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PRODUCTION OF ANHYDROUS SODA BASE LUBRICATING GREASES

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This invention relates to the production of lubricants and, more particularly, to substantially anhydrous soda soap greases containing small amounts of the higher polyalkylene glycols, that is, those above the trialkylene glycol, said glycols being exemplified by the polyethylene glycols, the polypropylene glycols, the polybutylene glycols, the polyamylene glycols, and the polyhexylene glycols. The soda soap greases of the present invention may contain a small amount of the liquid polyalkylene glycols having a molecular weight varying between about 200 and about 600, or a solid polyalkylene glycol having a molecular weight varying from about 1000 to 7000.

It is known that soda soap greases are exceedingly sensitive to rapid cooling from a highly heated liquid state to a solid state. This has made it necessary to slowly cool the grease from its hot liquid state adjacent its melting point and higher in a period usually varying from 12 to 16 hours when cooled in layers of three inches to five inches in thickness, bleeding of the oil from the grease being inhibited during this cooling period. In accordance with the present invention quick cooling is accomplished, and bleeding is prohibited by incorporating in the grease a small amount of a higher polyalkylene glycol thereof having the character set forth and cooling in the presence thereof, the percentage of polyalkylene glycol present in the grease ranging from about 0.05% to 1% and preferably from 0.1% to 0.25% or 0.3% taken on the weight of the grease, said cooling being preferably in thin layers averaging from $\frac{1}{16}$'' to about ½'' in thickness. Greater amounts may be used but are not necessary to accomplish the purpose of the present invention. Desirably, the amount of the polyalkylene glycol incorporated in the grease should not materially decrease the melting point of the grease. Some decrease in the melting point of the grease for certain purposes will not be harmful.

An additional object of the present invention is to prepare a completely reversible soda soap or soda base grease, said grease having been cooled slowly, or quickly within the spirit of the invention. A grease is designated "a reversible grease" if it is characterized by the property of being capable of being repeatedly melted to a liquid state and cooled to a solid state without any change in texture and mechanical properties, any cooling rate being utilized. When the polyalkylene glycol, and, particularly, polyethylene glycol is added in amounts less than about 1% taken on the weight of the grease, the soda base grease becomes reversible. While the amount of polyalkylene glycol added may vary from about .03% to 1%, it preferably varies from about 0.1% to .25% or 0.3% taken on the weight of the grease.

In the manufacture of sodium soap greases,

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in order to impart mechanical stability to the grease, and to diminish the tendency of the grease to bleed, it has been necessary to add to the grease 0.3% to 1% of sodium naphthenate based on the weight of the grease. It is an object of the present invention to produce substantially anhydrous sodium soap or sodium base greases which are mechanically stable and which show substantially no tendency to bleed, by incorporating in the grease from about .01% to .05% of a polyalkylene glycol of the character herein set forth. When an amount varying between .03% and .05% of a polyalkylene glycol of the character herein set forth is incorporated in the grease, the latter is reversible to the extent that it will not disintegrate on rapid cooling down, but the resulting grease is considerably harder than the worked grease. When .05% of a polyalkylene glycol is incorporated in the grease, the latter becomes completely reversible, and with this amount or a greater amount of the polyalkylene glycol present in the grease, the latter becomes capable of being quickly cooled; that is, within a time substantially less than usually employed and preferably less than two hours when the grease is cooled in layers varying between about ¼ inch and about 3 inches in thickness. When the polyalkylene glycol is present in excess of .05% taken on the weight of the grease, an easily pliable grease is obtained even on instantaneous cooling.

In accordance with the present invention, the higher molecular weight polyalkylene glycols of the character herein referred to and, more particularly, the polyethylene glycols, are added to lubricating greases of the anhydrous soda soap or soda base type during or after the cooking operation, and the resulting greases may be cooled from their liquid state at extremely rapid rates of the character herein set forth without any deleterious effect on the physical or chemical properties of the grease, that is, there is no bleeding of the grease, the latter, under certain circumstances, becoming completely reversible.

The invention will be illustrated by the following examples:

Example 1

The following ingredients are mixed and cooked:

	Grams	
Stearic acid	200	(3.35%)
Hydrogenated castor oil	35	(0.58%)
Polyethylene glycol (1500 molecular weight)	10	(0.166%)
Coastal pale oil, 100 vis	500	(8.35%)
Sodium hydroxide	32	(.535%)
or		
Metallic sodium	18.5	
Coastal pale oil, 100 vis	630	(10.5%)
Coastal red oil, 2000 vis	4600	(76.519%)

The stearic acid, hydrogenated castor oil, polyethylene glycol, the coastal pale oil, and the saponifying agent, either sodium hydroxide or metallic sodium, are all mixed together and the temperature raised to 360° F. until the reaction mass assumes a syrupy appearance. There is then added additional coastal oil and additional red oil, and the temperature is maintained at about 360° F. while stirring until a substantially completely homogeneous mass is obtainable. The hot grease is then poured into a pan of any suitable size, as for example, a pan measuring 24" by 60", the depth of the grease layer being ½". A cold stream of air is played upon the grease until the grease solidifies.

There is produced a non-bleeding transparent chassis grease of excellent mechanical stability having the ASTM worked penetration of 296 decimillimeters after 60 strokes, and 318 decimillimeters after 300 strokes. The resulting grease had a melting point of 348° F., and acidity equivalent to 0.08% oleic acid.

Example 2

The following ingredients are mixed and cooked following the procedure set forth in Example 1:

	Grams
Stearic acid	390 (6.6%)
Hydrogenated castor oil	84 (1.42%)
Polyethylene glycol (molecular weight 600)	12 (.204%)
Metallic sodium	41 (.68%)
Coastal pale oil, 100 vis	720 (12.2%)
Coastal red oil, 2000 vis	4800 (78.896%)

The above mixture is cooked at a temperature of 375° F. until the mass assumes a homogeneous state. It is thereafter poured into a flat pan carrying a grease layer of about ⅜" in depth and cooled in a cold stream of air. The resulting grease is characterized by the property of being non-bleeding, slightly fibrous, and has good mechanical stability. It is suitable as a wheel bearing grease.

The ASTM penetration after 60 strokes was 250 decimillimeters, and after 300 strokes, 268 decimillimeters. The grease had a melting point of 363° F.

Example 3

The following ingredients were mixed and cooked together:

	Grams
Hydrogenated fish oil fatty acids	200 (7.1%)
Caustic soda	28 (0.985%)
Neutral paraffinic oil, 200 vis. at 100° F	1220 (43.0%)
Paraffinic bright stock (aircraft lubricating oil), 120 vis. at 210° F	1400 (48.775%)
Polyethylene glycol, molecular weight 1500	4 (.14%)

After cooking the above grease to between 360° F. and 375° F., the grease was poured into a pan of ⅜" in depth and cooled in a cold air stream. A stable reversible grease was produced having a melting point of 358° F.

The grease had an ASTM penetration, after 60 strokes, of 305 decimillimeters, and after 300 strokes, 328 decimillimeters.

In each of the above examples, the grease assumed a temperature of about 95° F. within twenty minutes after pouring into the cooling pans, the surrounding air having a temperature of about 75° F.

A specimen was taken from each of the batches set forth in Examples 1, 2, and 3 and poured onto a steel plate in a layer having about ¼" thickness. These specimens cooled from the batch temperature of about 360° F. to 375° F. to room temperature in about ten minutes, and the resulting greases were stable, reversible, did not bleed, and, in general, had good physical and mechanical properties, the penetration and the melting points of the respective greases being as hereinbefore set forth in connection with Examples 1, 2, and 3.

In order that the description of the cooling step be standardized, it may be stated that in accordance with the present invention, a grease will cool from between 300° F. and 400° F. to about 90° F. to 100° F. in about five to twenty minutes when a specimen of the grease is poured on a steel plate at a temperature varying between 300° F. and 500° F. in a layer having a thickness of ¼".

The above set forth grease, containing from .05% to 1% of a polyalkylene glycol, is a completely reversible grease, thereby distinguishing from all prior known soda base greases which, although they were mechanically stable and had a relatively high melting point, were not reversible; that is, the prior art soda base greases could not be melted and cooled for a plurality of cycles, as for example, four to fifteen cycles and/or at any rate of cooling without change in texture and mechanical properties.

The method of incorporation of the polyalkylene glycols into the soda base greases is not limited to the cooking procedure disclosed in connection with Examples 1 and 2, said procedure being set forth primarily for the purpose of illustration and not by way of limitation, said batches being illustrative of standard batches, and the procedure being illustrative of the standard procedure used in the production of anhydrous soda soap or soda base greases. Therefore, in carrying out the present invention, any of the prior art grease cooling procedures may be employed, and the grease may be mixed and cooked through a wide range of temperatures varying from room temperature; that is, about 68° F. to about 500° F. The polyalkylene glycols, in percentages ranging from 0.01% to 1% may be incorporated prior to cooking, or during cooking, or they may be incorporated in a soda base grease which has already been prepared and cooled by melting the grease and mixing it with a polyalkylene glycol of the character herein set forth, namely, one having a molecular weight between 200 and 7000.

Most of the herein described polyalkylene glycols are oil soluble. They may be, therefore, dissolved, directly in the oil. However, the polyalkylene glycols may be brought into aqueous solution, or an aqueous emulsion may be formed thereof and the grease cooked in the presence of the aqueous emulsion provided all of the water is substantially eliminated or evaporated out of the grease during the cooking operation or thereafter so that there is produced a substantially anhydrous soda soap or soda base grease. By a substantially anhydrous soda soap grease is meant one that has a water-content of less than about 0.2% to .25% based on the weight of the grease and preferably has a water-content varying from less than .01% to 0.1%.

The following examples illustrate the manufacture of soda base or soda soap greases which are characterized by excellent mechanical stability and show substantially no tendency to bleed.

As previously pointed out, to diminish the tendency of soda base greases to bleed, it has been customary to add 0.5 to 1% of sodium naphthenate. In accordance with the present invention, much smaller amounts of polyalkylene glycols may be added to the grease in place of the sodium naphthenate, and the resulting grease has better mechanical stability and, in general, fails to disintegrate under conditions where ordinary anhydrous sodium base greases do disintegrate, although they have been prepared by the incorportion therein of an anti-disintegration material, as for example, sodium naphthenate. With exceedingly small percentages of the polyalkylene glycols, as for example, .01% to .04%, the greases are not capable of being cooled quickly within the spirit of the present invention, but as the percentage approaches and exceeds 0.05%, the anhydrous soda base greases may be quikly cooled as herein set forth.

Example 4

The following batch was mixed:

	grams
Stearic acid	600 (7.7%)
Sodium hydroxide	82 (1.05%)
Paraffinic neutral oil, 100 vis. at 100° F.	2800 (36%)
Coastal red oil, 2000 vis. at 100° F.	4400 (55.25%)

The above mass was cooked at 360° F. and poured into pans to a depth of 3½ to 4 inches, and showed upon cooling excessive bleeding, about 10% or more of the oil bleeding or separating during a cooling time of 12 to 16 hours. The same grease, to which there was added .02% of polyethylene glycol having an average molecular weight of between 200 to 7000 was cooked and cooled under the same conditions as the grease without the polyethylene glycol, and there was produced a perfectly dry, substantially anhydrous soda base or soda soap grease having a melting point of 356° F. and an ASTM penetration, after 60 strokes, of 292 decimillimeters and, after 300 strokes, 326 decimillimeters and acidity of 0.1% oleic acid equivalent.

Example 5

A soda base grease was prepared from the following batch of constituents:

	grams
Stearic acid	170 (8.5%)
Hydrogenated castor oil	30 (1.5%)
Sodium hydroxide for saponification of the stearic acid and hydrogenated castor oil	27 (1.35%)
Paraffinic neutral oil, 100 vis. at 100° F.	720 (36%)
Coastal red oil, 2000 vis. at 100° F.	1080 (53.65%)

The above batch was cooked at 360° F. and poured into cooling pants in layers of 3½" to 4" in depth, the grease being poured at approximately 350° F. This grease was cooled in approximately 12 to 16 hours and had an ASTM penetration, after 60 strokes, of 264 decimillimeters which within six hours' exposure to the rubbing action of the Shell Oil Company Roller Tester, softened from a micropenetration of 92 to that of 233 decimillimeters.

The same batch of constituents was mixed with .05% of polyethylene glycol having an average molecular weight of 1500, and then cooked

in the usual manner. There was produced a grease having an ASTM penetration, after 60 strokes, of 220 decimillimeters which increased in softness, after 9½ hours in a Shell roller tester only from 74 to 104 decimillimeters penetration as determined using the Shell Microcone.

The beneficial effects obtained from adding exceedingly small percentages of polyalkylene glycols, as for example, the higher polyethylene glycols of the character herein set forth or the equivalent polypropylene glycols, or the equivalent polybutylene glycols may be obtained using any of the prior art batches used for the production of anhydrous soda soap greases. The remarks made in connection with Examples 1 to 3 are also applicable to that form of the invention set forth in Examples 4 and 5. More specifically, it is desired to point out that the fatty acid constituent, which may be a saturated fatty acid or an unsaturated fatty acid, which may be used in carrying out the present invention includes stearic acid, 12-hydroxy stearic acid, 9, 10-dihydroxy stearic acid, 4-hydroxy palmitic acid, isostearic acid, iso-palmitic acid, 12-hydroxy 9-oleic acid (ricinoleic acid), oleic acid, lineoleic acid, hydrogenated fish oil fatty acids, palm oil fatty acids, cotton seed oil fatty acids. Further, abietic acid, and/or the corresponding glycerides thereof, and/or naphthenic acids may be incorporated in the grease making batch.

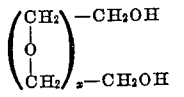
The grease making batch may also comprise any combination of the aforementioned materials in grease making proportions, all as known in the prior art. The glycerides of the saturated and unsaturated fatty acids may also be used.

In general in carrying out the present invention, the saponifiable organic constituent of the grease making batch may be any of the saponifiable organic constituents usually used in the production of grease. The fatty acids usually used in grease making are, in general, the saturated fatty acids containing up to 32 carbon atoms and usually from 14 to 32 carbon atoms; and the unsaturated acids containing up to 22 carbon atoms and usually ranging from 18 to 22 carbon atoms. Instead of using the fatty acids, the glycerides thereof may be used as well as the monohydric alcohol esters of said fatty acids or the wax esters of said acids. The saponifiable constituent of the grease making batch may be a vegetable oil or an animal oil or fat usually used in the production of anhydrous soda base greases. In short, any of the prior art saponifiable media may be used which are set forth in Klemgard's book entitled, "Lubricating Greases; Their Manufacture and Use" (1937) published by the Reinhold Publishing Company, New York. The saponifying medium may be sodium hydroxide or metallic sodium, and the present invention may be carried out when using metallic sodium in accordance with the disclosure of my copending application Ser. No. 625,966, now U. S. Patent No. 2,445,935 granted July 27, 1948.

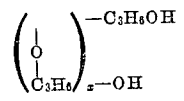
In general, the polymerized higher polyalkylene glycols having between 2 and 6 carbon atoms in the alkylene groups are effective in carrying out the present invention, but those containing the ethylene and propylene groups are preferred. However, the butylene, amylene, and hexylene glycols may be used. The average molecular weight of the polyethylene glycols used in carrying out the present invention may vary from 200 to 7000 or 400 to 7000, the preferred molecular weight varying from 1000 to 4000. It ap-

pears that the most effective average molecular weight is about 1500.

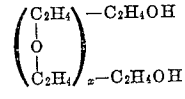
Polyethylene glycol has the following formula:



Referring to the above formula, each alkylene group within the parenthesis contains a carbon atom. Therefore, both alkylene groups within the parenthesis contain two carbon atoms; similarly, the propylene glycol has three carbon atoms in the alkylene group, and the polybutylene glycol has four carbon atoms in the two alkylene groups. The formula for the polypropylene glycol is:



The formula for the polybutylene glycol is as follows:



In all of the examples given, the polyethylene glycol may be replaced by polymerized polypropylene glycol or polymerized polybutylene glycol, said glycols having an average molecular weight in excess of 200, and usually between 200 and 7000.

The greases of the present invention may carry a sodium soap in the amount in which it is customarily present in sodium soap greases, the prior art greases being well set forth in Klemgard's book previously referred to. More specifically, the soda soap greases of the present invention may carry from 1% to 50% of a sodium soap, but more usually carry from 1% to 15%, and, preferably, carry from 3.5% to 7½%, or 10%.

It is desired to point out that the higher polyalkylene glycols are composed of a mixture of several polymers, for example, polyethylene glycol 400 consists of various glycols varying from a minor portion of tetraethylene glycol with increasing amounts of nona ethylene glycol and then increasing up to the pentadecaethylene glycol. Therefore, it is the average molecular weight which is specified and wherein the present specification polyalkylene glycols or polyethylene glycols are referred to, they define the higher glycols having an average molecular weight in excess of 200 and preferably in excess of 400, those with an average molecular weight in excess of 1000 being very effective in carrying out the present invention.

In accordance with the present invention there has been provided an anhydrous reversible soda base lubricating grease, said grease containing from 1% to 50% of a soda soap and, preferably, between 3.5% to 15% of a soda soap base. The anhydrous grease contains from about .01% to 1% of a polyalkylene glycol of the character set forth. The anhydrous grease becomes completely reversible when the amount of polyalkylene glycol is around .05%. With all amounts of the polyalkylene glycol, the grease becomes bleedless, and when the grease has present between about .05% to 1% or greater amounts, the grease is capable of being quickly cooled within the spirit of the present invention.

The invention in one of its forms comprises cooling a hot fluid anhydrous sodium soap lubricating grease to its solid state in the presence of a polyalkylene glycol having an average molecular weight in excess of 200, the amount of the polyalkylene glycol ranging from .01% to about 1%. The present invention is also directed to a method of preventing bleeding of oil from an anhydrous lubricating grease containing a lubricating oil base and a sodium soap by incorporating in the grease from .01% to about 1% of a polyalkylene glycol having an average molecular weight in excess of 200. The method is also directed to accelerating the cooling of a hot liquid sodium soap lubricating grease through a cooling range of at least 200° F. to a solid state adjacent room temperature and in the absence of any bleeding comprising incorporating in the grease a polyalkylene glycol in an amount greater than .05%, said polyalkylene glycol having an average molecular weight in excess of 200.

The percentages and percentage ranges herein set forth are taken on the weight of the grease.

The laws governing the rate of cooling of viscous or solid systems, such as a grease system, is well set forth in a book entitled "Heat Transmission" by William H. McAdams, Second Edition, McGraw Hill and Company, Inc., New York, 1942. It is there stated that the heat conduction in greases follows an inverse relationship between the cooling rate and the square of the thickness of the grease slab undergoing cooling. For example, if the middle plane of the grease slab cools in forty minutes, said grease slab having a thickness of 1", then a slab of ½" thickness will cool in ten minutes, and a slab of ¼" thickness will cool in 2½ minutes. In other words, by doubling the thickness of the grease layer, the time for cooling is not doubled, but quadrupled. Actually, when cooling a grease slab from both sides from about 350° F. initial temperature to 100° F. final temperature in a stream of air of 80° F. the actual cooling time will be somewhat longer due to (1) the heat transfer resistance of the air film limiting the rate of heat removal in the short initial period of cooling the hot grease and (2) the liberation of the heats of gelation (crystallization) and transition of the anhydrous soap during certain stages of the cooling process, the absolute amount of heat liberated being in proportion to the concentration of the soap being present in the grease, and it has been discovered that this is substantially unaffected by the presence of the polyalkylene glycols in the amounts stated.

In accordance with the present invention a hot grease in layers of about ¼" to about 1" will cool from about 350° F. or a little higher to a room temperature of 100° F. in less than two hours; that is, between 30 seconds and two hours.

While in carrying out the present invention the raw materials are cooked together in the presence of the polyalkylene glycol, the latter may be added to the cooled grease by agitation, and then the mass may be heated to above 300° F. and allowed to cool. This will produce a grease which does not bleed and which can be quickly cooled in layers of ¼" to 1" in less than 2 to 4 hours.

During the cooking of the grease, there may be introduced therein small amounts of any of the prior art aluminum or calcium soaps, and by small amounts is meant less than 2% of any prior art aluminum soap or less than 2% of any prior art calcium soap, or the amount of prior art aluminum soap or prior art calcium soap in the

grease together may be less than 2%, and the properties of the grease which are conferred thereon due to the use of the polyalkylene glycols will be retained by the grease. More specifically, the amount of the aluminum soap and/or calcium soap may vary between 0.1% to 2% taken on the weight of the grease. However, after the sodium soap grease of the present invention has been once cooked in the presence of the polyalkylene glycol and cooled, said grease can be mixed when cooled with any amount of aluminum soap grease or calcium soap grease. For example, there may be incorporated into the soda base grease 1% to 70% of aluminum soap grease or 1% to 70% of a calcium soap grease, or mixtures thereof, said greases being incorporated into the cold sodium soap grease. Any of the polyalkylene glycols herein broadly and specifically set forth may be mixed with each other in any proportion and used in the place of a single polyalkylene glycol.

In the trade, the anhydrous soda base greases usually contain less than .25% of water.

I claim:

1. An anhydrous soda base lubricating grease containing .05% to about 1% of a polyethylene glycol having an average molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

2. An anhydrous soda base lubricating grease containing .05% to about 1% of a polyethylene glycol having an average molecular weight varying between about 200 and about 7000, said percentage range being taken on the weight of the grease.

3. An anhydrous soda base lubricating grease containing from .05% to about 1% of a polyethylene glycol having an average molecular weight varying between about 1000 and about 4000, said percentage range being taken on the weight of the grease.

4. An anhydrous reversible soda base lubricating grease containing about 1% to 50% by weight of a soda soap and about 0.01% to about 1% of a polyethylene glycol having a molecular weight greater than 200.

5. An anhydrous reversible soda base lubricating grease containing .1% to .3% of a polyalkylene glycol having an average molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

6. An anhydrous bleedless reversible soda base lubricating grease containing about 0.01% to about 1% of a polyalkylene glycol in which the total carbon atoms present in the alkylene groups of the glycol varies from 2 to 6 inclusive, said polyalkylene glycol having an average molecular weight in excess of 200, said glycol additive being present in amount sufficient to inhibit bleeding of said grease lubricant.

7. An anhydrous bleedless soda base lubricating grease containing .01% to about 1% of a polypropylene glycol having a molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

8. A substantially anhydrous bleedless soda base lubricating grease containing .01% to .05% of a polyalkylene glycol having an average molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

9. A substantially anhydrous bleedless soda base lubricating grease containing .01% to .05% of a polyalkylene glycol having an average molecular weight varying between 400 and 7000, said percentage range being taken on the weight of the grease.

10. An anhydrous bleedless soda base lubricating grease containing .1% to .5% of a polyalkylene glycol in which the total carbon atoms present in the alkylene groups varies from 2 to 6 inclusive, said polyalkylene glycol having a molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

11. An anhydrous bleedless soda base lubricating grease containing .1% to .5% of a polyethylene glycol in which the total carbon atoms present in the ethylene groups varies from 2 to 6 inclusive, said polyethylene glycol having a molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

12. An anhydrous bleedless lubricating grease containing a grease producing amount of a sodium soap of 12-hydroxy stearic acid and having present .01% to .05% of a polyalkylene glycol in which the total carbon atoms present in the alkylene groups varies from 2 to 6 inclusive, said polyalkylene glycol having a molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

13. A lubricating grease composition consisting essentially of mineral lubricating oil thickened to a grease consistency by the sodium soap of substantially saturated higher fatty acids and containing about 0.1% of polyethylene glycol having a molecular weight of about 1000.

14. A soda soap base lubricating grease containing 0.05% to about 1% of a polyethylene glycol having an average molecular weight in excess of 200, said percentage range being taken on the weight of the grease.

15. A lubricating grease composition comprising mineral lubricating oil thickened to a grease consistency by the sodium soap of substantially saturated higher fatty acids and containing about 0.05% to about 1% of polyethylene glycol having an average molecular weight between about 200 and about 7000.

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