

Aug. 11, 1953

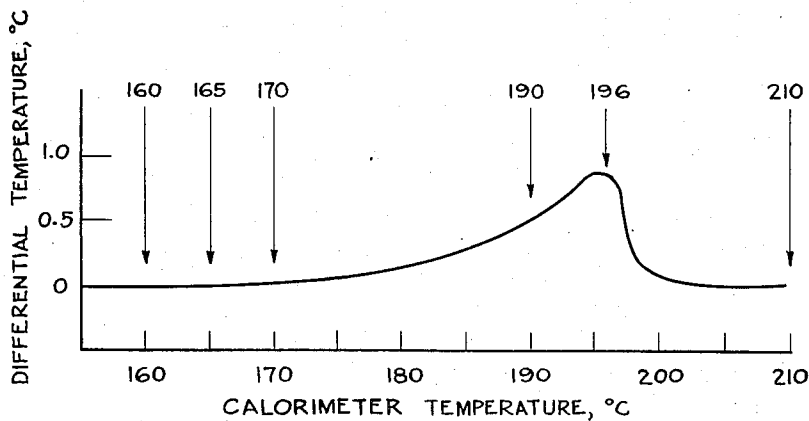
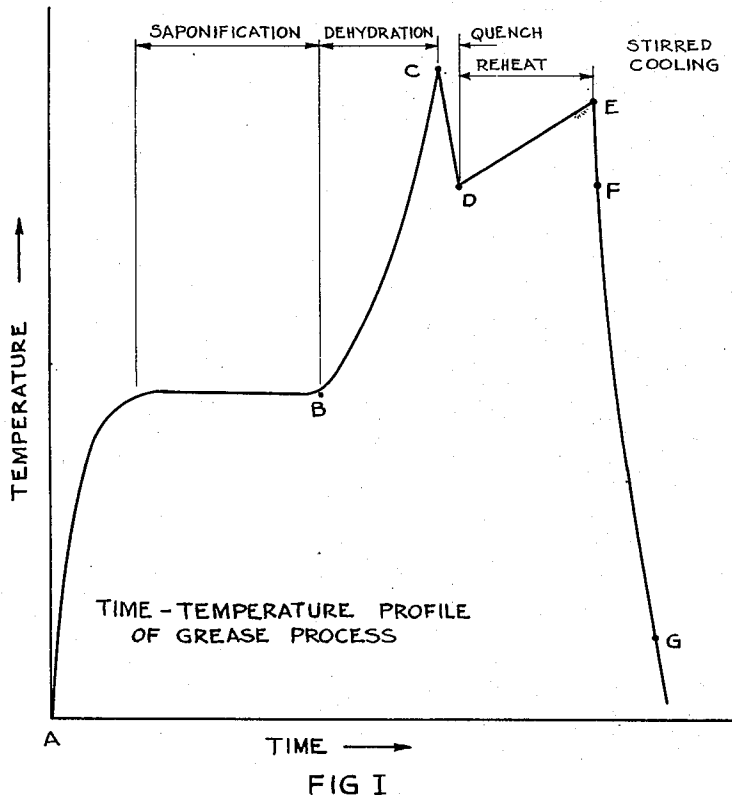
R. J. MOORE

2,648,634

METHOD OF PREPARING LUBRICATING GREASE COMPOSITIONS

Filed July 14, 1950

3 Sheets-Sheet 1



INVENTOR:

ROBERT J. MOORE

BY:

*James Jodorovic*  
HIS ATTORNEY

Aug. 11, 1953

R. J. MOORE

2,648,634

METHOD OF PREPARING LUBRICATING GREASE COMPOSITIONS

Filed July 14, 1950

3 Sheets-Sheet 2

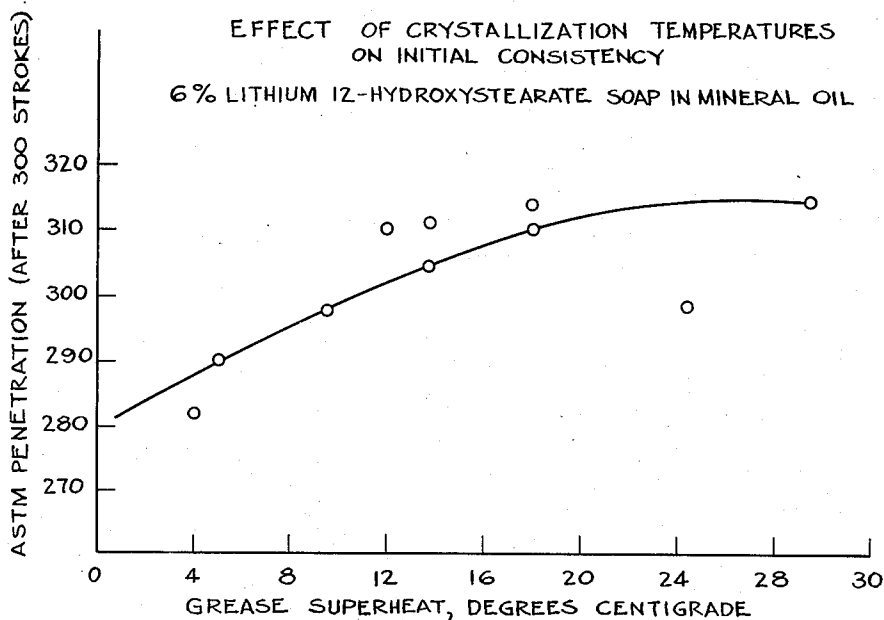


FIG. III

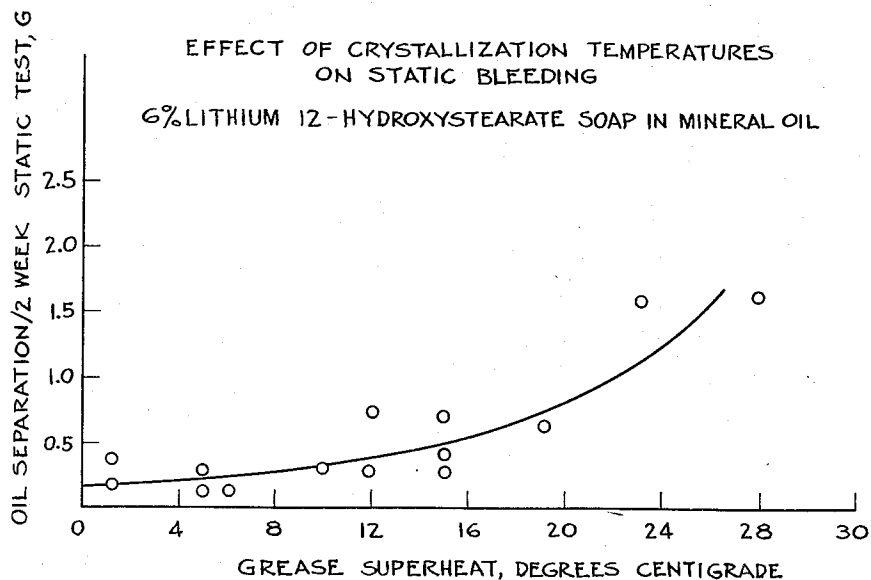


FIG. IV

INVENTOR:

ROBERT J. MOORE

BY:

*James Jodorovic*

HIS ATTORNEY

Aug. 11, 1953

R. J. MOORE

2,648,634

METHOD OF PREPARING LUBRICATING GREASE COMPOSITIONS

Filed July 14, 1950

3 Sheets-Sheet 3

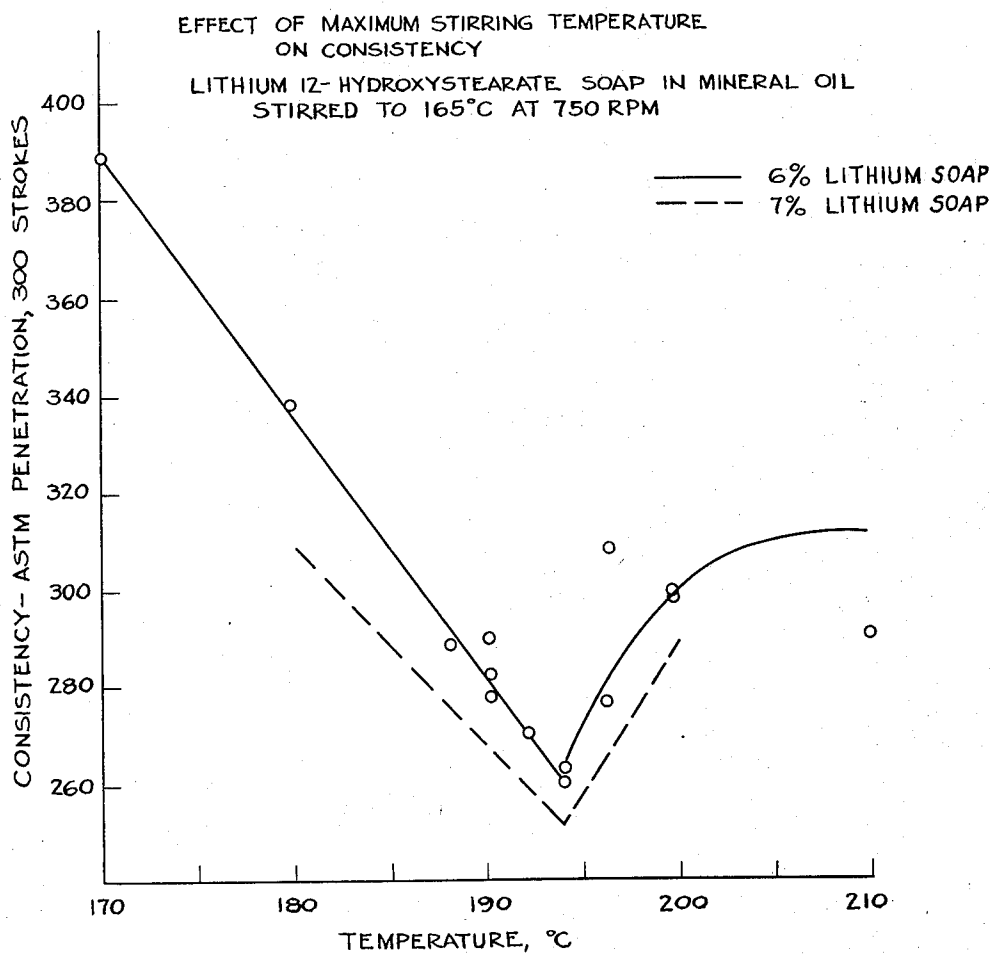


FIG. V

INVENTOR:

ROBERT J. MOORE

BY:

*James Todorovic*  
HIS ATTORNEY

## UNITED STATES PATENT OFFICE

2,648,634

## METHOD OF PREPARING LUBRICATING GREASE COMPOSITIONS

Robert J. Moore, Oakland, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application July 14, 1950, Serial No. 173,754

13 Claims. (Cl. 252-41)

1

This invention relates to improved grease compositions. More particularly, this invention pertains to a method of producing improved grease compositions which are capable of maintaining their consistency under variable conditions, resist bleeding, and possess good mechanical and dimensional stability.

A general deficiency encountered in most greases is the change in consistency which is observed on storage or after being worked for some time. On storage, greases generally tend to harden. Hardening is believed to be due to the interaction of active groups associated with the soap micelles therein which leads to the increase in the consistency of greases. Such hardening is undesirable for it introduces numerous lubricating difficulties such as in grease pumping equipment, handling and the like.

Another deficiency encountered in greases is their lack of resistance to shear as well as other types of mechanical forces which are generally exerted upon greases under various working conditions. Thus, in the lubrication of ball and roller bearings, greases may be subjected to temperatures in excess of 250° to 300° F., which temperatures accelerate oxidation, and, coupled with high shearing stresses, cause the greases to break down in structure. Thus, the greases are incapable of adhering to the surfaces to be lubricated, resulting in bearing corrosion, wear and failure. As a result it is essential that good greases, therefore, resist shearing stresses, particularly over wide temperature ranges.

Bleeding is another phenomenon which is frequently encountered in grease compositions. The causes for bleeding are at present not completely understood. Generally, it has been assumed that bleeding is the result of syneresis, but this does not appear to be entirely correct in view of the present findings which will be set forth hereinafter. However, to inhibit bleeding various precautionary measures have been taken which are time-consuming, costly and not very successful. Non-bleeding greases are produced by either reducing the soap content generally to less than about 5% by weight or by increasing the soap content to a maximum. These methods of stabilizing greases against bleeding have, however, proved to be unsatisfactory because in the case of reducing the soap content to less than 5% by weight, 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 undesirably high consistency.

It is an object of this invention to produce grease compositions having outstanding mechanical stability under dynamic and static conditions. It is another object of the invention to produce greases having good thermal reversibility and which are capable of resisting shearing stresses over wide temperature ranges. Still another object of this invention is to provide a method of

2

making improved grease compositions either by batch or continuous processes. Furthermore, it is an object of this invention to produce a multi-purpose grease of outstanding lubricating properties.

The foregoing objects will be better understood and others will become apparent from the detailed description of the invention, which will be made with reference to the accompanying drawings, wherein:

Figure I is a temperature profile of a grease-making process according to the invention.

Figure II is a differential thermal analysis of a particular grease made according to this invention.

Figure III is a graphical representation of the influence of solution temperature upon the penetration value of a grease.

Figure IV is a graphical representation of the influence of solution temperature expressed as "superheat," upon the bleeding characteristics of a grease.

Figure V is a graphical representation of the influence of maximum reheat temperature upon grease consistency.

Broadly stated, the present invention resides in the discovery that an improved grease can be obtained by forming a solution of a gelling agent or mixture of gelling agents in a suitable carrier or liquid lubricant, rapidly cooling said solution, reheating the resulting admixture to about the solution temperature and then cooling the mixture while subjecting it to shearing action. Specifically, as applied to soap-base greases, it has now been discovered that a superior grease composition is obtained by the process which comprises the steps: saponifying a fatty acid glyceride or a fatty acid in admixture with a suitable liquid lubricant or carrier, such as a mineral lubricating oil, with an alkaline-acting saponifying agent, for example, a metal compound, such as lithium hydroxide, to form a soap concentrate of the resulting soap in the liquid lubricant, such as one containing about 30% by weight soap; heating the resulting admixture to or slightly above substantial solution temperature of the soap in the liquid lubricant; rapidly quenching the resulting solution with additional liquid lubricant or carrier as may be required to yield the desired concentration of soap in the liquid lubricant to produce a grease structure; reheating the quenched material to slightly below solution temperature and thereupon cooling the reheated material, while subjecting it to shearing, to about 30° C. below said solution temperature.

The preparation of superior greases, particularly soap base greases, is contingent upon the distribution of the gelling agent therein, e. g., a soap, in the form of fibers or elongated "crystals" having a fairly high length to width ratio. The efficiency of utilization of a gelling agent as

a thickening agent depends upon the degree to which the gelling agent is present as discrete fibers, in contrast to more or less isometric crystals or bundles of fibers. The amount of gelling agent required to achieve a given consistency or mechanical stability is dependent upon this efficiency of utilization. It follows, then, that an important point in a grease preparative procedure is the step where the gelling agent is produced in the desired form. For example, in the manufacture of a soap-base grease, the crystallization step for the precipitation of the soap is largely determinative of the character of the grease product.

In the conventional method of manufacturing a mineral oil-soap grease, precipitation of the soap gelling agent occurs during saponification of the fats or fatty acids. After dehydration of the resulting soap-oil concentrate, it is diluted with additional oil to the desired consistency and weight per cent of soap. However, by this method the form of the precipitated gelling agent (soap) is dependent upon the growth-conditions present during saponification. The growth-conditions present at that time do not insure crystallization under the best conditions for the formation of the gelling agent in the desired and most efficient form.

The process of the invention will be better understood by reference to Fig. I. Fig. I represents in temperature profile a specific application of the process of the invention to the manufacture of a soap grease admixed with a mineral oil.

As represented in Fig. I, when a mixture of oil and suitable saponifiable and saponifying agents is heated gradually the temperature of the system changes with time as indicated by line AB with the formation of a soap-mineral oil concentrate containing, for example, about 30% by weight soap. On further heating of the resulting mixture to dehydrate it until a substantially homogeneous solution is formed, the temperature of the system changes as represented by line BC. When the homogeneous mass is then quench-cooled as by the addition of the remaining mineral oil in order to bring the weight percentage of soap therein to the desired amount and, also, to form finely divided fiber soap gelling agent as a result of the rapid cooling, the temperature of the system changes as indicated by line CD. On reheating the resulting admixture to a temperature (represented by point E) slightly below the solution temperature and thereafter cooling the reheated material, with stirring, to packaging temperature, or to about 30° C. below (indicated by point F) the solution temperature of the mixture (the temperature of point F being about the same as the temperature of point D), the temperature of the system changes with time as indicated by line DEFG.

By solution temperature is meant that temperature, as indicated by differential thermal analysis of the particular gelling agent-liquid lubricant system, at which the temperature differential of the cells within the calorimeter has reached its greatest value. Solution temperature may be characterized as that temperature at which substantially complete solution of the gelling agent in the liquid lubricant takes place, i. e., that temperature at which the gelling agent therein is present as discrete molecules or at most molecular aggregates (crystal nuclei) approximating colloidal dimensions in size. Solu-

tion temperature may be further characterized as that temperature at which the Tyndall beam disappears in the mixture. This is a convenient and accepted criterion of solution in colloid systems.

To provide a better understanding of the principles which underlie the requirement for specific processing temperatures, as for example, the solution temperature, it is advantageous to compare these temperatures with changes in the gelling agent-liquid lubricant system indicated by differential thermal analysis. The changes which take place in going from a solid-liquid mixture (gel) at room temperature to a homogeneous substantially complete solution at solution temperature are much more complex than the more familiar solvent-solute systems. Several changes at different temperatures are involved and processing techniques must be coordinated therewith.

A differential thermal analysis of a lithium 12-hydroxy-stearate-mineral oil system is shown in Fig. II. This figure shows the occurrence of phase changes (manifested by changes in temperature-time relationships of the sample) at temperatures which correlate well with the mechanical behavior of the grease when heat is added thereto or removed therefrom. Significant temperatures are found at about 196° C. and about 165° C. An examination of the phenomenon of "solution" of lithium 12-hydroxystearate soap in a mineral lubricating oil shows that the action is more complex than merely increasing solubility with increasing temperature. For example, even at 0.1% by weight soap concentration the solution temperature is still about 196° C. A suitable and likely explanation of the broad transition temperature range (165° to 196° C.) is that the transition temperature range can be likened to a type of depolymerization where the polymer exists by virtue of hydrogen bonds. These normally do not have the sharp transitions found with well-defined crystalline materials. Thus a considerable portion of the heat input between 165° C. and 196° C. is absorbed in "loosening" the structure of the solid soap particles and at higher temperatures a true solution is formed. Using this interpretation as a working model a fairly adequate explanation of the processing requirements and subsequent mechanical properties of the grease can be presented, although it is to be understood that any theory utilized for a better understanding of the invention, regardless of the validity of such theory, is immaterial to the carrying out of the combination process of the invention.

It has been found that the solution temperature of a gelling agent in a liquid lubricant carrier is influenced by the viscosity and/or the molecular weight of the carrier used. Accordingly, if lighter or heavier molecular weight carriers, such as mineral oils, are used, processing temperatures should be adjusted accordingly. For example, it has been found that the solution temperature of lithium 12-hydroxystearate in mineral oils of varying viscosity increases with increasing viscosity, although no differences were observed when oils of varying degrees of refinement were used. The data in Table I show the change in solution temperature of lithium 12-hydroxystearate with change in viscosity of a mineral lubricating oil. The mineral oils used were solvent extracted, acid treated, mineral oil distillates, although a similar situation holds when unextracted raw lube distillates are used.

5  
TABLE I

| Viscosity in Centistokes at 100° F. | Solution Temp., ° C. |
|-------------------------------------|----------------------|
| 20.....                             | 191                  |
| 32.....                             | 194                  |
| 100.....                            | 196                  |
| 325.....                            | 199                  |

As indicated hereinbefore, of the various processing factors in the formation of a superior grease, the initial formation of the gelling agent fibers is probably the most important. The degree of supersaturation and the number of crystal nuclei present in a solution are controlling factors on the size distribution of the solute particles (gelling agent) which are precipitated. Sudden lowering of the temperature of the solution to create a high degree of supersaturation and assuring ample crystallization sites (crystal nuclei) so that the solid phase can precipitate at many points, enhances the production of many small crystals or fibers. The effect of this size distribution and its relationship to specific conditions under which it is achieved on several grease properties is set forth hereinafter.

The specific crystallization conditions used to effect precipitation of the gelling agent from its solution in the liquid lubricant carrier can be related to the resulting consistency or penetration by an expression involving (1) the temperature to which the gelling agent solution was heated, which temperature controls the number of available crystal nuclei remaining in the solution and (2) the temperature to which the solution was quenched, as by rapid cooling or by quenching with additional lubricant carrier, which temperature determines the amount of supersaturation existing at the moment of crystallization. Thus, specifically, considering the temperature limits of 196° and 165° C. (as determined by thermal analysis) which represent the solution temperature and the temperature at which a lithium 12-hydroxystearate soap-mineral oil system is "frozen," respectively, the excess of the sum of the temperatures to which the mixture is heated for solution and then quenched over the sum of the temperatures represented by 196° and 165° C., is termed the amount of "superheating" and has been correlated with initial consistency (after 300 strokes ASTM) in Fig. III, for various lithium 12-hydroxystearate-mineral oil greases. As shown by Fig. III, those samples of a lithium 12-hydroxystearate grease which were heated to a temperature (solution temperature) just sufficient to dissolve all of the lithium soap but not to destroy the crystal nuclei therein (which latter would happen if the solution temperature was substantially exceeded), and thereupon quenched (as by rapid cooling or the addition of coil oil), had appreciably lower penetration values, as measured by ASTM Test Procedure D217-48 titled "Cone Penetration of Grease." In general, it has been found that those greases manufactured according to the invention with only a minor amount of superheat, preferably not over 10° C., have very satisfactory penetration values.

To demonstrate this effect further a lithium-12-hydroxystearate grease sample was heated to well above solution temperature (204° C. for about 10 minutes) to destroy the crystal nuclei, the grease was then seeded with about 0.035% of its weight of a pre-formed grease of suitably sized fibers to provide new crystallization sites

6

and rapidly cooled to about 175° C. The resulting grease had a penetration value of 288 instead of an expected 310 or greater.

It has also been observed that after precipitation of the gelling agent by quenching a solution of the gelling agent in a liquid lubricant carrier, extended heating for a period of about ½ to 1 hour at temperatures somewhat below the solution temperature, such as about 5° to 20° C. below said solution temperature, for example at a temperature of from about 180° to about 190° C. for a lithium 12-hydroxystearate mineral oil grease, leads to progressive softening of the finished grease. It is considered that during this heating period chance cross links in the gelling agent's "fiber bundles" become consolidated so that in the subsequent stirring operation there is more breakage of the preferred long fibers.

The control of bleeding grease by regulation of the gelling agent fiber size therein is considered in this invention to be a problem involving filtration of the liquid lubricant carrier therein from the mass of gelling agent fibers. Formerly, it was considered that bleeding was the result of syneresis or the resultant "forcing out" of the lubricant-carrier liquid phase (e. g., mineral lubricating oil) due to the shrinkage of the gelling agent solid phase. Accordingly, in the present view the entangled gelling agent fibers (e. g., soap) act like a filter mat from which oil separates under the influence of gravity so that where a liquid "head" of carrier exists there is a tendency for the liquid carrier to collect at the low point. This separation (flow) is resisted by (1) the capillary attraction of the gelling agent fibers for the liquid carrier and (2) by the rigidity or gel strength of the grease mass supporting the static "head" of liquid carrier.

Accordingly, in view of the above hypotheses, bleeding should be less for a system comprising the liquid lubricant carrier held by relatively fine fibers. Since it is possible to prepare a grease under conditions, according to the invention, conducive to the formation of finer fibers, it is, therefore, possible to thereby directly control bleeding.

A series of experiments were performed wherein samples of 6% by weight lithium 12-hydroxystearate grease in mineral oil were produced under varying conditions and the bleeding propensities of these samples were determined.

The bleeding test found most satisfactory is one based on static bleeding in a half-pound tin of grease and performed in the following manner. A vertical groove was cut to the bottom of the grease sample with a spatula (⅞ in. wide) and the sample stored at room temperature. After two weeks and again after six weeks, the free oil was decanted and measured, allowing a one-hour drain period. The groove was used primarily to decrease the testing time. The data obtained are graphically illustrated in Figure IV and they reveal that when crystallization temperatures, as indicated by a greater amount of "superheat," are such that as a result relatively coarse soap fibers are formed, there is an increased tendency towards bleeding. In general, the maximum temperature of the gelling agent solution should be limited to a few degrees, preferably not over 5° C., above the solution temperature in order to obtain greases having low bleeding losses. Also the temperature of the gelling agent solution should be lowered (quenched) sufficiently and quickly to provide a high degree of supersaturation and thereby assure the growth of only small crystals. It is preferred that the

temperature after quenching should be between about 15° C. to about 50° C., preferably about 30° C., below the solution temperature but may be greater or lesser according to the materials used and results desired.

It is pointed out that a high temperature, i. e., a temperature appreciably greater than the solution temperature, is to be avoided because of the resulting destruction of crystal sites (crystal nuclei) thereby. Furthermore, heating for an extended period of time at a temperature only slightly (2–10° C.) above solution temperature is to be avoided because crystal nuclei (molecular aggregates) are destroyed thereby. Thus a lithium soap grease prepared by holding a concentrate thereof in mineral oil at a temperature above solution temperature, for example, 10 minutes at 200° C. (solution temperature 196° C.) before quenching by adding thereto additional mineral oil, gave a considerably higher rate of bleeding than did a similar sample which was quenched immediately after reaching 200° C., although the degree of "superheating" was the same for both samples.

The critical relationship between crystallization temperature and crystal size of the gelling agent can be minimized by quenching a more dilute solution of the gelling agent. Accordingly, instead of quenching a 30% by weight concentrate of gelling agent with the remainder of the liquid carrier to produce a 6% grease, a suitable alternative procedure would be to quench a relatively low "concentrate," say about 7% by weight gelling agent (which would contain about 84% of the total liquid lubricant carrier in the finished grease) with the additional liquid lubricant carrier required to give a 6% grease. The additional liquid carrier should be at an appropriately relatively lower temperature, about –10° C., in order to obtain rapid quenching and the proper quench temperature. Thus 6% by weight lithium 12-hydroxystearate mineral oil grease made in the above manner to give a temperature after quenching of 179° C. from a solution at a temperature of 200° C. (i. e., 18° C. superheat) would be expected, according to Fig. IV, to have a bleeding value of at least 0.5 gm. Actually a bleeding value of only 0.05 gm. was obtained. In addition, it is pointed out that a grease produced by quenching a dilute solution requires less vigorous stirring to form a smooth grease because aggregation of the precipitated crystal fibers is inhibited. It is, of course, realized that instead of preparing a soap concentrate, it is possible to prepare a grease containing all the components thereof in the desired proportions, thereby eliminating the necessity of adding additional carrier. The heated grease may then be quenched as by rapid cooling in a heat exchanger and further treated in accordance with the invention.

In summary, to produce a superior substantially non-bleeding grease, excellent results are obtained when a gelling agent (soap) and liquid carrier (mineral oil) are heated to, or slightly, about 1° to 5° C., preferably about 1° to 2° C., above solution temperature, maintained at that temperature for only a relatively short time (1–10 minutes), so that although the melt appears to be substantially uniform and homogeneous there remain therein molecular aggregates or crystal nuclei; quenched from a fairly dilute melt with additional liquid carrier to a temperature substantially below the solution temperature, about 30° C. below; reheated to a temperature slightly, from about 2° to about 5° C., preferably about 2°

C., below solution temperature and then vigorously agitated while being cooled to a temperature substantially below (about 30° C.) the solution temperature.

5 Dimensional stability or the resistance to slumping, particularly at elevated temperatures, is an important property of a grease relating to the ability of the grease to stay in place during use. Slumping takes place under gravity when the mass of the grease exceeds the ability of the fiber cross links of the gelling agent therein to support the structure. As the temperature increases the individual points of contact supporting the mass become weaker, leading to eventual collapse of the "scaffolding" supporting the grease and holding the oil therein.

Not only is the crystallization (precipitation) step important in determining the distribution of the gelling agent (soap) fibers but also other steps of the process involving aggregation of the fibers have considerable effect upon dimensional stability. Obviously, if the fiber bundles formed by aggregation are not completely dispersed by the shearing action during cooling or if only a relatively few large fibers have been formed in the crystallization step, there will be few contact points holding the entire grease mass together and greases of this type will slump very easily. Dimensional stability (slumping tendency) can be fairly well correlated with processing conditions and temperature (i. e., solution and quench temperature, expressed as "superheat"). Slumping data for a range of "superheat" temperatures are set forth in Table II below. The data show that only those samples prepared at the lower temperatures (small amount of superheat), according to the teaching of the invention, resisted slumping at 110° C.

The test used to evaluate slumping tendency is a simple modification of the well-known wheel-bearing test. 100 grams of grease is spread uniformly on the inside of a 600 cc. beaker to give a cylinder of grease approximately ¼" thick and 3" high and placed about ¼" above the bottom of the beaker. The beaker containing the sample is placed in an oven at 110° C. for one hour and the extent of slumping estimated from the proportion (percentage) of the bottom of the beaker covered by the grease. Bleeding can also be estimated in this test.

TABLE II

Effect of crystallization temperatures on static bleeding and dimensional stability

[6% lithium 12-hydroxystearate in mineral oil stirred from 190° C. to 165° C.]

|    | Bleeding,<br>gms./2<br>weeks | Slump<br>Test,<br>110° C. | Super-<br>heat, <sup>1</sup><br>° C. | Max.<br>Melt.<br>Temp.,<br>° C. | Quench<br>Temp.,<br>° C. | ASTM<br>Penetra-<br>tion, 300<br>Strokes |
|----|------------------------------|---------------------------|--------------------------------------|---------------------------------|--------------------------|------------------------------------------|
| 60 | 0.1-----                     | pass----                  | 5                                    | 196                             | 170                      | 287                                      |
|    | 0.1-----                     | do-----                   | 6                                    | 199                             | 168                      | 300                                      |
|    | 0.2-----                     | do-----                   | 0                                    | 197                             | 164                      | 290                                      |
|    | 0.2-----                     | do-----                   | 5                                    | 196                             | 170                      | 299                                      |
| 65 | 0.3-----                     | do-----                   | 1                                    | 197                             | 163                      | 307                                      |
|    | 0.3-----                     | do-----                   | 8                                    | 197                             | 172                      | 296                                      |
|    | 0.3-----                     | 25%-----                  | 10                                   | 200                             | 171                      | 299                                      |
|    | 0.3-----                     | 25%-----                  | 12                                   | 200                             | 173                      | 289                                      |
|    | 0.3-----                     | 75%-----                  | 15                                   | 205                             | 171                      | 284                                      |
|    | 0.4-----                     | 50%-----                  | 15                                   | 205                             | 171                      | 312                                      |
|    | 0.7-----                     | 100%-----                 | 12                                   | 202                             | 171                      | 310                                      |
| 70 | 0.7-----                     | 100%-----                 | 19                                   | 207                             | 173                      | 317                                      |
|    | 1.7-----                     | 100%-----                 | 23                                   | 200                             | 184                      | 301                                      |
|    | 1.7-----                     | 100%-----                 | 28                                   | 211                             | 188                      | 320                                      |

<sup>1</sup> Superheat: The sum of the temperatures in degrees centigrade above 165° C. for the quench temperature and above 196° C. for the melt temperature.

When a gelling agent (e. g., lithium 12-hydroxystearate) is precipitated from its hot liquid carrier (e. g., mineral oil) solution, the resulting crystals usually have a tendency to aggregate into fairly large masses or clumps. This results in a "grainy" grease, or gelling agent (soap)-liquid carrier (oil) slurry having none of the properties of a grease. As pointed out hereinbefore, this tendency to form "clumps" can be lessened by crystallizing the gelling agent from a dilute solution. In general, however, it is necessary to subject the grease mixture to a shearing action in order to disperse and break up these crystal aggregates. The shearing can be carried out at room temperature but the energy required would be excessive. However, at a temperature somewhat below the solution temperature (e. g., for a lithium 12-hydroxystearate-mineral oil grease a temperature of between about 165° and 195° C.) the crystal bonds are much weaker and a smooth grease can easily be prepared by stirring the hot slurry. The effect of maximum stirring temperature upon grease consistency is shown by Figure V, wherein a lithium 12-hydroxystearate grease concentrate was heated to about 200° C. and then portions were quenched with additional mineral oil to give greases containing 6% and 7% by weight soap. Thereafter portions of these greases were reheated to certain selected temperatures and then stirred at 750 R. P. M. in a closed kettle while cooling to about 165° C. The various greases were then tested as to their consistency (ASTM penetration tests—300 strokes) and the values noted were plotted against maximum stirring temperature, as illustrated by Figure V. The increased effectiveness of stirring at higher temperature up to solution temperature, is strikingly evident therefrom. However, when the greases are reheated above the solution temperature, all the fibers (crystals) previously formed by quenching disappear and the subsequent recrystallization which takes place during the relatively slow cooling and stirring period leads to the formation of a rather coarse, grainy grease since a slow rate of cooling is conducive to the formation of very large fibers (crystals).

It is pointed out that if stirring after reheating is stopped before the grease has cooled substantially below the solution temperature, i. e., at least 15° C. below solution temperature, fiber reaggregation takes place so that high penetration values are obtained. Furthermore, if stirring of the grease is continued to room or packaging temperature, that is, to a temperature at least about 100° C. below solution temperature, a small amount of softening of the grease occurs due to the mechanical breakdown of the fiber structure of the grease.

Bleeding resistance and dimensional stability are affected by maximum stirring temperatures to the extent that dispersion of the fibers is promoted by higher temperatures. For example, for a 6% lithium 12-hydroxy-stearate-mineral oil grease, bleeding resistance improved when the maximum stirring temperature was increased to 194° C. instead of 190° C. In general, the maximum stirring temperature should be slightly below between about 1° to 5° C., preferably about 2° C. below the solution temperature.

Although the practice of the invention and discussion of the various operational factors involved have been illustrated with mineral oil base greases containing lithium 12-hydroxystearate as gelling agent (soap), the invention is applicable

to other combinations of soaps and oils. The gelling agents used to form the grease may be soaps of fatty acids and/or their glycerides. The saponifiable material may be higher fatty acids or mixtures of the same having from 10 to 32 carbon atoms and they may be saturated, unsaturated or polar-substituted fatty acids, such as capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, myristoleic, palmitoleic, oleic, linoleic, ricinoleic, eucric acids, cottonseed oil fatty acids, palm oil fatty acids, hydrogenated fish oil fatty acids, and their mixtures and/or their glycerides, such as lard, beef, rapeseed, palm, menhaden, herring oils, etc. Other acids may be included, among which are: acid produced by oxidation of petroleum oil and waxes, rosin acids, tall oil acids, abietic acids, including dehydroabietic acid and dihydroabietic acid; naphthenic acids, petroleum sulfonic acids and the like.

A particularly preferred class of saponifiable materials is the class of hydroxy fatty acids and their glycerides, such as dimethyl hydroxy caprylic acids, dimethyl hydroxy capric acids, hydroxy physetoleic acid, ricinoleic acid, ricinoleic acid, 12-hydroxystearic acid, 9,10-dihydroxystearic acid, 4-hydroxypalmitic acid, linusic acid, sativic acid, lanoceric acid, dihydroxygadoleic, dihydroxybehenic acid, quince-oil acid and the like. The preferred hydroxy fatty acids are those in which the hydroxy group is at least 12 carbon atoms removed from the carboxyl group. Also, it is preferable to use hydroxy fatty acids having at least 10 carbon atoms and up to about 32 carbon atoms and preferably those having between 14 and 32 carbon atoms in the molecule. Instead of using the free fatty acids containing a hydroxy radical their glycerides can be used, such as castor oil or hydrogenated castor oil or mixtures of free hydroxy fatty acids and their glycerides can be used. Mixtures of hydroxy and non-hydroxy fatty acids can be used to form soaps for use in the invention.

The saponifying agent used to make the soap may be alkaline acting metal compounds of Li, Na, K, Cs, Ca, Sr, Ba, Cd, Zn, Pb and Co, and preferably the oxides, hydroxides and carbonates of the alkaline metals of valences from 1 to 3. Mixtures of soaps can be used and the soaps can be made in situ or pre-made soaps can be used to form the grease. Specific examples of preferred soaps and mixtures thereof are the alkali metal fatty acid soaps, such as lithium stearate, lithium hydroxystearate, lithium ricinoleate, lithium soap of hydrogenated fishoil fatty acids, lithium soap of mixed stearic and hydroxystearic acids, sodium stearate, sodium hydroxystearate, sodium oleate, potassium oleate, potassium rosinate, calcium stearate, calcium hydroxystearate, barium hydroxystearate, barium stearate, barium soap of mixed stearic and hydroxystearic acids, lithium soap of mixed oleic and hydroxystearic acids, sodium soap of mixed stearic and hydroxystearic acids; barium soap of mixed stearic and oleic acids; lead ricinoleate; mixed soaps of lithium stearate and sodium stearate, mixed soaps of lithium hydroxystearate and sodium stearate; mixed soaps of lithium hydroxystearate and calcium stearate, etc. Amine soaps, such as triethanolamine oleate can be used in combination with metal soaps or as the only gelling agent.

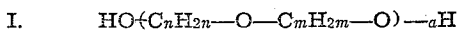
Instead of using only soaps as the gelling agent, mixtures of soaps and other gelling agents, such as organic or inorganic aerogels, silica aerogels,

alumina aerogels, nylon or cellulose fibers can be used in addition to the soap as the gelling agent.

The soap content of grease compositions of this invention may vary over wide limits between about 3 to 20% and may be as high as 50% by weight. In practice, it is possible by choice of suitable grease-forming lubricant bases to manufacture satisfactory lubricating greases containing only about 10% or less by weight of the soap mixtures. Very satisfactory products are obtained with a total soap content of about 6% to 8% by weight of the finished grease.

The grease-forming lubricant bases used in preparing the greases of the present invention may vary widely in character and include mineral oil of wide viscosity range, the range varying from about 100 SSU at 100° F. to about 2000 SSU at 100° F. The viscosity index of the oil can vary from below zero to about 90 or higher and can have an average molecular weight ranging from about 250 to about 900 or higher. It may be highly refined and solvent treated if desired by any known means. A preferred mineral oil is one which has a viscosity of 300 to 700 SSU at 100° F., a viscosity index of from 40 to 90, or even higher, and an average molecular weight of 350 to 750. Instead of using straight mineral oil as the base, synthetic oils and lubricants may be substituted in part or wholly for the mineral oil. Among the synthetic lubricants which can be used are: polymerized olefins; polyalkylene glycols and their partial or complete ethers and esters; organic esters, e. g., 2-ethyl-hexyl sebacate, dioctyl phthalate, tri(ethylhexyl) phosphate; polymeric tetrahydrofuran; polyalkyl silicone polymers, e. g., dimethyl silicone polymer; alkylated aromatics, such as waxylated naphthalenes, etc. Under some conditions of lubrication, minor amounts of a fixed oil such as castor oil, lard oil, etc., may be admixed with the hydrocarbon oil and/or synthetic oil used in making grease compositions of this invention.

Particularly useful stabilizing agents for grease compositions of this invention are the alkylene glycol and/or alkylene thio glycol polymers, including their mixtures, as well as their monoester and/or ether derivatives. The alkylene glycol polymeric materials, also named polyoxyalkylene diols, can be represented by the following general structural formula:



wherein  $m$  and  $n$  are the same or different integers in a given molecule and  $a$  is an integer. Preferably the polymeric alkylene glycols as represented by the above general formula should be such that the product of the factor  $a$  and the number of carbon atoms within the brackets should be at least 6 and more.

The 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 be from about 200 to about 7,000 and the preferred molecular weight being from about 600 to 6,000, it being understood that such compositions are always mixtures of various molecular species of different molecular weights.

To greases of this invention there may be added 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 soap or alkali and alkaline earth metal naphthenates, acetates, hydroxybenzoate, alpha-hydroxystearate, alpha-hydroxypropionate, beta-hydroxypropionate, gamma-hydroxyvalerate, Ca salt of alkylphenol-formaldehyde condensation product, Zn dibutyl-dithiocarbamate, etc.

Minor amounts of oxidation inhibitors can be added to grease compositions of this invention with benefit, such as N-butyl paraphenylene diamine. Also effective as oxidation inhibitors are alpha or beta naphthylamine, phenyl-alpha- or beta-naphthylamine, alpha-alpha or beta-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 greases and the preferred agents comprise esters of phosphorus acids such as triaryl-, alkylhydroxy-, alkyl-, 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, dicresol 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 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., urethanes, allophanates, carbazides, carbazones, etc.; or rubber, polyisobutylene, polyvinyl esters, etc.; viscosity index (V. I.) 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 stearic and oleic acids and pour point depressors such as chlorinated naphthalene to further lower the pour point of the lubricant base.

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

This invention is a continuation-in-part of my copending patent application, Serial No. 105,381, filed July 18, 1949 now U. S. Patent 2,614,079.

I claim as my invention:

1. A method of preparing a grease composition

which comprises: heating a mixture of an organic liquid lubricant and a fibrous metallic soap of an aliphatic monocarboxylic acid having at least 10 carbon atoms per molecule, said soap being selected from the group consisting of alkali metal soaps and alkaline earth metal soaps to a temperature between the minimum solution temperature, at which temperature said soap at least colloiddally disperses in said lubricant, and 5° C. thereabove, for a period between 1 and 10 minutes; quenching the solution so formed to a temperature between about 15° C. and 50° C. below said minimum solution temperature; reheating the cooled mixture to a temperature between about 1° C. and about 10° C. below said minimum solution temperature; cooling the reheated mixture while subjecting it to shearing, to a temperature between 15° C. and 100° C. below the minimum solution temperature; and cooling the resulting grease to lower temperatures in the substantial absence of shearing.

2. A method of preparing a grease composition which comprises: heating a mixture of a liquid hydrocarbon lubricant and a fibrous alkali metal soap of an aliphatic monocarboxylic acid having at least 10 carbon atoms per molecule to a temperature between the minimum solution temperature, at which temperature said soap at least colloiddally disperses in said lubricant, and 5° C. thereabove, for a period between 1 and 10 minutes; quenching the solution so formed to a temperature between about 15° C. and 50° C. below said minimum solution temperature; reheating the cooled mixture to a temperature between about 1° C. and about 10° C. below said minimum solution temperature; cooling the reheated mixture, while subjecting it to shearing to a temperature between 15° C. and 100° C. below the minimum solution temperature; and cooling the resulting grease to lower temperatures in the substantial absence of shearing.

3. A method of preparing a grease composition which comprises: heating a mixture of a liquid hydrocarbon lubricant and a fibrous lithium soap of an aliphatic monocarboxylic acid having at least 10 carbon atoms per molecule to a temperature between the minimum solution temperature, at which temperature said soap at least colloiddally disperses in said lubricant, and 5° C. thereabove, for a period between 1 and 10 minutes; quenching the solution so formed to a temperature between about 15° C. and 50° C. below said minimum solution temperature; reheating the cooled mixture to a temperature between about 1° C. and about 10° C. below said minimum solution temperature; cooling the reheated mixture, while subjecting it to shearing to a temperature between 15° C. and 100° C. below the minimum solution temperature; and cooling the resulting grease to lower temperatures in the substantial absence of shearing.

4. The method according to claim 1 wherein the organic liquid lubricant is a mineral lubricating oil.

5. The method according to claim 1 wherein the soap is a metal hydroxy fatty acid soap and the organic liquid lubricant is a mineral oil.

6. The method according to claim 3 wherein the soap is a lithium hydroxy fatty acid soap and the organic liquid lubricant is a mineral oil.

7. The method according to claim 3 wherein the soap is lithium 12-hydroxystearate and the organic liquid lubricant is a mineral lubricating oil.

8. The method according to claim 2 wherein the soap is a sodium fatty acid soap and the organic liquid lubricant is a mineral lubricating oil.

9. The method of producing a lithium soap grease composition which comprises: heating an admixture of lithium 12-hydroxystearate and mineral oil to about 195° C.; rapidly cooling the resulting solution to a temperature between about 160° C. and about 180° C. by adding additional mineral oil thereto; reheating the resulting cooled material to a temperature between about 185° C. and about 196° C. but below solution temperature and cooling while working the reheated material to a temperature between about 150° and about 175° C. and thereafter statically cooling the resulting grease to ambient atmospheric temperature.

10. The method according to claim 9 wherein the proportions of oil and soap in the first heating step are such as to yield about a 30% concentration of soap in the total composition.

11. The method according to claim 9 wherein the proportions of oil and soap in the first heating step are such as to yield about a 7% concentration of soap in the total composition and wherein the amount of mineral oil added in the first cooling step in such as to reduce the soap content to about 6%.

12. The method of producing a lithium soap grease composition which comprises: heating an admixture of a lithium hydroxystearate and mineral oil to about solution temperature; rapidly cooling the resulting solution to a temperature between about 15° and 50° C. below said solution temperature; reheating the resulting cooled material to a temperature about 1° C. to about 10° C. below said solution temperature and cooling while working the reheated material to a temperature about 15° and 50° C. below said solution temperature.

13. The method of producing a lithium soap grease composition which comprises heating a mixture of lithium hydroxy stearate and mineral oil to about solution temperature; rapidly cooling the resulting solution to a temperature between about 15° and about 50° C. below said solution temperature; reheating the resulting cooled material to a temperature about 1° C. to about 10° C. below said solution temperature and cooling while working the reheated material to a temperature about 15° and 50° below said solution temperature, said initial heating having been carried out to a maximum temperature not higher than the minimum solution temperature for a time not greater than about ten minutes.

ROBERT J. MOORE.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

| Number    | Name                | Date           |
|-----------|---------------------|----------------|
| 1,943,806 | Becker et al. ....  | Jan. 16, 1934  |
| 2,397,956 | Fraser .....        | Apr. 9, 1946   |
| 2,450,255 | Puryear et al. .... | Sept. 28, 1948 |
| 2,497,133 | Morway et al. ....  | Feb. 14, 1950  |