich in stearin, or saturated or hydrogenated fats and oils or unsaturated oils other than rapeseed oil could be converted into desirable high temperature greases. While grease products having high melting points have been obtained from these raw materials, the products are extremely hard and dry and unsuitable for ball or roller bearings requiring soft unctuous greases. This situation is unsatisfactory particularly whenever there exists a shortage of rapeseed oil as it has actually occurred during war time. Efforts to produce a good quality high temperature grease from such rapeseed oil substitutes as mixtures of 50% oleic acid and 50% erucic or behenic acid with 2% glycerine were likewise unsuccessful when the known process for producing such greases from rapeseed oil was employed. The present invention eliminates these difficulties.

It is, therefore, an important object of the present invention to provide soap-thickened, good quality high temperature greases based on raw materials other than rapeseed oil. Other objects and advantages will appear from the following description of the invention.

It has now been found that glyceride-type fats and oils and mixtures approximating the composition of such fats and oils may be used quite generally in place of rapeseed oil for the production of high temperature greases of excellent quality provided a large excess of alkali over the amount required for saponification of the glycerides or neutralization of the fatty acid is employed, and saponification or neutralization proper is followed by heating of the reaction mixture to such temperatures substantially exceeding 520° F. as are conducive to alkali fusion of the glycerine with accompanying evolution of hydrogen. While the reaction mechanism is not fully understood, it may be postulated that, in the second high temperature stage, the glycerine split off during the earlier saponification stage or otherwise introduced into the reaction mixture is dehydrated to form acrolein or a dimer thereof. Upon continued heating, the acrolein or its dimer is converted into a salt by alkali fusion either directly or via the Cannizzaro reaction. Alkali fusion of the alcohol formed in the Cannizzaro reaction may also occur. Reactions of the following type may be involved:

(1)

$$\overset{\text{Fat}}{CH_2OOCR\cdot CHOOCR\cdot CH_2OOCR} + 3NaOH \xrightarrow{\text{Saponi-fication}} \overset{\text{Glycerine}}{CH_2OH\cdot CHOH\cdot CH_2OH} + \overset{\text{Soap}}{3RCOONa}$$

(2)

$$CH_2OH\cdot CHOH\cdot CH_2OH \xrightarrow{\text{Dehy-dration}} CH_2{=}CH{-}CHO + 2H_2O$$

(3)

$$CH_2{=}CH{-}CHO + NaOH \xrightarrow{\text{Fusion}} CH_2{=}CH{-}COONa + H_2$$

(4)

$$CH_2{=}CH{-}CHO + NaOH \xrightarrow{\text{Canniz-zaro}} CH_2{=}CH{-}COONa + CH_2{=}CH{-}CH_2OH$$

5)

$$CH_2{=}CH{-}CH_2OH + NaOH \xrightarrow{\text{Fusion}} CH_2{=}CH{-}COONa + 2H_2$$

Reaction 1 illustrates the conventional saponification reaction of the first, low-temperature stage of the invention. The second, i. e., the high temperature, stage may involve Reactions 2–5.

In carrying out the present invention, the amount of alkali is preferably at least twice that required completely to saponify the fat or neutralize the fatty acid used. The first stage of the invention consists in slowly heating the reaction mixture until saponification or acid neutralization is completed. This is satisfactorily accomplished at a temperature below 400° F. Thereafter, heating is continued at temperatures in the range of about 530°–570° F. until foaming caused by gas evolution ceases. It is particularly to be noted that this second reaction does not initiate below this range when employing suitable starting materials other than rapeseed oil.

Within this range, the temperatures required in the second stage are higher for saturated or hydrogenated fats and fatty acids than for unsaturated saponifiable materials. In the case of the former, alkali fusion accompanied by gas evolution and foaming may begin at about 550° F. and stop at about 570° F., as compared to about 530° and 550° F. for the corresponding temperatures in the case of unsaturated saponifiable materials. On the other hand, when rapeseed oil is used in accordance with the known procedure, saponification is completed at about 300°–350° F. and gas evolution and foaming begin at about 450° F. and terminate at about 500° F.

Soap-forming base materials useful for the purposes of the present invention are quite generally saturated or unsaturated or hydrogenated naturally occurring glyceride-type fats and oils of animal or vegetable nature, such as tallow, hog fat, etc., which begin to react with alkali to produce hydrogen at temperatures above about 520° F., as well as mixtures of saturated and/or unsaturated high molecular weight fatty acids with glycerine. Mixtures of glycerides with fatty acids and glycerine can, of course, be used. Of the saturated acids, those containing 12–30 carbon atoms, such as lauric or myristic, and preferably palmitic, stearic, behenic acids are operable. The preferred unsaturated acids are those containing at least 18 and up to about 22 carbon atoms. However, the acids containing conjugated bonds such as the acids of oiticica, tung and similar drying oils should be used if at all in small quantities since they tend to polymerize giving undesirable properties. When mixtures of fatty acids and glycerine are used, the proportion of glycerine is preferably that corresponding to or approximating the glyceride of the fatty acid involved and should not exceed about twice that amount. In the latter case, correspondingly larger amounts of alkali should be used.

As in the case of greases based on rapeseed oil, the addition of small amounts, say, about ¼ to about 2% based on the finished grease, of an oil soluble sulfonic compound derived from petroleum should be added to increase the soft and unctuous quality of the grease and its temperature stability. A petroleum sulfonic acid or an alkali metal soap thereof may be used for this purpose. Other conventional grease additives, such as antioxidants, especially amino compounds, dispersants, extreme pressure agents containing sulfur, etc., may be added.

Regarding suitable lubricating oil bases, mineral oils or unsaponifiable synthetic oils should be used until alkali fusion is completed. For example, a non-paraffinic mineral oil may be employed in this stage of the process. After fusion and after recrystallization of the soap at a temperature below 300° F., any desired type of lubricating oil including ester-type synthetic oils may be added.

Greases, in accordance with the invention, quite generally, may be prepared as follows. The glyceride or a mixture of high molecular weight fatty acids with glycerine is charged together with about 50% of the total lubricating oil requirement to a heated grease kettle and warmed to about 130°–150° F. Alkali metal hydroxide, preferably sodium hydroxide is added in an amount at least twice, but preferably greater than twice, as much as that required to saponify the fat or acid. An excess of 100–125% over saponification requirements should be used, preferably in the form of a 50% aqueous solution of NaOH. The temperature is then raised to about 350°–400° F. and the balance of the lubricating oil is added. Heating is continued to melt the mass completely and beyond this point until foaming begins, becoming appreciable at temperatures of about 530°–550° F. Foaming is usually violent enough to require top stirring which prevents overflowing. The temperature is further raised until foaming commences to recede, which takes place after a temperature rise of about 20° F. This temperature which usually falls between about 550° and 570° F. is maintained for about 20–40 minutes until foaming has ceased.

The grease may then be allowed to cool to about 300°–330° F. whereupon at least a portion of the remaining excess alkali may be neutralized by the addition of fat or fatty acid. The grease should have a free alkalinity of less than 1.0%. Thereafter, further quantities of lubricating oil may be added to adjust the grease consistency to the desired degree. Concentrations of 15–30 wt. percent, based on the finished grease, of total soap-type thickener are suitable for the purposes of the invention.

Regarding the cooling stage, it is noted that cooling times of about 8–22 hours have been used heretofore when working with rapeseed oil. Similar cooling times may be employed in the present process. It has been found, however, that the cooling time may be shortened to as little as 6–10 hours for the temperature interval from about 570° F. to about 200° F. when sufficient acid is added during the cooling process completely to neutralize any excess free alkalinity remaining after fusion and to have even a slight excess of acid in the finished grease, as it is disclosed and claimed more broadly in the copending Morway application Serial No. 289,898, filed May 24, 1952, now abandoned, and assigned to the same interests. In addition to substantial savings in processing equipment due to the shortened cooling times, the greases so prepared have satisfactory lubrication life without any loss in high temperature quality.

Greases obtained in accordance with the present invention have dropping points substantially in excess of 400° F. They have a soft, unctuous consistency at temperatures above 20° F. and retain the same over a wide temperature range.

The invention will be further illustrated by the following specific examples which represent preferred modifications of the invention.

EXAMPLE I

About 20 parts by weight of hydrogenated tallow and 36 parts by weight of low cold test naphthenic type mineral oil having a viscosity of 80 S. S. U. at 210° F. (oil A) were charged to a fire heated grease kettle and warmed to 150° F. About 6 parts by weight of sodium hydroxide in a 50% aqueous solution was charged, the quantity of NaOH being more than twice that required to saponify the fat. The temperature was then raised to 400° F. where an additional 36 parts by weight of a low cold test naphthenic type mineral oil having a viscosity of 40 S. S. U. at 210° F. (oil B) was added. Heating was continued. At 500° F., the grease was completely molten with only slight foam formation. At 550° F. foaming became more evident and at 560° F. the kettle was completely filled with foam requiring top stirring to retain the product in the kettle. At 570° F. the foaming commenced to recede. The batch was held between 550° and 570° F. for ½ hour.

A sample taken at 500° F. had a dropping point of 457° F. while a sample taken at 570° F. had a dropping point of 482° F.

The grease was cooled while stirring to 330° F. when sufficient hydrogenated tallow was added to neutralize ⅓ of the remaining excess caustic. A sufficient amount of oil B was added to hold the soap concentration at 20% by weight. The cold grease had the following properties.

Dropping point, ° F.	411
Percent free alkalinity as NaOH	1.00
Penetrations, 77° F., mm./10:	
Unworked	230
Worked, 60 strokes	260
Worked, 100,000 strokes	360
Appearance—excellent, smooth, uniform short fiber product	
Water solubility—5% loss in AN-G-15[1] water washing test	

[1] Method described in AN-G-15 Government specification.

The gas evolved during fusion had the following composition:

	Percent
Hydrogen	81.0
Carbon dioxide	2.3
Saturated hydrocarbons	14.4
Unsaturated hydrocarbons	2.3

This analysis confirms the evolution of hydrogen during the fusion process and thus tends to substantiate reactions 3 and 5 given above.

EXAMPLE II

Formulation	Parts by Weight
Oleic Acid	20.00
Glycerine	2.00
Sodium Hydroxide	4.75
50% Solution of Sodium Petroleum Sulfonate in Mineral Oil	1.00
Phenyl-α-Naphthylamine Oxidation Inhibitor	1.00
Condensation Product of Salicylal and Ethylene Diamine	0.50
Blend of Oil A and Oil B having Viscosity of 50 S. S. U. at 210° F	70.75

This grease was prepared essentially as described in Example I with the exception that after addition of the second batch of mineral oil, heating was continued to 530° F. The temperature was held at this level until foaming had ceased. After cooling the grease had the following properties:

Penetrations, 77° F., mm./10:	
Unworked	Too soft.
Worked, 60 strokes	Too soft.
Worked, 100,000 strokes	Fluid.
After high shear-type homogenization at 4,000 p. s. i.	227.
Norman-Hoffman, hrs. to 5 p. s. i., drop in oxygen pressure (after homogenization)	170.
Spindle life, hours (after homogenization)	1507.
Percent free alkalinity as NaOH	0.28.
Dropping point, ° F	465.

It will be seen that this grease has a highly satisfactory dropping point and may be homogenized to acquire satisfactory penetration characteristics.

EXAMPLE III

The advantages of the present invention over prior art types of procedures are best illustrated by the following experiments.

Experiment A

A grease was prepared by the process of U. S. Patent No. 2,265,791 from the following ingredients:

Ingredients	Parts by Weight
Rapeseed Oil	22.00
Sodium Hydroxide	4.75
50% Solution of Sodium Petroleum Sulfonate in Mineral Oil	1.00
Phenyl-α-Naphthylamine Oxidation Inhibitor	1.00
Condensation Product of Salicylal and Ethylene Diamine Oxidation Inhibitor	0.50
Blend of Oil A and Oil B, Having Viscosity of 50 S. S. U. at 210° F	70.75

The rapeseed oil and ½ of the mineral oil was charged to a fire heated grease kettle and warmed to 150° F. while agitating. The sodium sulfonate-mineral oil solution was added followed by a 40% aqueous solution of the sodium hydroxide. The temperature was raised and the soap formed was dehydrated at 300°-350° F. At this temperature the balance of the mineral oil was slowly added while continuing to raise the temperature. At 425° F. a second reaction initiated as indicated by foam formation. This foaming continued while the temperature was raised to 500° F. At this temperature foaming ceased, heating was discontinued and the grease cooled while agitating to 275° F. when the inhibitors were added. The grease was further cooled to 200° F. and filtered while drawing in packages.

Experiment B

In an attempt to prepare a high quality grease by the prior art process but using ingredients other than rapeseed oil, a grease was prepared essentially as in Experiment A from the following ingredients:

Ingredients	Parts by Weight
Oleic Acid	10.00
Hydrofol A. B. Acids [1]	10.00
Glycerine	2.00
Sodium Hydroxide	4.75
50% Solution of Sodium Petroleum Sulfonate in Mineral Oil	1.00
Phenyl-α-Naphthylamine Oxidation Inhibitor	1.00
Condensation Product of Salicylal and Ethylene Diamine, Oxidation Inhibitor	0.50
Blend of Oil A and Oil B, Having Viscosity of 50 S. S. U. at 210° F	70.75

[1] Hydrofol A. B. acids composition, percent:

Myristic	1.7
Palmitic	13.3
Stearic	16.9
Arachidic	37.4
Behenic	28.4
Myristoleic	0.1

At temperatures up to 500° F. at which the experiment was terminated no secondary reaction involving foaming or gas evolution had occurred.

Experiment C

The same ingredients as in Experiment B were used and treated as in Experiments A and B except that heating was continued above 500° F. At 530° F., the second reaction initiated. It was completed at 550° F. This grease was then finished as in Experiments A and B.

These three greases were tested with the results tabulated below.

	Experiments		
	A	B	C
Top Manufacturing Temperature, ° F	500	500	550
2nd Reaction Occurs, ° F	425	None	530
2nd Reaction Terminates, ° F	500	--------	550
Penetrations, 77° F. mm./10:			
Unworked	260	265	--------
Worked 60 strokes	285	290	285
Worked 100,000 strokes [1]	360	fluid	375
Dropping Point, ° F	500	360	520+
Water Solubility		Soluble	
Percent Free Alkalinity as NaOH	0.22	1.15	0.17
Norma Hoffman Bomb Oxidation Test Hrs. to 5 p. s. i. Drop in Oxygen Pressure:			
Uninhibited	18	--------	24
Inhibited	150	--------	170
Homogenization: [2] Worked Penetration	170	--------	186

[1] Fine hole worker plate 270—1/16" holes.

[2] Ultimate hardness after high shear type homogenization at 4,000 p. s. i.

The superiority of the grease in Experiment C which corresponds to the present invention is manifest. This grease has the highest dropping point and has good penetration and oxidation characteristics.

The present invention is not limited to any theory of the process of grease manufacture nor to the specific examples set forth above. The relative proportions of the grease constituents may be varied within the limits indicated to obtain greases of different consistency and varying characteristics.

In the following claims, the terms "saponifying," "saponifiable" and "saponification" refer to the formation of soaps by an alkali treatment of fats, oils and/or fatty acids.

What is claimed is:

1. The process of preparing lubricating greases adapted for lubrication at high temperatures which comprises saponifying in a mineral lubricating oil in grease-making proportions a saponifiable material selected from the group consisting of (1) mixtures consisting of saturated high molecular weight fatty acids and glycerine, (2) mixtures consisting of unsaturated high molecular weight fatty acids and glycerine, said glycerine being present in an amount corresponding to that present in the glycerides

of said fatty acids and (3) glycerides of high molecular weight fatty acids, with an amount of sodium hydroxide which is about 100 to 125% more than that required to saponify said material, heating the resulting mixture to complete the saponification of the fatty acids, continuing heating at a temperature of about 530° to 570° F. until hydrogen gas evolution recedes, and then cooling to obtain said lubricating grease.

2. The process of claim 1 wherein said saponification is carried out in the presence of a small amount of an oil-soluble sulfonic compound derived from petroleum.

3. The process of claim 1 wherein said high molecular weight fatty acids have from about 12 to 30 carbon atoms per molecule.

4. The process of preparing lubricating greases adapted for lubrication at high temperatures and containing a major proportion of mineral lubricating oil, which comprises charging to a reaction vessel about 50% of said proportion of lubricating oil, and a minor grease-making proportion of a soap-forming material consisting of a mixture of high molecular weight fatty acids having about 12 to 30 carbon atoms per molecule with an amount of glycerine corresponding to that present in the glycerides of said acids, heating the resulting mixture to a temperature of about 130° to 150° F., adding to said heated mixture sodium hydroxide in an amount of about 100 to 125% more than that required to saponify said material, thereafter raising the temperature of the mixture to about 350° to 400° F., adding the balance of said lubricating oil to the mixture so heated, continuing heating to a temperature of about 530° to 550° F. at which foaming and hydrogen evolution begins, further heating to a level between about 550° to 570° F. at which foaming commences to recede, maintaining said temperature level from about 20 to 40 minutes until foaming and hydrogen evolution has substantially ceased, and then cooling to obtain said lubricating grease composition.

5. The process of claim 4 wherein said soap-forming material comprises a free fatty acid selected from the group consisting of oleic, myristic, palmitic, stearic, arachidic, behenic and myristoleic acids.

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