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ALKALI BASE LUBRICATING GREASES

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15 Claims. (Cl. 252—42)

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This invention relates to the production of lubricants and, more particularly, to alkali soap greases containing small amounts of the monoether derivatives of higher polyalkylene glycols, the radical replacing the hydrogen atom of one of the hydroxy radicals to form the ether being an alkyl or alkylaryl radical having at least 6 and preferably from 8 to 32 carbon atoms, the monoethers of trialkylene glocol, said glycols being exemplified by the polyethylene glycols, the polypropylene glycols, the polybutylene glycols, the polyamylene glycols, and the polyhexylene glycols are particularly preferred. The alkali soap greases of the present invention may contain a small amount of the monoether derivatives of 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 monoether derivative of a higher 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 monoether of 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 alkali metal soap or alkali metal 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

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a monoether derivative of a polyalkylene glycol and particularly a monoether derivative of 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 monoether of polyalkylene glycol thereof added may vary from about .03% to 1%, it preferably varies from about 0.1% to .25% on the weight of the grease.

It is an object of the present invention to produce substantially anhydrous sodium soap or sodium base greases or other alkali base greases, e. g. lithium and potassium soap 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 monoether of a polyalkylene glycol of the character herein set forth. When an amount varying between .03% and .05% of a monoether 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 monoether of a polyalkylene glycol is incorporated in the grease, the latter becomes completely reversible, and with this amount or a greater amount of the monoether of a 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 monoether of a 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 monoethers of polyalkylene glycols of the character herein referred to and, more particularly, the monoethers of polyethylene glycols, are added to lubricating greases of the anhydrous soda soap or soda base type during or after the cooling 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 I

The following ingredients are mixed and cooked:

Stearic acid	200 gms. (3.35%)
Hydrogenated castor oil	35 gms. (0.58%)
Dodecanoxy polyethoxy ethanol	10 gms. (0.16%)
Coastal pale oil, 100 vis.	500 gms. (8.35%)
Sodium hydroxide	25 gms. (.535%)
or	
Metallic sodium	18.5 gms.
Coastal pale oil, 100 vis.	630 gms. (10.5%)
Coastal red oil, 2000 vis.	4600 gms. (76.519%)

The stearic acid, hydrogenated castor oil, dodecanoxy polyethoxy ethanol, 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 obtained. 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 300 strokes. The resulting grease had a melting point of 348° F., and acidity equivalent to 0.08% oleic acid.

EXAMPLE II

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

Stearic acid	390 gms. (6.6%)
Hydrogenated castor oil	84 gms. (1.42%)
12-hydroxy-9,10-octadecenoxy polyethoxy ethanol	12 gms. (.204%)
Sodium hydroxide	53 gms. (.68%)
Coastal pale oil, 100 vis	720 gms. (12.2%)
Coastal red oil, 2000 vis	4800 gms. (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 III

The following ingredients were mixed and cooked together:

Hydrogenated fish oil fatty acids	200 gms. (7.1%)
Caustic soda	28 gms. (0.985%)
Neutral paraffinic oil, 200 vis. at 100° F	1200 gms. (43.0%)
Paraffinic bright stock (aircraft lubricating oil) 120 vis. at 210° F	1400 gms. (48.775%)
3,5-diisobutyl phenoxy decaethoxy ethanol	4 gms. (.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 I, II, and III, 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 I, II, and III.

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 monoether of a polyalkylene glycol, is a completely reversible grease, thereby distinguishing from all prior known alkali base greases which, although they were mechanically stable and had a relatively high melting point, were not reversible; that is, the prior art alkali 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 monoethers of polyalkylene glycols into the alkali base greases is not limited to the cooking procedure disclosed in connection with Examples I and II, 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 monoethers of 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 monoether of polyalkylene glycol of the character herein set forth, namely, one having a molecular weight between 200 and 7000.

Most of the herein described polyalkylene glycol monoether derivatives are oil soluble. They may be, therefore, dissolved, directly in the oil. However, the polyalkylene glycol monoether derivatives 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 alkali soap or alkali base grease. By a substantially anhydrous alkali 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 glycol monoether derivatives 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 incorporation therein of an anti-disintegration material, as for example, sodium naphthenate. With exceedingly small percentages of the polyalkylene glycol monoether derivatives, as for example, 0.01% to 0.04%, 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 sodi base greases may be quickly cooled as herein set forth.

EXAMPLE IV

The following batch was mixed:

Stearic acid	600 g. (7.7%)
Sodium hydroxide	82 g. (1.05%)
Paraffinic neutral oil, 100 vis. at 100° F	2800 g. (36%)
Coastal red oil, 2000 vis. at 100° F	4400 gms. (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 12-hydroxy-9,10 octadecenoxy polyethoxy ethanol was cooked and cooled under the same conditions as the grease without the 12-hydroxy-9,10 octadecenoxy polyethoxy ethanol 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 V

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

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

The above batch was cooked at 360° F. and poured into cooling pans 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 12-hydroxy-9,10 octadecenoxy polyethoxy ethanol 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 glycol monoether derivatives, for example, the higher polyethylene glycol monoether derivatives of the character herein set forth or the equivalent polypropylene glycol monoethers, or the equivalent polybutylene glycol monoethers 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 I to III was also applicable to that form of the invention set forth in Examples IV and V. 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, iso-stearic acid, iso-palmitic acid, 12-hydroxy 9-oleic acid (ricinoleic acid) oleic acid, montanic acid, linoleic acid, hydrogenated fish oil fatty acids, palm oil fatty acids, cotton seed oil fatty acids.

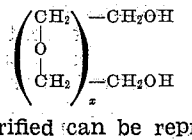
The grease making batch may also comprise any combination of the aforementioned materials in grease making proportions, all as known in the prior art. The glycerides of the saturated and unsaturated fatty acids may also be used.

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 alkali 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.

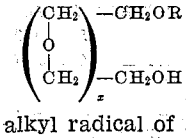
In general, the ethers may be obtained by etherifying polymerized higher polyalkylene glycols having between 2 and 6 carbon atoms in the alkylene groups are effective in carrying out the present invention, but those containing the ethylene and propylene groups are preferred.

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

Polyethylene glycol has the following formula:

I 

and when etherified can be represented by:

II 

where R is an alkyl radical of at least 6 carbon atoms and preferably 8 to 20 carbon atoms of an alkaryl radical having at least 8 carbon atoms in the alkyl group.

Referring to the above Formula I each alkylene group within the parentheses contains a carbon atom. Therefore, both alkylene groups within the parentheses 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.

In addition to the above ether compounds which have been specifically mentioned the following may also be used:

Nonanoxy polyethoxy ethanol
Undecanoxy polyethoxy ethanol
Tetradecanoxy polyethoxy ethanol
Hexadecanoxy polyethoxy ethanol
Octadecanoxy polyethoxy ethanol
Nonanoxy methoxy ethanol
Dodecanoxy methoxy ethanol
Dodecanoxy ethoxy methoxy ethanol
Nonanoxy polypropoxy ethanol
Dodecanoxy isopropoxy ethanol
Dioctyl phenoxy nonanoxy ethanol
Dioctyl phenoxy decaethoxy ethanol

Broadly a class of half glycol-ether compounds suitable as additives for greases of this invention may be represented by the formula

$$ROCH_2OZOH$$

where R represents an alkyl or alkaryl group or the residue of a compound having a long carbon-linked chain or other hydrophobe radicals having 6 to 32 or more carbon atoms and corresponding to the carbon-linked chain of a fatty acid or the hydrophobe radical of a resin, naphthenic or alicylic acid and Z represents the residue of a polyhydroxy alcohol, usually a polyoxyethylene glycol which contains a number of ethylene groups. However, if desired, instead of the half-ethers as represented by the above formula, a whole ether may be also used by etherifying both of the terminal hydroxy groups of glycol compounds. In such cases both of the hydrogens may be replaced by the R radical as defined above or the wholly etherified compound may be represented by

$$ROCH_2OZOR_1$$

where R is the same as above and R_1 may be an alkyl radical of from 1 to 32 carbons or an alkylaryl or alkoxyaryl radical.

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 10%.

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 monoether of a polyalkylene glycol of the character set forth. The anhydrous grease becomes completely reversible when the amount of a monoether of a polyalkylene glycol is around .05%. With all amounts of the monoether of 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 rot fluid anhydrous sodium soap lubricating grease to its solid state in the presence of a monoether of a polyalkylene glycol having an average molecular weight in excess of 200, the amount of the monoether of a 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 monoether 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 monoether of polyalkylene glycol in an amount greater than .05%, said monoether of a 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 heat of gelation (crystallization) and transition of the anhydrous soap during cer-

tain 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 glycol monoethers 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 thirty 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 glycol monoether 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 glycol monoethers herein broadly and specifically set forth may be mixed with each other in any proportion and used in the place of a single monoether of a polyalkylene glycol.

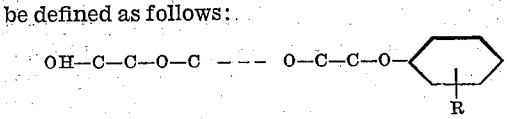
In the trade, the anhydrous soda base greases usually contain less than .25% of water.

A further example illustrating the present invention follows:

EXAMPLE VI

The following ingredients are mixed and cooked: 140 gms. of stearic acid, 26 gms. of 12-hydroxy stearic acid; 25 gms. of caustic soda in aqueous solution and 746 gms. of 100 paraffin oil, and 1150 gms. of 2000 coastal red oil. There is added about 1.5 grams of a polyethylene glycol with an aromatic ring in the molecule.

The molecular weight of the glycol portion of the herein described compounds of polyethylene glycol may be about 400, and the total molecular weight of the polyethylene glycol ether may be about 684. These polyethylene glycol ethers may be defined as follows:

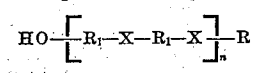


where R is an alkyl chain having a length of 1 to 8 carbon atoms, inclusive.

This aromatic ether of the polyalkylene glycol or more specifically as the aromatic ether derivative of the polyethylene glycol in which the aromatic nucleus is connected by means of an ether group to the glycol chain.

0.075% of the above ether is added to the hot grease after the same has been partially or completely cooked, said ether being homogeneously distributed through the hot grease. Thereafter, the latter is poured into a vessel of 3 inches' diameter and cooled in a thin layer in about two hours. The resulting grease has a smooth slightly fibrous texture and has a melting point (ASTM) of 358° F. The penetration after 60 strokes is 240 and after 300 strokes, 350 decimillimeters. The outstanding mechanical stability of the grease is evidenced by the Shell Roller Test method. At 0 hours the roller test method gives a micropenetration of 105; after 67 hours, a penetration of 170; and after 115 hours, 180, said figures being expressed in decimillimeters of micropenetration. These compounds are essentially polyethylene glycols with an aromatic ring or nucleus in the molecule.

In all cases the oxygen atoms of the ether compounds may be replaced wholly or in part by sulfur atoms so as to form the thioether derivatives and a particularly desirable class of compounds may be represented by the formula



where R_1 represents an alkylene radical, R represents an alkyl radical of at least 6 and preferably 6 to 32 carbon atoms, the X's may be oxygen, sulfur and/or their mixtures and n is an integer of at least one.

EXAMPLE VII

In a suitable grease-making kettle approximately 3.7% of hydrogenated fish oil fatty acids and 3.7% of hydrogenated castor oil fatty acid, 1.0% lithium hydrate solution and about 10% of a 100 SUS at 100° F. paraffin oil were admixed and heated while stirring to a temperature of between about 380° F. and about 400° F. An additional amount of about 50 to 55% of 100 SUS at 100° F. paraffin oil and about 30% of 2000 SUS at 100° F. coastal pale oil was added very slowly and the temperature of the mixture maintained at between about 380 to 385° F. When a homogeneous mass was formed about 0.01% dodecanoxy polyethoxy ethanol was added to the grease. The hot fluid mass was poured into flat pans to a depth of less than 1 inch and exposed to a current of cooling air so that the grease cooled down to around about 150° F. in less than 30 minutes. The cooled grease was milled to form a more improved non-bleeding lithium soap grease.

EXAMPLE VIII

A grease of this invention was made by admixing approximately 3.4% of a hydrogenated fish oil fatty acid, 7.0% of 12-hydroxy stearic acid, 1.6% of lithium hydrate and 12% of 100 SUS at 100° F. paraffin oil and heating said mixture to form a homogeneous mass. To it, approximately 50% of 100 SUS at 100° F. paraffin oil and 25% of a 2000 SUS at 100° F. coastal red oil and about 0.1% of dodecanoxy polyethoxy methoxy ethanol having an average molecular weight of 1500 was slowly added and the mixture heated to about 380° F. and about 420° F. until a homogeneous mass was obtained. The hot grease was poured in a ⅛" layer into a container and cooled by playing a cold stream of air over it so that it cooled down to about 140° F. in less than 30 minutes.

EXAMPLE IX

A grease having the following formulation was cooked in a conventional manner, and subsequently pumped in a thin stream onto a cooling belt where it is chilled from about 380° F. to about 200° F. or less within 10 minutes. The chilled grease is then broken up by a screw conveyor and pumped through 60 mesh screens into an agitator equipped tank, where it is stirred for about 4 hours and pumped from there through 60 mesh or finer screens to a storage tank.

Composition of grease

8% 12-hydroxy-stearic acid
2% hydrogenated fish oil fatty acid
1.52% lithium hydrate
27% 100 SUS at 100° F. paraffin base oil
63% 2000 SUS at 100° F. naphthene base oil
0.1% dioctyl phenoxy decaethoxy ethanol

During the cooking of the grease, there may be introduced therein small amounts of any of the prior art soaps, and by small amounts is meant less than 2% for additional benefits. However, after a grease of the present invention has been once cooked and cooled, said grease can be admixed with any amount of a desirable soap grease. For example, there may be incorporated into a cold lithium base grease of this invention about 1% to 70% of either aluminum soap grease or sodium soap grease.

To stabilize greases of the type described against oxidation it is advisable to add minor amounts of oxidation inhibitors to the grease. Among the antioxidants which are effective with grease compositions of the type disclosed are: N-alkyl paraphenylenediamine and condensed polynuclear aromatic mono-amines. Such inhibitors are N-butyl paraphenylenediamine, N-N-dibutyl paraphenylenediamine, etc. Also effective as oxidation inhibitors are alpha or beta-naphthylamine, phenyl-alpha or beta-naphthylamine, alpha-alpha, beta-beta, or alpha-beta dinaphthylamine, diphenylamine, tetramethyldiamino diphenylmethane, petroleum alkyl phenols, and 2,4-ditertiary butyl-6-methyl phenol.

Corrosion inhibitors which are particularly applicable with compositions of this invention are N-primary amines containing at least 6 and more than 18 carbon atoms in the molecule such as hexylamine, octylamine, decylamine, dodecylamine, octadecylamine, heterocyclic nitrogen containing organic compounds such as alkyl substituted oxazolines and oxazoline salts of fatty acids.

Extreme pressure agents can be added to such grease and the preferred comprise esters of phosphorous acids such as triaryl, alkylhydroxy, aryl, or aralkyl phosphates, thiophosphates or phosphites, etc. neutral aromatic sulfur compounds such as diaryl sulfides and polysulfides, e. g. diphenyl sulfide, dicresol sulfide, dibenzyl sulfide, methyl butyl diphenol sulfide, etc., diphenyl selenide and diselenide; discresol selenide and polyselenide, etc., sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc., in which the sulfur is tightly bound; sulfurized long-chain olefins obtained by dehydrogenating or cracking of wax; sulfurized phosphorized fatty oils, acids, esters and ketones, phosphorous acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorous acids with hydroxy fatty acids; chlorinated hydrocarbons such as chlorinated paraffins, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc., or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients which can be added are antiwear agents such as oil-soluble urea or thiourea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc.; or rubber, polyisobutylene, polyvinyl esters, etc.; VI improvers such as polyisobutylenes having a molecular weight above about 800, volatilized paraffin wax, unsaturated polymerized esters of fatty acids and monohydric alcohols, etc.; oiliness agents such as stearic and oleic acids and pour point depressors such as chlorinated naphthalene to further lower the pour point of the lubricant.

The amount of the above additives can be added to grease compositions of this invention in around about 0.01% to less than 10% by weight, and preferably 0.1 to 5.0% by weight.

Improved grease products of this invention can be attained by quickly cooling said greases in the manner fully described in applicant's copending application Serial No. 666,790, filed May 2, 1946, now Patent No. 2,527,789 dated October 31, 1950. Essentially this comprises in cooling greases in a rather rapid manner in the absence of any shearing stress, that is while the grease is maintained in a quiescent state.

By quick cooling is meant cooling in such a manner that the grease cools from 400° F. and above to room temperature, in a period of less than 1 hour and preferably in less than 30 minutes.

One method of cooling greases in this manner is to feed the hot grease on to a steel belt or the like so as to form a relatively thin continuous layer on the steel belt and subject it to a current of air or other cooling medium, so that the grease while being carried along on the belt is cooled in a uniform fashion free from shearing stress. By cooling in this manner, an unusually smooth grease is obtained which has a higher consistency with less soap than a grease containing a greater amount of soap but cooled by convenient means.

Many modifications as to cooling can be made made without departing from the scope or spirit of the invention. Thus, the grease can be cooled on a belt moving at a controlled rate and the cooling medium directed countercurrent to the flow of the grease. Also the thickness of the grease layer should be controlled because with grease layers above about one inch in thickness, the rate of cooling becomes prohibitively low. Generally the thickness of a grease while being cooled should be between $\frac{1}{16}$ to $\frac{1}{4}$'' in thickness.

The length of a belt suitable for commercial grease production should be at least 100 ft. long and moved at a speed of about 13 feet per minute so that the total cooling time of a hot grease down to a jelled mass should be in the neighborhood of about 7 to 10 minutes.

To improve the mechanical stability of the grease still further it can be milled or homogenized after being quickly chilled. This can be accomplished by breaking up the chilled mass in a screw conveyor and pumping it through 60 mesh screens into a suitable agitator such as a tank equipped with agitators or a Cornell homogenizer where it is worked until constant penetration value is attained. The grease is then pumped through 60 mesh of finer screens to storage tanks or packaged.

Greases of this invention are applicable for general automotive use, they are excellent air-

craft greases, and they are equally applicable for general industrial use.

This is a continuation-in-part of the copending application Serial No. 655,887, filed March 20, 1946.

I claim as my invention:

1. A mechanically stable, thermally reversible, non-bleeding soda soap grease comprising a major amount of mineral lubricating oil, a minor amount of from 5% to 25% of a soda soap and from 0.01% to 1% of dodecanoxy polyethoxy ethanol.

2. A mechanically stable, thermally reversible, non-bleeding soda soap grease comprising a major amount of mineral lubricating oil, a minor amount of from 5% to 25% of a soda soap and from 0.01% to 1% of 12-hydroxy-9,10-octadecenoxy polyethoxy ethanol.

3. A mechanically stable, thermally reversible, non-bleeding soda soap grease comprising a major amount of mineral lubricating oil, a minor amount of from 5% to 25% of a soda soap and from 0.01% to 1% of 3,5-diisobutyl phenoxydecaethoxy ethanol.

4. A mechanically stable, thermally reversible, non-bleeding lithium soap grease comprising a major amount of mineral lubricating oil, a minor amount of from 5% to 25% of a lithium soap and from 0.01% to 1% of dodecanoxy polyethoxy ethanol.

5. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of mineral lubricating oil, from 5% to 25% lithium 12-hydroxy stearate and from 0.01% to 1% of dodecanoxy polyethoxyethanol.

6. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of mineral lubricating oil, from 5% to 25% lithium stearate and from 0.01% to 1% of dodecanoxy polyethoxyethanol.

7. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of mineral lubricating oil, from 5% to 25% of a lithium soap of a hydroxy fatty acid having up to 32 carbon atoms, and from 0.01% to 1% of a monohydrocarbyloxy polyethoxyethanol wherein the hydrocarbyl radical is an alkyl radical having 6 to 32 carbon atoms.

8. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of mineral lubricating oil, from 5% to 25% of a soda soap of a hydroxy fatty acid having up to 32 carbon atoms, and from 0.01% to 1% of a monohydrocarbyloxy polyethoxyethanol wherein the hydrocarbyl radical is an alkyl radical having 6 to 32 carbon atoms.

9. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of a hydrocarbon oil, from 5% to 25% of a lithium soap and from 0.01% to 1% of a monohydrocarbyloxy polyethoxyethanol wherein the hydrocarbyl radical is an alkyl radical having 6 to 32 carbon atoms.

10. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of a hydrocarbon oil, from 5% to 25% of a soda soap and from 0.01% to 1% of a monohydrocarbyloxy polyethoxyethanol wherein the hydrocarbyl radical is an alkyl radical having 6 to 32 carbon atoms.

11. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of a hydrocarbon oil from 5% to 25% of an alkali metal soap and from 0.01% to 1% of a monohydrocarbyloxy polyethoxyethanol wherein the hydrocarbyl radical is an alkyl radical having 6 to 32 carbon atoms.

12. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of a hydrocarbon oil, from 5% to 25% of an alkali metal soap and from 0.01% to 1% of a monohydrocarbyloxy polyethoxyalkanol wherein the hydrocarbyl radical is an alkyl radical having from 6 to 32 carbon atoms.

13. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of a hydrocarbon oil, from 5% to 25% of an alkali metal soap and from 0.01% to 1% of a monohydrocarbyloxy polyalkoxyalkanol wherein the hydrocarbyl radical is an alkyl radical having from 6 to 32 carbon atoms.

14. A mechanically stable, thermally reversible, non-bleeding grease, comprising a major amout of a liquid oleaginous material, from 5% to 25% of an alkali metal soap, and from 0.01% to 1% of a monohydrocarbyloxy polyalkoxyalkanol.

15. A mechanically stable, thermally reversible, non-bleeding grease comprising a major amount of a lubricating oil, from 5% to 25% of an alkali metal soap and from 0.01% to 1% of a monohydrocarbyl ether of a polyalkylene glycol, said monohydrocarbyl group having from 6 to 32 carbon atoms and wherein said alkylene radicals of the polyalkylene glycol have from 2 to 6 carbon atoms each.

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