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MANUFACTURE OF LUBRICATING GREASES BY THE IN SITU ALKALI FUSION OF ALCOHOLS

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The present invention relates to an improved method of preparing lubricating greases and to grease compositions produced by this method. More specifically, the invention pertains to improvements in the manufacture of grease thickeners and to greases containing such thickeners. In its broadest aspect, the invention provides for making grease thickeners by fusing high molecular weight alcohols with caustic alkali, producing a metal soap from the acid so formed and incorporating this metal soap into a lubricating oil in grease making proportions. In a preferred embodiment of the invention, the fusion is carried out in the presence of lubricating oil.

Lubricating greases normally consist of lubricating oils thickened by alkali and alkaline earth metal soaps or other thickeners to a solid or semi-solid consistency. The soaps may be prepared by the neutralization of high molecular weight fatty acids or by the saponification of fats which is usually carried out in a portion of the oil to be thickened. Saponification of fats has been the preferred grease making method heretofore chiefly because greases produced in the absence of glycerine or similar materials have tendencies to become crumbly, to sweat oil and to break down into soft granular masses of reduced lubricating value. More recently, fatty acids are being frequently employed in combination with the glycerides for various purposes, such as improvements in structure of the grease, its high temperature characteristics, etc.

The present invention pertains to highly valuable, stable lubricating greases in which the high molecular weight fatty acids are replaced or at least supplemented by a new grease making material. It has now been found that such greases may be prepared by incorporating into lubricating oils a grease thickener obtained by fusing high molecular weight alcohols with alkali, particularly caustic soda or potash at temperatures of about 450°–650° F., preferably about 500°–560° F. for a time sufficient to form the alkali metal salt of the acid corresponding to the alcohol used. The chemical reaction taking place during the fusion process may be illustrated by the following equation:

$$RCH_2OH + MOH \rightarrow 2H_2 + RCOOM$$

wherein R may be a radical containing 10–30 carbon atoms and M is an alkali metal such as sodium or potassium.

The discovery of the utility of alkali fusion of high molecular weight alcohols for grease making greatly increases the wealth of raw materials available for grease production. Heretofore, ester-type fats, oils or high molecular weight fatty acids have been used exclusively in the manufacture of soap-thickened greases and these starting materials have been believed indispensable for the purpose. All these materials have numerous other industrial uses, a situation conductive to the development

of shortages forcing frequent variations in grease making procedures and grease characteristics. The discovery of an entirely new and large class of suitable raw materials eases this situation considerably.

Three factors further contribute to the value of high molecular weight alcohols as grease making materials. In the first place, their use introduces no complication into the grease making procedure. While alkali fusion of the alcohol may be carried out in a separate preliminary acid-forming stage, the greases are preferably produced essentially in a single process step in which the high molecular weight alcohol is fused with alkali in the lubricating oil base in grease making proportions and at grease making conditions, although at somewhat higher temperatures. At the conclusion of the fusion process a finished grease is obtained.

Secondly, no water is formed during the reaction so that no excessive foaming occurs. Slight foaming caused by the evolution of hydrogen is not a great inconvenience.

Finally, alcohols useful for the purposes of the present invention have become available in large quantities as intermediate or final products of various synthesis processes and more particularly as products and by-products of the well-known "Oxo" synthesis. The last named process involves the catalytic reaction of olefins with carbon monoxide and hydrogen at elevated temperatures, say about 300°–400° F., and pressures of about 2500–4000 p. s. i g. in the presence of group VIII metal catalysts, particularly cobalt catalysts, to form saturated aldehydes having one carbon atom more than the olefin originally used. The aldehyde is catalytically hydrogenated to the corresponding alcohol which is recovered by distillation from the reaction mixture leaving the so-called "Oxo-bottoms," consisting of higher boiling materials rich in alcohols. The present invention is applicable to high molecular weight alcohols so prepared and recovered overhead from the distillation stage. However, a highly desirable embodiment of the invention involves the use of the Oxo bottoms as such in the new grease making process.

Quite generally, alcohols may be used which have about 10–30 carbon atoms per molecule and a sufficiently high boiling point to prevent excessive volatilization during the fusion process. As to the type of alcohols suitable for the invention, straight chain saturated alcohols give good results. Examples of such alcohols are cetyl and stearyl alcohols. Particularly desirable starting materials are the branched chain primary alcohols, such as those obtained by oxonation of polymerized olefins or olefins from cracked waxes, cracked petrolatums and other high molecular weight hydrocarbon products, for example Fischer-Tropsch olefins.

When applying the invention to the fusion of Oxo-bottoms in accordance with one of the embodiments of the invention, the distillation residue of the hydrogenated oxonation product of a wide variety of oxonation reactions may be used. Quite generally, the distillation bottoms obtained in the successive oxonation, hydrogenation and distillation of mono-olefins having 7–30 carbon atoms or more per molecule are preferred for the purposes of the invention.

These Oxo-bottoms are of rather complex composition. For example, in the manufacture of iso-octyl alcohol from a C_7 olefin prepared by propylene-butylene copolymerization, the final distillation of the crude C_8 alcohol to a dry point of about 392° F. in the A. S. T. M. distillation test results in a bottoms fraction representing about 7–15 wt. percent of the crude alcohol charged to the distillation zone. This bottoms fraction consists of C_8 and C_9 alcohols as well as C_{16}–C_{18} alcohols, C_{24} acetals, C_{16}+ esters,

C_8–C_9 acids and heavier acids. A typical composition is about as follows:

	Weight percent
C_8–C_9 alcohols	12.0
Crude higher alcohols (C_{16}–C_{18})	18.0
C_{24} acetals	1
C_{16}+ esters	32
C_{16} esters + miscellaneous	19
C_8–C_9 acids	6
Crude heavy acids (C_{16}–C_{18})	12

Typical inspection data (after caustic wash) are given below.

Specific gravity @ 20/20	0.85
Acidity	Neutral
Hydroxyl number	109/130
Distillation, ° F.:	
Initial	392
80% point	770

Oxo-bottoms of the type defined above and those of lesser volatility obtained in many other Oxo processes are suitable for the purposes of the invention provided they contain substantial proportions of free or combined alcohols within the desired molecular weight range of about 10–30 carbon atoms per molecule. These distillation bottoms may be used as such without prior refining treatment. They may be reacted with alkali or with alkali dispersed in a suitable lubricating oil, the alkali being employed in an amount sufficient to convert all saponifiable and fusible constituents into alkali metal soaps and salts. Constituents of the Oxo-bottoms which do not react at the conditions of alcohol fusion, such as certain ethers, acetals, and hydrocarbons, are readily removed from the reaction mixture by distillation at the relatively high temperatures of the fusion process, which usually exceed 500° F. However, it is often preferred to retain these constituents as modifiers in the grease in which case elevated pressures may be employed. Acids and the acid groups of esters are, of course, converted into soaps and salts and are retained in the finished grease.

When carrying out the alcohol fusion in the lubricating oil itself so as to form the grease thickening soap in situ in accordance with the preferred embodiment of the invention, it has been observed that the alkali has a strong tendency to settle out of the reaction mixture to the bottom of the reactor in the form of a cake which does not fully participate in the reaction. Highly efficient stirring or agitation will counteract this tendency. However, in many cases more efficient stirring is required than may be obtained in conventional grease kettles and special equipment would have to be used.

It has now further been found that the settling tendency of the alkali in the lubricating oil-alcohol mixture is negligible when a sufficient amount of a solid suspending agent is present in the reaction mixture. Most desirable suspending agents are those which serve simultaneously as grease thickeners, such as soaps of high molecular weight fatty acids, silica gel, carbon black, bentones, Attapulgus clay modifications, etc.

Soaps, particularly sodium soaps of high molecular weight fatty acids are preferred for this purpose. However, the melting points of most of these soaps in lubricating oil is rather low, usually below 400° F. Thus, at the high reaction or fusion temperature of about 500° F. or thereabove, these soaps are liquid when used as such and do not entirely counteract the settling tendency of the alkali. This difficulty may be overcome in accordance with a specific embodiment of the invention by using the salt, preferably the alkali metal salt, of a low molecular weight acid in addition to the high molecular weight fatty acid soap. In this manner, soap-salt complexes are formed which melt well above 500° F. and thus form an excellent suspending agent.

These soaps or soap-salt complexes are preferably

formed in situ by neutralization of the corresponding acids in the alcohol-oil mixture with alkali added in amounts sufficient for this neutralization and the subsequent fusion which takes place at considerably higher temperatures. High molecular weight acids useful for this purpose include hydrogenated fish oil acids, C_{12}–C_{22} naturally occurring acids of animal or vegetable origin, etc. These acids may be used in amounts ranging from about 2–30 wt. percent based on the finished product. Suitable low molecular weight acids include acetic, furoic, acrylic and similar acids to be used in proportions of about 1–10 wt. percent based on the finished product. Easters of the high and/or low molecular weight acids, particularly those containing mono basic acid esters may be used in place of the free acids in corresponding proportions. In this case, the alcohol portions of the esters are converted into acids and the corresponding soaps by alkali fusion. If esters of low molecular weight alcohols are used, elevated pressures may be employed to prevent volatilization of the alcohols. Of course, esters of nonvolatile low molecular weight alcohols, such as polyhydroxy alcohol esters, e. g. sorbitol acetate, glycol acetate, etc. may be used. Particularly the high molecular weight type of acids or their esters used for this purpose may also be prepared by alkali fusion of Oxo products. In this case, a portion of the product of the alkali fusion process in which the principal grease thickener is prepared in accordance with the invention may be returned to the fusion stage to serve as an agent preventing settling of the alkali.

Soaps of high molecular weight fatty acids and/or soap-salt complexes of the type specified may be incorporated in the greases of the present invention to improve high temperature or other characteristics even if no suspending agents are required. Thus, it has been found that the use of soaps derived from branched-chain alcohols as the sole grease thickeners often tend to form rubbery or cohesive structures which may be undesirable. However, when these branched-chain soaps are mixed with straight chain soaps derived from fatty acids, this cohesive structure is largely eliminated or modified to an extent that is desirable for certain purposes.

The soaps formed by alkali fusion of alcohols in the presence of other fatty acid soaps consistently yield excellent smooth greases. Other conventional thickeners, antioxidants, corrosion inhibitors, tackiness agents, load-carrying compounds, viscosity index improvers, oiliness agents, and the like may be added prior, during and/or after the fusion process as will be apparent to those skilled in the art.

The base oil used as menstruum during the fusion process should be a mineral lubricating oil. After the fusion is completed, synthetic lubricating oils, such as a dibasic acid ester (e. g. di-2-ethyl hexyl sebacate, adipate, etc.), polyglycol type synthetic oils, esters of dibasic acids and polyhydric alcohols, etc., as well as alkyl silicates, carbonates, formals, acetals, etc., may be used alone or in addition to mineral lubricating oil to bring the grease to the desired consistency. The oil base preferably comprises about 50 to about 95% of the total weight of the finished grease.

As indicated above, the process of the invention may be carried out in two stages. When so operating, the alcohol to be fused may be added over a period of several hours, say 5–15 hours, in substantially stoichiometric proportions, to a molten mixture of alkali and mineral oil, preferably a heavy paraffinic oil, maintained at fusion temperatures of, say, about 450–550° F. When all the alcohol has been added, heating may be continued at these temperatures until gas evolution substantially ceases. The acid formed may be recovered from the reaction mixture after cooling, by dilution with water followed by extraction of the oil and any unreacted alcohol with a light hydrocarbon solvent, such as heptane or the like, and acidification of the aqueous raffinate. If desired,

the free acid may be purified by vacuum distillation. The acid so prepared may then be introduced into a lubricating oil base stock, other high and/or low molecular weight fatty acids as well as other grease additives may be added and the mixture may be converted into a grease by the addition of at least sufficient caustic alkali, preferably in aqueous solution, to neutralize the acids present. Conventional grease making conditions including temperatures of about 350°–500° F. may be used in this stage. The soap derived from the alcohol by alkali fusion should form at least 20 wt. percent and preferably about 30–50 wt. percent of the grease thickener or about 2.0–20 wt. percent of the finished grease. The remainder of the grease thickener is preferably made up by a suitable soap-salt complex of the type described above. The proportion of soap derived from alcohol to soaps and salts derived from other acids may be about 1:4 to 4:1 and preferably is about 1:1.

In order to prepare a grease by alkali fusion of the alcohol in situ in accordance with a more desirable embodiment of the invention, the grease making procedure may be quite generally as follows. A mineral lubricating oil base is mixed with solid alkali, preferably in flake or pellet form. The mixture is heated to about 450°–500° F. whereupon the alcohol is slowly added in increments or continuously over a period of about 1–20 hours under vigorous stirring. A reaction temperature of about 475°–550° F., preferably about 500°–560° F., is maintained throughout the alcohol addition. After all the alcohol has been added, heating at these temperatures is continued until evolution of hydrogen ceases or until the desired conversion has been obtained. The reaction mixture is quenched or allowed to cool and may then be diluted with further amounts of lubricating oil to the desired grease consistency.

A similar procedure is employed when the alcohol is subjected to alkali fusion in situ in the presence of suspending agents, such as soaps of high molecular weight fatty acids or complexes of such soaps with low molecular weight fatty acid salts in accordance with the preferred embodiment of the invention. In this case, all the acids needed to form the suspending agent are added to the mineral oil together with the alcohol. Thereafter, sufficient caustic alkali to neutralize the acids and convert the alcohol to soap is added, preferably in the form of an aqueous solution of about 40–50% and the mixture is heated at a saponification temperature of about 300°–400° F. until the acids are converted to soaps and salts and all the water is volatilized. Alkali fusion is then carried out substantially as described above, except that less violent stirring is required.

In the case of the use of Oxo-bottoms as the source for the alcohols, the choice of suitable proportions of base oil, Oxo-bottoms and caustic alkali depends on the composition of the Oxo-bottoms. Quite generally, it may be stated that the Oxo-bottoms may be employed in the same proportions as the alcohols unless the amount of reactionable material is exceptionally low.

The invention will be best understood by reference to the following specific examples which represent preferred modifications of the invention.

Example I

A 1 gallon nickel reactor with a stainless steel cover which was fitted with a stirrer, thermometer well, condenser and an alcohol feed line was charged with:

370 g. NaOH flakes
330 g. KOH flakes
325 g. heavy white oil

This mixture was maintained at 460°–530° F. while 2600 g. of C_{13} Oxo alcohol was added over a period of 12 hours. The Oxo alcohol had been obtained by the oxonation of C_{12} polypropylene at conventional conditions. This product is believed to be substantially a mixture of C_{13} branched-chain primary alcohols.

The reaction temperature was maintained for one more hour after all the alcohol had been added. During the entire time of the reaction the H_2 evolved was measured through a wet test meter. The hot product was removed from the reactor by suction and poured into water. The resulting mixture was extracted with heptane to remove the white oil and any unreacted alcohol. Acidification of the aqueous solution resulted in the separation of the C_{13} acid. It was further purified by vacuum distillation. This acid was used to make a grease as follows:

Ingredients:	Percent
C_{13} acid prepared as mentioned above	10.0
Hydrofol acids [1]	10.0
Acetic acid glacial	4.0
Phenyl alpha naphthylamine	1.0
Sodium hydroxide	6.5
Naphthenic type lubricating oil distillate having a viscosity of 55 S. S. U. at 210° F.	68.5

[1] Hydrogenated fish oil acids, approximately equivalent to stearic acid in molecular weight and unsaturation.

The two high molecular weight acids and ½ the mineral oil were charged to a fire heated kettle equipped with efficient stirring mechanism and heated to 150° F. The acetic acid was charged just prior to addition of a 40% aqueous solution of the sodium hydroxide. The temperature was slowly raised and the soaps dehydrated. When completely dehydrated the balance of the oil was added and the temperature raised to 480° F. The phenyl alpha naphthylamine oxidation inhibitor was added and the grease cooled while agitating. The product was smooth and quite stiff; it had the appearance of a smooth uniform short-fiber grease and a worked penetration of 200 mm./10.

The above product was heated to 400° F. and 1500 grams of a naphthenic type lubricating oil distillate having a viscosity of 55 S. S. U. at 210° F. was slowly added. The resultant grease had the following composition and properties after heating to 480° F. and cooling.

Ingredients:	Weight percent.
C_{13} Oxo acid prepared as above	5.00.
Hydrofol acids	5.00.
Acetic acid glacial	2.00.
Phenyl alpha naphthylamine	0.50.
NaOH	3.25.
Naphthenic type lubricating oil distillate having a viscosity of 55 S. S. U. at 210° F	84.25.
Percent free alkalinity or acidity: Acidity as oleic acid	0.06.
Properties:	
Appearance	Smooth, uniform, straw colored, short fiber product.
Penetrations, 77° F., mm./10:	
Unworked	275.
Worked, 60 strokes	278.
Worked, 100,000 strokes	185.
Dropping point, °F.	476.
BEC Test 204 ball bearing operating at 3400 R. P. M.:	
80° F.	Excellent lubrication.
220° F.	Excellent lubrication. No leakage thru seal.
Norma-Hoffman Bomb oxidation test, hours to 5 p. s. i. drop in oxygen pressure	175.

Example II

Ingredients:	Weight percent
C_{13} Oxo alcohol	10.0
Hydrofol acids	10.0
Acetic acid glacial	4.0
Phenyl alpha naphthylamine	1.0
NaOH	6.5
Naphthenic type lubricating oil distillate having a viscosity of 55 S. S. U. at 210° F	68.5

The alcohol, fish oil acids and ½ mineral oil were charged to a fire-heated kettle and warmed to 150° F. The glacial acetic acid was charged followed immediately by a 40% aqueous solution of NaOH. The mass was heated to 300° F. until the acids were converted to soaps and salt and essentially all water was volatilized. The balance of the oil was added and the mass heated to 550°–560° F. and held at this temperature for about 2 hours. During this period at elevated temperatures the alcohol was fused, forming soaps of the corresponding acid and hydrogen. The mass was then cooled, while working, to 300° F., the phenyl alpha naphthylamine oxidation inhibitor was added and the grease further cooled to 200° F. The product formed was a stiff, firm grease.

If a softer product is desired, additional oil may be added. This oil may be of a different type having low volatility, better viscosity-temperature relationship and more oxidation stability. Even if unsatisfactory as a medium for the original soap dispersion and soap crystallization, it will give an excellent dilution effect to the already dispersed soap. The diluted grease may be filtered and the uniformity, smoothness, and homogeneity desired by the trade may be obtained by subsequent homogenization or milling under high rates of shear.

Example III

Ingredients:	Weight percent
Hydrofol acids	10.00
C_{16} "Oxo" alcohol [1]	10.00
Glacial acetic acid	4.00
Sodium hydroxide	6.50
Phenyl alpha napthhylamine	1.00
Naphthenic type lubricating oil distillate having a viscosity of 55 S. S. U. at 2105 F	68.50

[1] Branched chain primary alcohol prepared by oxonation of C_{15} polypropylene in a conventional manner.

The alcohol, hydrofol acid and mineral oil (½ portion) were charged to a fire-heated kettle equipped with efficient means of agitation. After heating to 150° F., the acetic acid was added, followed immediately with a 40% solution of sodium hydroxide. Heating was continued and the temperature raised to 350° F. At this time the grease was of good solid consistency and dry. The balance of the oil was added and the grease heated to 560° F. and held at this temperature until free alkalinity determinations on spot samples had shown substantially complete reaction of the alcohol. The mass was allowed to cool and at 300° F., the phenyl alpha naphthylamine was added. The grease was filtered and packaged at 200° F. If desired, the grease at this temperature may be diluted with further oil and homogenized to the desired consistency. A small amount of unreacted alcohol left in the grease acts as an excellent modifying and smoothing agent. Excess free alkalinity may be neutralized with fatty acid if desired.

Properties:	
Percent free alkalinity as NaOH	1.00
Dropping point, ° F	500+
Penetrations, 77° F., mm./10:	
Unhomogenized:	
Unworked	392
Worked, 60 strokes	436
Worked, 100,000 strokes	340

Homogenized:	
Unworked	194
Worked, 60 strokes	239
Worked, 100,000 strokes	320
Norma-Hoffman oxidation, hours to 5 p. s. i. drop in oxygen pressure	110
Water washing, percent loss	0.0

The above grease was diluted with a mixed base dewaxed and solvent refined oil of the SAE 20 grade and homogenized in the ratio of 61% grease and 39% of the additional lubricating oil. The properties of this product were as follows:

Appearance	Yellow short-fiber grease.
Dropping point, ° F	450.
Worked penetration, 77° F.	345.
Water washing, percent loss	55.
Spindle life, hours at 250° F. and 10,000 R. P. M	>2000.

Example IV

Ingredients:	Weight percent
Stearyl alcohol	10.00
Hydrofol acids	10.00
Acetic acid glacial	4.00
Sodium hydroxide	6.50
Phenyl alpha naphthylamine	1.00
Naphthenic type lubricating oil distillate having a viscosity of 55 S. S. U. at 210° F	68.50

Prepared in a manner similar to that of Example III.

Properties:		
Appearance	Excellent, smooth uniform product	
Free alkalinity, percent (as NaOH)	0.83	
Penetrations, 77° F., mm./10:		*After Gaulin homogenization*
Unworked	333	177
Worked, 60 strokes	344	190
Worked, 61,000 strokes [1]	184	
Dropping point, ° F	461	
Water washing test, percent loss	None	
Norma-Hoffman oxidation, hours to 5 p. s. i. drop in oxygen pressure		114

[1] Worker plate—270-1/16" diameter holes.

The invention is not limited to the specific figures of the foregoing examples. The relative proportions of the grease constituents may be varied within the limits indicated above to obtain greases of different consistency and varying characteristics.

What is claimed is:

1. The process of preparing a lubricating grease which comprises mixing a mineral lubricating oil with alkali, sufficient in amount for fusion and saponification, heating the resulting mixture to a temperature in the range of 450° to 500° F., slowly adding to the heated mixture over a time in the range of 1 to 20 hours a stoichiometric proportion of an alcohol while maintaining a fusion-reaction temperature within the range of 475° to 560° F., continuing heating at the fusion-reaction temperature until gas evolution ceases, cooling the reaction mixture, and diluting the reaction mixture with additional lubricating oil to obtain the desired grease consistency, said alcohol consisting of a branched chain primary aliphatic alcohol having from about 10 to 30 carbon atoms per molecule, prepared by the catalytic reaction of an olefin having one carbon atom less than said alcohol with carbon monoxide and hydrogen at a temperature in the range of 300° to 400° F. and a pressure in the range of 2500 to 4000 p. s. i. g. in the presence of a group VIII metal catalyst, followed by catalytic hydrogenation of the aldehyde so formed.

2. The process of preparing a lubricating grease which comprises admixing an alcohol, a high molecular weight carboxylic acid having from about 12 to 22 carbon atoms per molecule and a dispersing proportion of a mineral lubricating oil, adding alkali to the mixture sufficient in amount for fusion and saponification, heating the resulting mixture to a temperature in the range of 300° to 400° F.,

adding additional lubricating oil to the heated mixture to obtain the desired grease consistency, heating the diluted mixture to a fusion-reaction temperature in the range of 475° to 560° F., continuing heating at said fusion-reaction temperature until gas evolution ceases, and then cooling the reaction mixture to obtain a lubricating grease, said alcohol consisting of a branched chain primary aliphatic alcohol having from about 10 to 30 carbon atoms per molecule, prepared by the catalytic reaction of an olefin having one carbon atom less than said alcohol, with carbon monoxide and hydrogen at a temperature in the range of 300° to 400° F. and a pressure in the range of 2500 to 4000 p. s. i. g. in the presence of a group VIII metal catalyst, followed by catalytic hydrogenation of the aldehyde so formed.

3. The process of claim 2 wherein said alcohol is contained in the bottoms remaining after distilling a more volatile product alcohol from the hydrogenated product of the aldehye hydrogenation step.

4. The process of claim 2 wherein a low molecular weight monocarboxylic acid is added to the mixture of said alcohol, high molecular weight carboxylic acid and mineral lubricating oil prior to the addition of alkali.

5. The process of claim 4 wherein said low molecular weight carboxylic acid is acetic acid.

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