This invention relates to a novel method of preparing grease compositions. More particularly, this invention pertains to a novel process of making alkali and/or alkaline earth soap grease compositions which are stable under static or dynamic conditions, resist bleeding and possess excellent lubricating properties over wide temperature ranges.

It is well established that the quality of a grease varies substantially with the method of making it. Thus, lubricating grease compositions made from identical materials, but in which the method of making said grease has been varied, will result in one case in a grease having excellent stability and lubricating properties and in the other case the resulting grease will be extremely poor. A study of this problem makes it more and more evident that with some types of greases a controlling factor, which will determine the quality and property of the grease, is the final structure of the gel or soap used to make the grease. Unless the fibrous or micellar structure of the grease is controlled or modified by an initial or intermediate stage, a more or less complete loss of their grease-like structure and flow away from the bearing surface being lubricated and thereby leave the bearing unprotected.

The ability of controlling or modifying the fiber, crystalline or micellar structure or soaps or gelling agents used in forming grease during the conventional grease making process is extremely difficult. One means of overcoming this difficulty has been the use of crystalline or micellar modifiers in many cases, however, they do more harm than good, and in some cases additives which possess the ability of acting as crystalline or micellar modifiers, cause corrosion, act as pro-oxidants and the like.

Bleeding is also a phenomenon frequently encountered in grease compositions which is manifested by an undesirable separation of soap and base lubricant. This action has also been termed "syneresis" and is thought to be due in part to the presence of an undesirable soap structure.

Generally, in order to inhibit bleeding and improve the texture of greases special precautionary measures are taken, such as employing slow or rapid means of cooling, or extensively working the grease in special homogenizers, e.g. the Cornell homogenizer and the like. Such procedures are usually time-consuming and add greatly to the cost of the grease. Other ways of producing stable, non-bleeding greases have been attempted by either reducing the soap content generally to less than about 5% by weight and by increasing the soap content to a maximum. These methods of stabilizing greases against bleeding have also proved to be unsatisfactory because in the case of reducing the soap content to less than 5%, such greases become limited in their use due to the low soap content, while increasing the soap content to a maximum makes the grease too costly and such products generally possess an undesired consistency.

It is an object of this invention to produce greases by a novel process. Another object of this invention is to produce greases by a novel process which is stable under static and dynamic conditions. Another object of this invention is to produce greases by a novel process which resists bleeding. Still another object of this invention is to provide a method of making greases having a definite micellar or soap structure. Still another object of this invention is to provide a method of making greases in a batch or continuous process whereby mechanically stable, non-bleeding products are produced. Still another object of this invention is to produce a grease of desired consistency with a minimum amount of soap.

Broadly, this invention comprises a method of making alkali and/or alkaline earth soap greases involving the following essential steps. A premade soap or saponifying agents and saponifiable materials are admixed with a portion of the base oil required to make the grease and the mixture heated above the melting point of the soap or mixtures thereof until a homogeneous mass has been obtained. If only a portion of the base oil has been used to form the homogeneous mass, the remainder of the base oil can be added at this point together with any additives or modifying agents which might be desired to have present in the final product. The homogeneous grease mass is then cooled from above its temperature of transition to the jelly phase to below this transition temperature but above 100°C and the grease is heat-treated at a convenient temperature between 100°C and the transition temperature in a quiescent state until the desired soap fiber growth has been attained. The grease can then be slowly cooled with or without stirring down to room temperature or shock-chilled to room temperature, homogenized, if desired, and packaged.

The essence of this invention then is to heat-treat alkali and/or alkaline earth soap greases while they are in the expanded gel phase until a recrystallization and consolidation of soap.
crystallites into the desired fiber form have been attained. The gel phase may be defined as a two phase system comprising solid crystalline soap and a liquid phase consisting of either soap-oil jelly or pure oil. The jelly phase of the system under discussion may be defined as being a non-crystalline mixture of soap and oil and may be considered as a single-phase system or a pseudo-solution. Within the limits of the expanded gel phase, recrystallization and consolidation of soap crystallizes proceeds at a rate depending upon the temperature so that a lower temperature can be compensated for by increased heating time. By plotting a cooling curve for a particular soap grease (temperature versus time) and integrating that portion above 100°C, and below the jelly phase, a term comprising the product of time (t) and temperature (T°C) can be obtained which can be correlated with the mechanical stability of the resulting grease. That is, for a given mechanical stability

\[ (t) \quad (T-100) = K \]  

The soap used to make greases of this invention may be made by saponification of various fats, fatty acids, derivatives of fats and oils such as fatty acids derived from vegetable, animal, marine and fish oils, and hydrogenated fatty acids thereof; preferably containing from 8 to 40 carbon atoms, synthetic fatty acids produced from hydrocarbon, naphthenic acids, rosin acids, tall oil acids and the like.

Specifically, the natural fats and fatty acid materials derived therefrom which can be used to form soaps include:

- **I. Animal:**
  - Tallow (beef, mutton, goat) etc., lard oil, bone oil, neat's-foot oil, wood fat, horse fat oil, etc.

- **II. Vegetable oils:**
  - Caster oil, cashew nut oil, peanut oil, coconut oil, jojoba seed oil, olive oil, palm oil, corn oil, cottonseed oil, rapeseed oil, ravi-son oil, sesame oil, soybean oil, linseed oil, etc.

- **III. Marine and fish oils:**
  - Codfish oil, cod liver oil, dog fish oil, dolphin oil, herring oil, mnenhaden oil, porpoise oil, salmon oil, sardine oil, seal oil, shark oil, whale oil, etc.

- **IV. Hydrogenated residuum or distillate fractions obtained from any of the oils listed above.**

- **V. Specific fatty acids which can be used to form the soap may include saturated alkyl mono-carboxylic acids:**
  - Caprylic, undecylic, lauric, myristic, palmitic, stearic, arachidic, lignoceric, montanic, melastic acids, etc.

- **VI. Unsaturated alkyl mono-carboxylic acids:**
  - Oleic, linoleic, erucic, elapanodonic, linoleic, brassylic, elallic, elacostearic, stearo-leic acids, etc.

Mixtures of fatty materials and derivatives thereof may be used to form soap. Thus, an excellent soap for grease compositions may be made from a mixture of hydrogenated fish oil fatty acids and hydrogenated caster oil.

The proportions of fatty material used are governed in part by the type of mineral oil base used for compounding the greases as well as its intended use.

The soap may be made by saponifying the above type fatty materials, their mixtures, with metal oxide, hydroxides, carbonates, etc., or in the presence of several metal compounds, or organic bases.

A. Metals selected from the periodic table, e.g.,-

- Group I—lithium, sodium, potassium, rubidium, cesium.

- Group II—calcium, strontium, barium, magnesium, zinc, and cadmium.

In order more clearly to set forth the invention, reference is now made to the accompanying drawing, which is a flow diagram illustrating a method of producing alkali and/or alkaline earth soap greases by the meaning of this invention.

It is understood that modifications as to equipment, its arrangement, type and kind of materials and their proportions can be resorted to without departing from the spirit of the invention as presented in the subjoined claims.

Referring to the flow diagram, the invention can be carried out as follows: Into a slurry tank 1 a pre-made soap or soap mixtures or materials used for making desired soaps and base oil are added through lines 3 and 2, respectively, and other additives such as oxidation and corrosion inhibitors, anti-bleeding agents, oiliness agents, fillers and the like are added to the grease they can be introduced into the slurry tank 1 through conduit 3 or through conduit 21 at a convenient time. The oil and soap are heated to between about 60° and 90°C, and preferably to ±80°C and then led through conduit 4 to conduit 14 to a slurry homogenizer 7 where the oil-soap mixture is worked at a temperature of about 120°C. The mixture can then be returned to the slurry tank 1 through lines 42 and 43 for further working or by-passed through line 4 through pump 6 and line 4’ into heating tank 8. If the mixture is returned to slurry tank 1 for further working it is subsequently discharged from the tank into line 4 through a booster pump 5 on through line 4’ and pump 5, through line 4” and into heating tank 8. If only a portion of the base oil has been used the balance of the oil is added at this point through line 21, and the entire mixture is stirred and heated at a temperature of from 180° to 250°C until a homogeneous mixture has been attained. During this stage of the process additives can be added to the grease if so desired. The heating vessel 8 may be a heating kettle or a heating “votator” or any suitable equipment for making a desired grease composition. The hot grease is then discharged from the vessel 8 at a controlled rate through lines 5 and 6’ with the aid of pump 10 so that when it reaches the time tank 11 it is at the temperature where it is just changing its phase from a jelly phase to a gel phase. The grease is allowed to remain in the time tank 11 at a temperature and for a time 2 to 10 hours which would allow for the maximum recrystallization and consolidation of soap crystallites into fibers of desired length and structure while in a quiescent state. For a grease having a desired mechanical stability, the time and temperature factors can be determined by Formula 3, column 3. The grease is discharged from this tank and may be conducted through lines 12 and 14 into a slow cooling tank 45 or conducted through lines 12 and 13 into an apparatus 44 where the grease can be quickly cooled to room temperature. This can be accomplished by use of a steel belt on which the grease is spread in very thin layers and is subjected to a cooling medium or a chilled steel cylinder or a Carbondale chiller or the like can be used. If desired, a portion of
the grease can be cooling in 44 and a portion in 45 and when both have been cooled down to room temperature the grease can be conducted through lines 13’, 14’ and 15 into storage tank 18 or the entire grease can be slowly cooled to room temperature in 45. The grease is accumulated in storage tank 18 and may be conducted through line 36 to packing containers 20 or homogenized in a homogenizer 19 at a temperature ranging from room temperature to about 90°C and then discharged through line 19 into packing containers 20.

Modifications to the process outlined above can be made. For example, the mixture of soap and oil from slurry tank 1 can be introduced directly into heating vessel 8 through lines 4, 14, 38, 43, 44 and 4’. A portion of the grease from heating tank 8 can then be returned to the slurry tank 1 or slurry homogenizer 7 where it is admixed with new grease, while the balance of the grease is processed to its final grease stage. Also during the heating stage of greases of this invention in heating tank 8 other soaps, such as, aluminum, zinc, or lead soaps can be added through conduit 50. The grease in its production stages is conducted to or by-products equipment by means of conduits, as noted in Figure 1, each having attached thereto control valves 22.

To illustrate the process of making greases by this invention, a specific example, namely, the method of making and heat-treating a soda base grease, will be herein fully described following the flow diagram.

The composition of the grease is as follows:

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<th>Components</th>
<th>lb./500 lb. grease</th>
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<tbody>
<tr>
<td>Hydrogenated fish oil acids</td>
<td>7.0</td>
</tr>
<tr>
<td>Hydrogenated castor oil</td>
<td>1.0</td>
</tr>
<tr>
<td>Polyethylene glycol having an average molecular weight of 600</td>
<td>0.045</td>
</tr>
<tr>
<td>Sodium hydroxide dissolved in 2 lbs. water</td>
<td>1.12</td>
</tr>
<tr>
<td>Solvent Refined Mineral oil, 600 SSU at 100° F.</td>
<td>91.3</td>
</tr>
</tbody>
</table>

The acids and glycerides together with about twice their weight of oil and the caustic solution are introduced into slurry tank 1 and heated at about 80°C until the fatty materials have melted. The mixture is stirred vigorously to form a slurry and the temperature increased to above 100°C to drive off the water. During the heating and stirring, a modicum of a polymeric silicone, e.g., dimethyl silicone polymer may be added if foaming becomes excessive. The slurry is then led through conduit 4, 4’ and 4” with the aid of pumps 5 and 6 into tank 8 where the temperature is increased to 180 to 250°C and the balance of the oil, preferably pre-heated to around 120°C, is slowly added through line 21 and the entire mixture is agitated and maintained at above 100°C until a homogeneous jelly stage has been attained. At this point the polyethylene glycol is introduced through conduit 50 and the mixture is maintained at the above elevated temperature. The grease is then discharged through conduit 9 and 9’ with the aid of pump 18 at a rate that by the time it reaches the tank 11 the temperature of the grease is below 172°C. The grease is allowed to remain in the tank 11 in a quiescent state for about 8 hours at a temperature of from 160° to 170° C. If a substantially lower temperature is to be used for heat conditioning the grease should not be brought down to below 160-170°C in less than half an hour. At the end of this heat treatment the grease is transferred to a cooling vessel 45 where it is allowed to cool to around room temperature and then led to homogenizer 18 for working to a homogeneous consistency and texture, after which it is packed in containers 20. Greases produced by this method require less soap than greases produced by conventional methods. Generally, excellent greases can be produced by the present method using only 3 to 8% soap. However, if desired, larger amounts up to 30% soap and soap mixtures can be used.

Using the Formula I it is possible to accumulate data for particular types of greases from which a master curve can be plotted and from which the heat conditioning required to obtain a given mechanical stability can be predicted. Figure 2 is a master curve for the soda base grease described in the preceding paragraph. For this particular grease it can be noted from Figure 2 that an increase in mechanical stability (measured by the Shell Roll Test) is obtained with increase in heat conditioning up to an equivalent of 8 hours at 170°C. Beyond this degree of heat conditioning, a moderate decrease in mechanical stability is noted which may be related to some type of embrittlement of the fibers.

Other grease compositions which can be produced by this process may include, sodium stearate, sodium oleate, potassium oleate, calcium stearate, barium stearate-acetate, strotium stearate-acetate, sodium 12-hydroxy stearate-oleate, zinc stearate, magnesium stearate sodium palmitate, sodium soap of castor oil, sodium ricinoleate-steareate greases, and the like. These greases may contain anti-oxidants, e.g., phenyl-alpha-naphthylamine, fillers, etc.

The temperature at which the soap-oil system is converted from the gel (two phase) state to the jelly or solution state is affected by the mineral oil as well as by the specific soap used. In the case of the soda base grease described in the foregoing example, use of a higher molecular weight mineral oil substantially increases this transition temperature. If a lithium soap is used instead of sodium soap, the transition temperature is also increased.

To improve grease compositions made by the present method minor amounts of stabilizing agents can be added at a desired stage of the process.

A particularly desirable stabilizing agent which can be used with grease compositions of this invention are the alkylene glycol and/or alkylene thio glycol polymers as well as their mono-esters and other polymeric derivatives. The alkylene glycol polymeric materials can be represented by the following general structural formula:

\[ H - \left( \text{C}_n\text{H}_{2n+1}O - \text{C}_m\text{H}_{2m}O \right) \cdot \text{H} \]

wherein \( m \) and \( n \) are integers. Preferably the polymeric alkylene glycols as represented by the above general formula should be such that the factor "c" times the number of carbon atoms within the brackets should be at least 6 and more.

The polymeric alkylene glycols can be made by polymerizing in the presence of a catalyst such as iodine, hydrobromic acid and the like, ethylene, propylene, isobutylene, n-butylene oxides and/or their mixtures. Such polymers can also be produced by reacting a monohydric alcohol with an alkylene oxide. Thus, a suitable product can be made by reacting n-butanol with propylene oxide at about between 212 to 230° F. under pressure and in the presence of an alkali catalyst.
The polymerized higher polyalkylene glycols having between 2 and 6 carbon atoms in the alkylene group are most effective as additives of this invention and those containing the ethylene and propylene groups are preferred. The average molecular weight of the polyalkylene glycols may range from about 200 to about 7000 and the preferred molecular weight being from about 600 to 6000.

It is desired to point out that the higher polyalkylene glycols are composed of mixtures of several polymers, for example, a polyethylene glycol having a molecular weight of 400 consists of various glycols varying from a minor amount of monooethylene glycol and increasing up to the pentadecaethylene glycol. Therefore, it is the average molecular weight which is specified and wherein the present specification, polyalkylene glycols or polyethylenylene glycols or 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 of between 600 to 1500 being very effective in carrying out the present invention.

In lieu of the polyalkylene glycols, the ester and other derivatives can be used. The esters can be made from a variety of acids having between 1 to about 22 carbon atoms and preferably between about 10 to 18 carbon atoms. Acids which may be used are the aliphatic, aromatic, cyclic, sulfonic acids and the like. Fatty acids and especially the higher fatty acids are preferred and include such acids as lauric, myristic, palmitic, stearic, arachidic, behenic, oleic, ricinoleic, hydroxystearic, phenylactic, phenylstearic acids and the like. However, such acids as naphthenic acid, oil-soluble, petroleum sulfonic acids, tall oil fatty acids, aromatic acids, etc., e.g., salicylic and phthalic acids and the like may be used to form the esters. Specific examples of esters of this type are the polyethylene glycol monostearate, polyethylene glycol monolaurate and the like.

Ether derivatives of polyalkylene glycols may be made by any conventional method and the aromatic ethers of polyalkylene glycols having the general formula:

III

\[ RO(C_{n}H_{2n}O\cdots C_{m}H_{2m}O\cdots)Ar\cdot R' \]

wherein Ar is an aromatic radical having attached thereto at least one alkyl radical denoted by R' having from 1 to about 6 carbon atoms and wherein Y is a fatty acid derivative, u, m, and n and q are numbers selected from the group consisting of zero or 1.

During the cooking of grease of this invention there may be introduced small amounts of other soaps or salts, generally in amounts of less than 2% for additional benefits. For example, there may be incorporated into sodium soap grease as described above a minor amount of aluminum or lithium soap or alkali and alkaline earth metal naphthenates, acetates, etc. Minor amounts of oxidation inhibitors can be added to grease compositions of this invention such as N-butyl paraphenylenediamine. Also effective as oxidation inhibitors are alpha or beta naphthalamine, phenyl-alpha or beta naphthalimine, alpha-alpha, beta-beta dimethylphthalimine, diphenylamine, tetramethyl dianino diphenylethylene, 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 10 carbon atoms in the molecule such as hexylamine, octylamine, decylamine, dodecylamine, octadecylamine, heterocyclic nitrogen containing organic compounds such as alkyl substituted oxazoles and oxazoline salts of fatty acids.

Extreme pressure agents can be added to such grease the preferred agents comprise esters of phosphorus acids such as triaryl, alkyldihydroxy, alky1, aralkyl phosphates, thio phosphates, or phosphates, 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 selendie and diselenide, dicresol selendie 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 dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils, acids, esters and ketones, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with hydroxy fatty acids, chlorinated hydrocarbons such as chlorinated paraffins, aromatic hydrocarbons, terpenes, mineral lubricating oils, etc.; or chlorinated esters of fatty acids containing the chlorine in positions other than the alpha position.

Additional ingredients which can be added are anti-wear agents such as oil-soluble urea or thiourea derivatives, e.g., urethanates, alkoxyphosphates, carbazides, carboxanes, etc.; or rubber, polyisobutylene, polystyrene, etc.; VI improvers such as polyisobutylene having a molecular weight above about 800, volatilized paraffin wax, unsaturated polymerized esters of fatty acids and monohydric alcohols, etc.; oiliness agents such as steareic 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 about around 0.01% to less than 10% by weight and preferably 0.1 to 5.0% by weight.

Greases of this invention are applicable for general automotive uses, and are excellent aircraft greases, industrial greases and the like.

We claim as our invention:

1. The method of making grease compositions from soaps of the group consisting of alkali metal soap, alkaline earth metal soaps and mixtures thereof comprising forming a slurry of the soap and lubricating oil, said soap being present in an amount sufficient to form a grease, heating said slurry to a temperature of 180-250°C until a homogeneous non-crystalline mixture has formed and thereafter cooling said grease to its gelation phase and heat-treating said grease below 172°C, but above 100°C to produce a stable homogeneous grease.

2. The method as defined by claim 1 in which a small amount of an oxidation inhibitor is incorporated into the soap slurry.

3. The method of claim 1 in which a portion of the hot homogeneous non-crystalline oil-soap mixture is admixed with a new batch of soap slurry.

4. The method of claim 1 in which the grease after being heat-treated is slowly cooled to room temperature.

5. The method of claim 1 in which the grease
after being heat-treated is shock-chilled to room temperature.

5. The method of making a soda soap grease, which comprises forming a slurry of soda soap and a mineral lubricating oil, heating and slurry to a temperature of 180–250° C. until a homogeneous non-crystalline mixture has formed, cooling said grease to its gelation temperature and heat-treating said grease from below 172° C. to above 100° C. for from 2 to 10 hours, in a quiescent state, to produce a stable homogeneous grease.

6. The method of making a soda soap grease, which comprises forming a slurry of soda soap, polyalkylene glycol and a mineral lubricating oil, heating said slurry to a temperature of 180–250° C. until a homogeneous non-crystalline mixture has formed, cooling said grease to its gelation temperature and heat-treating said grease from below 172° C. to above 100° C. for from 2 to 10 hours in a quiescent state to produce a stable homogeneous grease.

7. The method of making claim 6 in which between 3 and 10% soda soap is used to form the grease.

8. The method of making a soda soap grease, which comprises forming a slurry of soda soap, polyalkylene glycol and a mineral lubricating oil, heating said slurry to a temperature of 180–250° C. until a homogeneous non-crystalline mixture has formed, cooling said grease to its gelation temperature and heat-treating said grease from below 172° C. to above 100° C. for from 2 to 10 hours in a quiescent state to produce a stable homogeneous grease.

9. The method of making a soda soap grease, which comprises forming a slurry of soda soap, 0.01 to 1% polyalkylene glycol and a mineral lubricating oil, heating said slurry to a temperature of 180–250° C. until a homogeneous non-crystalline mixture has formed, cooling said grease to its gelation temperature and heat-treating said grease from below 172° C. to above 100° C. for from 2 to 10 hours in a quiescent state to produce a stable homogeneous grease.

10. The method of making an improved soda grease, which comprises (1) heating a mixture of 7 parts of hydrogenated fish oil acids, 1 part of hydrogenated castor oil, 1.12 parts of NaOH (dissolved in 2 parts of water) and a portion of solvent refined mineral oil and heating said mixture to about 100° C. until dehydrated, (2) increasing the temperature to around 180° C. adding 0.045 part of polyethylene glycol having average molecular weight of 600 and the balance of the mineral oil so that the total mineral oil amounts to 91.3 parts and heating said mixture at said temperature until mixture is homogeneous, (3) cooling the grease to 160–170° C. and maintaining said grease at said temperature in a quiescent state for about 8 hours (4) and finally shock chilling said grease to room temperature and thereafter homogenizing said grease.

11. The method of making grease compositions which comprises forming a slurry of an alkaline metal soap and lubricating oil, said soap being present in an amount sufficient to form a grease, heating said slurry to a temperature of 180–250° C. until a homogeneous non-crystalline mixture has formed and thereafter cooling said grease to its gelation phase and heat treating said grease at a temperature between 100° C. and 172° C. to produce a stable grease composition.

12. A method according to claim 11 wherein heat treating is carried out for a period from 2–10 hours.

13. The method of making grease compositions which comprise forming a slurry of an alkaline earth metal soap and lubricating oil, said soap being present in an amount sufficient to form a grease, heating said slurry to a temperature of 180–250° C. until a homogeneous non-crystalline mixture has formed and thereafter cooling said grease to its gelation phase and heat treating said grease at a temperature between 100° C. and 172° C. to produce a stable grease composition.

ROBERT J. MOORE,
WALFRID SAARNI.

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