

2,850,454

## PRODUCTION OF GREASES BY ALKALI FUSION OF MATERIALS CONTAINING HYDROXY FATTY ACID AND GLYCERINE RADICALS

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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 obtained by heating a material containing the radicals of a high molecular weight hydroxy fatty acid and 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 of about 480°–500° 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 glycerides of C<sub>22</sub> long chain acids, such as erucic acid, as the source of the soap. Rapeseed oil, mustard seed oil and the rest of the Brassicid family are the only known commercial sources for these materials. Erucic acid is present in fish oil but cannot be readily separated therefrom. Actually, soap-thickened greases having similar properties have not been prepared commercially heretofore from other glyceride-type fats or oils nor from the corresponding fatty acids as such, nor from synthetic composites approximating rapeseed oil.

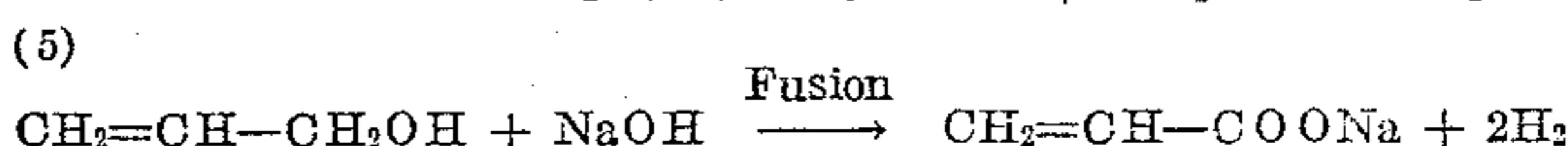
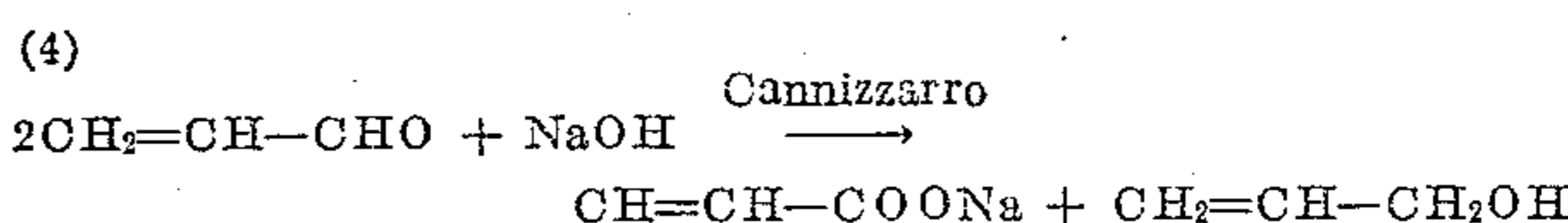
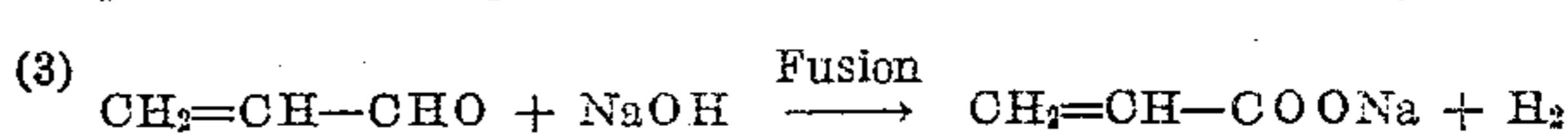
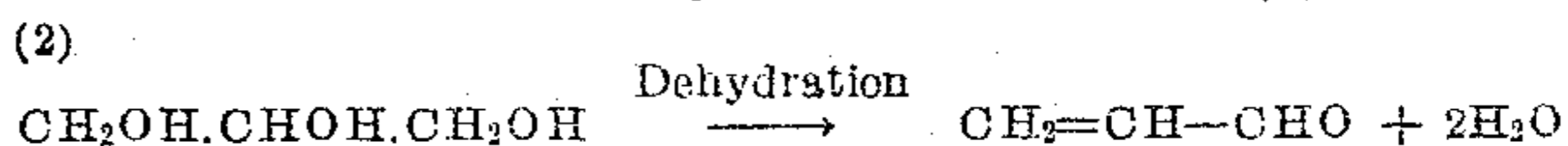
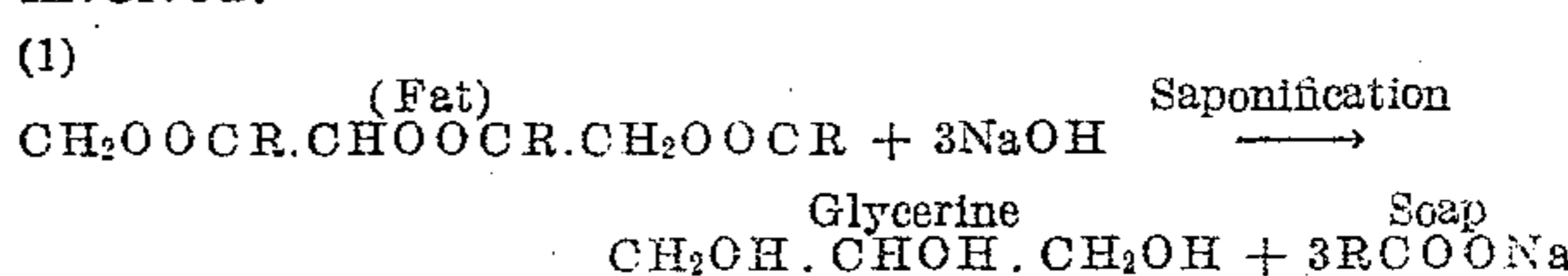
More specifically, prior to the present invention no commercial process was known by which unsaturated oils other than rapeseed oil could be converted into desirable high temperature greases. While grease products having high melting points have been obtained from these raw materials, the products are 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 containing the radicals of high molecular weight hydroxy fatty acids and mixtures approximating the

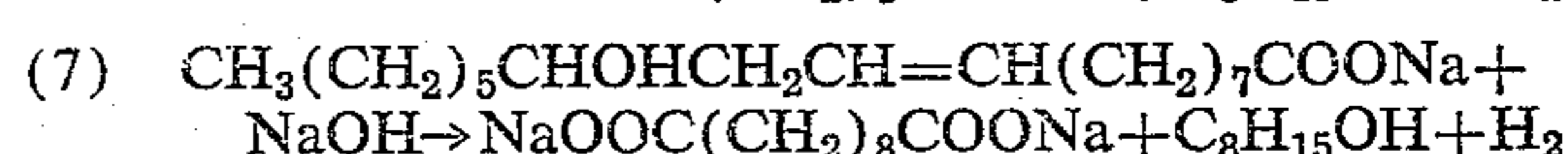
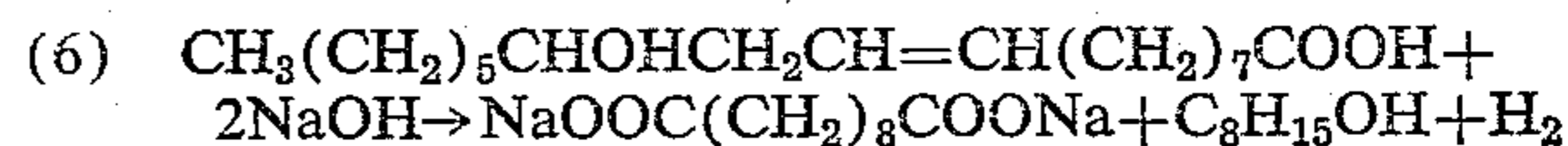
composition of such fats and oils may be used in place of rapeseed oil for the production of high temperature greases of excellent quality provided a large excess of alkali over the amount required for saponification of the glycerides or neutralization of the fatty acid is employed, and saponification or neutralization proper is followed by heating of the reaction mixture to such temperatures substantially exceeding 510° F. as are conducive to alkali fusion of the glycerine with accompanying evolution of hydrogen. Castor oil, which is the glyceride of ricinoleic acid, is the preferred glyceride of the invention. However, hydrogenated castor oil, i. e. castor wax, or mixtures of esters of hydroxy-stearic acids or other hydroxy fatty acids with glycerine may also be used.

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:



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).

The sodium acrylate produced forms a complex soap with the soap formed in accordance with Equation 1, such as sodium ricinoleate, to impart a high dropping point to the grease. A part of the acids of the castor oil or castor wax originally used or the sodium soaps thereof may form under fusion with sodium hydroxide at elevated temperatures sodium sebacate and octenol-2, as shown below.



The formation of these two products, possibly the alcohol, apparently plasticizes the grease to yield a soft unctuous product.

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 of 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 510°–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 the starting materials of the present invention.

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 containing hydroxy groups in their fatty acid radical, such as castor oil, castor wax, etc., which begin to react with alkali to produce hydrogen at temperatures above about 510° F., as well as mixtures of saturated and/or unsaturated high molecular weight hydroxy fatty acids with glycerine. Mixtures of hydroxy fatty acids and glycerine with non-hydroxy fatty acids or glycerides of hydroxy or non-hydroxy fatty acids can, of course, be used. The preferred unsaturated acids are those containing at least 18 and up to about 20 carbon atoms, particularly ricinoleic and hydroxy stearic acids. When mixtures of hydroxy fatty acids and glycerine are used, the proportion of glycerine is preferably that corresponding to or approximating the glyceride of the hydroxy fatty acid involved and should not exceed about twice that amount. In the latter case, correspondingly larger amounts of alkali should be used. The raw materials of the invention may be combined with rapeseed oil or other suitable fats, oils and fatty acids in a wide range of proportions.

As in the case of greases based on rapeseed oil alone, the addition of small amounts, say, about 1/4 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. This material also acts as a rust preventative. A petroleum sulfonic acid or an alkali metal soap thereof may be used for this purpose. Other conventional grease additives, such as anti-oxidants, 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 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 hydroxy 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 40–50% aqueous solution of NaOH. The temperature is then raised to about 300°–350° 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 510°–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 530° 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

##### Formulation

Ingredients:	Wt. percent
Castor oil	22.00
Sodium hydroxide	5.00
Sodium sulfonate blend (50% mineral oil and 50% Na sulfonate)	1.00
Phenyl alpha-naphthylamine (oxidation inhibitor)	1.00
Condensation product of propylene diamine and salicylaldehyde (oxidation inhibitor)	0.50
Naphthenic-type mineral oil having a viscosity of 50 S. S. U. at 210° F.	70.50

The castor oil, sodium sulfonate blend and 1/2 the mineral oil were charged to a fire-heated kettle and warmed to 150° F. The NaOH as a 40% aqueous solution was then added and heating continued until the grease was dehydrated. At 300° F., the balance of the mineral oil was added and the mass heated to 530° F. Heavy foaming initiated at 510° F. After foaming subsided at 530° F., the product was cooled while agitating to 300° F. The oxidation inhibitors were added and the grease cooled to 200° F. At this temperature the grease was filtered, homogenized and packaged. Analysis of the fatty acid extracted from the soap thickener in this grease shows that the fatty acid has undergone changes and differs from the original castor oil as follows:

	Mixed fatty acids from castor oil	Fatty acids extracted from grease
Iodine No.	88	43
Hydroxyl No.	219	61
Saponification No.	188	221
Acetyl No.	188	57

## 5

### EXAMPLE II

#### Formulation

Ingredients:	Wt. percent
Rapeseed oil.....	11.00
Castor oil.....	11.00
NaOH.....	5.00
Sodium sulfonate blend (50% mineral oil, 50% Na sulfonate).....	1.00
Phenyl alpha-naphthylamine.....	1.00
Condensation product of propylene diamine and salicylaldehyde.....	0.50
Naphthenic-type mineral oil having a viscosity of 50 S. S. U. at 210° F.....	70.50

The grease was prepared similarly as described in Example I.

### EXAMPLE III

#### Formulation

Ingredients:	Wt. percent
Castor Wax.....	14.67
Hydrofol <sup>1</sup> glyceride.....	7.33
NaOH.....	5.00
Sodium sulfonate blend (50% mineral oil, 50% Na sulfonate).....	1.00
Phenyl alpha-naphthylamine.....	1.00
Condensation product of propylene diamine and salicylaldehyde.....	0.50
Naphthenic-type mineral oil having a viscosity of 50 S. S. U. at 210° F.....	70.50

<sup>1</sup> Hydrofol acids are hydrogenated fish oil acids corresponding in saturation to commercial stearic acid.

The grease was prepared as described in Example I. The dropping point of this grease during manufacture was as follows:

Sample taken at 513° F.—398° F.

Sample taken at 530° F.—424° F.

The properties of the greases of Examples I, II and III are tabulated below in comparison with those of a grease prepared from rapeseed oil in the conventional manner.

PROPERTIES OF CASTOR OIL GREASES COMPARED WITH GREASE THICKENED WITH SOAP OF RAPESEED OIL

	Rapeseed oil grease	Example I	Example II	Example III
Composition, weight percent:				
Rapeseed oil.....	22.00	11.00		
Castor oil.....		11.00	22.00	
Castor wax.....				14.67
Hydrogenated fish oil glyceride.....				7.33
NaOH.....	4.75	5.00	5.00	5.00
Sodium sulfonate blend (50% mineral oil, 50% Na sulfonate).....	1.00	1.00	1.00	1.00
Phenyl alpha-naphthylamine.....	1.00	1.00	1.00	1.00
Condensation product of propylene diamine and salicylaldehyde.....	0.50	0.50	0.50	0.50
Mineral oils.....	70.75	70.75	70.75	70.75
Properties:				
Percent free alkalinity (NaOH).....	0.30	0.30	0.20	0.30
Dropping point, ° F.....	500+	500+	500+	500+
Penetrations, 77° F. mm./10—				
Unworked.....	252	240	309	276
Worked, 60 strokes.....	265	268	335	308
Worked penetration after homogenization to ultimate hardness.....	177	203	329	232
Norma-Hoffman oxidation, hours to 5 p. s. l. drop in O <sub>2</sub> pressure.....	110	150	100	272
Maximum temperature of manufacture, ° F.....	500	530	530	530

It has further been found that the grease of the present invention will prevent friction oxidation. In the lubrication of heavy truck front wheel bearings, the inner and

## 6

outer bearings of the wheel assembly are slipped over the wheel spindle. In actual practice the inner bore surfaces tend to turn only a small portion of a complete revolution while being subjected to heavy intermittent shock loads. This is a condition highly conducive to the occurrence of fretting corrosion. After short periods of operation with common soap-thickened lubricants, corrosion between the inner race bore surfaces and the spindle occurs. Further operation results in the spread of iron oxide into the bearing itself resulting in early bearing failure. A further complication is the welding of the bearing to the spindle, if this fretting corrosion is not observed early. When this occurs, the spindle must be removed and replaced. This is very expensive.

Lubrication of wheel bearings with the lubricant of the present invention materially reduces this oxidation corrosion and gives excellent lubrication for long periods of operation. Truck wheel assemblies employing a grease prepared as described in Example II have gone to brake band replacement, i. e. to approximately 75,000–90,000 miles, and even then the lubricant was in good condition. This effect is substantially superior to that of greases prepared with rapeseed oil in the conventional manner, which permit early occurrence of mild fretting corrosion.

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 acid.

What is claimed is:

1. A process of preparing lubricating greases containing a major proportion of lubricating oil, which comprises charging to a reaction vessel a mixture consisting essentially of about 50% of said proportion of a mineral lubricating oil and a minor grease making proportion of a soap-forming material containing the radicals of a high molecular weight hydroxy fatty acid having in the range of 18 to 20 carbon atoms per molecule and of glycerine in an amount corresponding to the glyceride of said acid, heating the mixture to a temperature in the range of 130° to 150° F., adding to said heated mixture sodium hydroxide in an amount in the range of 100 to 125% in excess of that required to saponify said soap-forming material, thereafter raising the temperature of the mixture to in the range of 300° to 350° F., adding the balance of said lubricating oil to the mixture so heated, continuing heating to melt the mass and beyond this point to a temperature in the range of 510° to 550° F. sufficient to liberate gas and cause foaming, further raising the temperature to a level in the range of 530° to 570° F. until foaming subsides, cooling the mixture to a temperature in the range of 300° to 330° F. and adjusting the free alkalinity of the mixture to less than one percent.

2. The process of claim 1 wherein said soap-forming material is castor oil.

3. The process of claim 1 wherein said soap forming material is hydrogenated castor oil.

4. A process for preparing lubricating greases suitable for high temperature service which consists essentially of the steps of mixing a portion of the mineral lubricating oil required in the finished grease and a saponifiable material selected from the group consisting of hydroxy fatty acid glycerides and mixtures of a hydroxy fatty acid with glycerine in glyceride proportions, with an alkali metal hydroxide, the amount of said metal hydroxide being sufficient to neutralize said saponifiable material and acidic products formed by decomposition of the glycerine under conditions hereinafter stated, heating the resulting mixture to a temperature sufficient to saponify said sa-

ponifiable material, but below the decomposition temperature of the glycerine, thereafter adding additional lubricating oil, further heating the resulting mixture to a temperature in the range of 510° to 550° F. sufficient to initiate decomposition of the glycerine into acidic compounds with the evolution of gas and the formation of foam, heating the mixture at least 20° F. above said last named temperature until the foaming has subsided, and thereafter cooling the resulting product.

5. The process of claim 4 wherein the saponification is carried out in the presence of about 0.25 to 2.0 percent, based on the finished grease, of an oil soluble sulfonic compound derived from petroleum.

6. The process of claim 4 wherein said hydroxy fatty acid is ricinoleic acid.

7. The process of claim 4 wherein said hydroxy fatty acid is a hydroxy stearic acid.

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