METHOD OF PREPARING LUBRICATING GREASE COMPOSITIONS

Inventors: Robert C. Jones
Robert J. Wall

By James Todorovic
Their Attorney
METHOD OF PREPARING LUBRICATING GREASE COMPOSITIONS

Figures II and III illustrate the effects of soap, temperature, and penetration on the consistency of the lubricating grease. The figures show how different factors interact to affect the final product.

Inventors: Robert C. Jones  
Robert J. Wall

By: James J. D. Wall  
their Attorney
Relationship between Pressure Drop and Recycle Rate with Respect to Consistency

Figure IV

Effect of Working on Consistency

Figure V

Inventors: Robert C. Jones
Robert J. Wall

By James Adonis
their Attorney
The resulting heated admixture is allowed to cool statically until a gel structure has been formed. The cooled gel is then usually subjected to a milling operation to homogenize it to a homogeneous grease composition. In general, however, heretofore both the apparatus and methods employed in such processes have proven unsatisfactory, especially when applied to the manufacture of quality and superior greases.

Quality greases are critical compositions, the size and state of aggregation of the gelling agent therein having a pronounced effect upon the physical properties of the finished grease, such as dimensional stability, resistance to bleeding, etc.

The preparation of superior greases, particularly mineral oil soap-base greases, is contingent upon the distribution of the gelling agent therein, e.g., a soap, such as a lithium hydroxy fatty acid soap, in the form of fibers or elongated "crystals" having a fairly high length to width ratio. The efficiency of utilization of the 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 isotropic crystals or bundles of fibers. The amount of gelling agent (yield) required to achieve a given consistency (penetration) 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 wherein the gelling agent is produced in the desired fiber (crystal) form; for example, in the manufacture of a soap-base grease, the crystallization step wherein the soap is precipitated.

It is an object of this invention to provide a method for the production of superior greases. It is another object of the invention to provide an improved method for the continuous manufacture of grease. A more specific object of this invention is to present a method for the manufacture of a superior alkali metal soap-base grease, such as a lithium hydroxy fatty acid soap grease. These and other objects of the invention will become apparent from the disclosure of this invention as set forth hereinafter.
illustrated when applied to the manufacture of a lithium hydroxy-fatty acid soap grease, specifically a lithium 12-hydroxy-oleate-mineral oil grease as fully described hereinafter with reference to Figure 1.

Figure I is a process flow diagram of an embodiment of the invention as applied to the preparation of lithium 12-hydroxy-oleate—mineral lubricating oil grease. Referring now to Figure I, a lithium 12-hydroxy-oleate and mineral oil slurry—concentrate, containing about 12% by weight of said soap plus desired additives was prepared in kettle 11, such as a standard Dopp kettle, equipped with a suitable agitator 12 and heated therein to some convenient temperature, say about 285° F. The temperature of about 285° F. was selected because it could easily be reached by employing steam as the heating medium without necessitating unduly high steam pressures. The resulting slurry at a temperature of about 285° F. leaves the kettle via line 14 and enters a high pressure preheating displacement pump 15 from which it is discharged at a suitable rate, e.g., about one-half pound per minute, via line 16 into a high capacity, forced film-type of heat exchanger (Votator type) 18 which is supplied with a suitable high pressure heating medium, such as Dowtherm. The soap—oil slurry is rapidly heated within the heat exchanger to a high temperature, T1, about 360° F., and emerges from said heat exchanger via line 18 wherein it is rapidly cooled (quenched) by contact with a relatively cool recycle dilute soap—oil stream from line 21 to some temperature, T2, in the neighborhood of 330—340° F., about 45° F. below temperature T1.

While the soap—oil admixture is quenched within line 19, work is being performed upon it by forcing it through a shearing device 25, such as a plug cock. Although any number of shearing devices are suitable, a plug cock is selected because of its simplicity, flexibility, low cost, etc. Furthermore, by adjusting the size of the opening in the plug cock a wide range of pressure drop, ΔP, across the same is possible. A relatively large portion of the quenched, sheared soap—oil admixture at a temperature T2 is withdrawn via line 16 by line 24 which leads to a high pressure positive displacement type pump 26, such as a gear pump which supplies the major portion of the energy required to accomplish the shearing within plug cock 29 and also the recycling of the soap—oil mixture via line 21. The temperature T3 is maintained and controlled by injection from line 20 into line 21 of oil, for example, a 750 SSU at 100° F. pale oil, such as is used to prepare the initial slurry concentrate. The injection oil in line 25 is supplied thereto via line 23 from a high pressure positive displacement type pump 29; the oil is heated by passing through heat exchanger 30 wherein the temperature of the injection oil emerging therefrom is maintained and/or controlled by suitable temperature control devices actuated by a selected temperature T5 in line 19 to control the amount of heat exchange fluid entering and leaving said heat exchanger 30 via lines 31 and 33, respectively.

A portion of the quenched, sheared soap—oil admixture from line 18 passes into a high capacity forced—film type of heat exchanger (Votator type) 32 which is supplied with a suitable coolant, such as water. The cooled grease emerges from heat exchanger 32 at some reduced temperature, for instance, in the neighborhood of 100° F., and is ready for packaging or for any other processing which may be desired.

In order to determine and demonstrate the critical influence of the various temperatures, such as the solution temperature, T1, and the quenched oil—soap temperature, T2, upon the finished grease, a number of experiments were performed wherein various temperatures for T1 and T2 were employed. Additionally, to demonstrate the effect of varying amounts of work (shearing) performed upon the grease during quenching as well as the influence of recycle ratio, R, thereupon, e.g., the weight ratio of the recycle stream to the product stream to cooler 22, a number of experiments were carried out wherein these factors were varied.

Specifically, the experiments consisted of basing a concentrated slurry of gelling agent and additives (about 12% by weight of the total composition) in a mineral oil (750 SSU at 100° F., pale oil), said slurry having been obtained by saponifying hardened castor oil glycerides with lithium hydroxide to obtain a lithium hydroxy—oleate type of soap which is supplied with a suitable coolant, such as water. The cooled grease emerges from heat exchanger 32, wherein it is rapidly cooled (quenched) by contact with a relatively cool recycle dilute soap—oil stream from line 21 to some temperature, T2, in the neighborhood of 330—340° F., about 45° F. below temperature T1.

While the soap—oil admixture is quenched within line 19, work is being performed upon it by forcing it through a shearing device 25, such as a plug cock. Although any number of shearing devices are suitable, a plug cock is selected because of its simplicity, flexibility, low cost, etc. Furthermore, by adjusting the size of the opening in the plug cock a wide range of pressure drop, ΔP, across the same is possible. A relatively large portion of the quenched, sheared soap—oil admixture at a temperature T2 is withdrawn via line 16 by line 24 which leads to a high pressure positive displacement type pump 26, such as a gear pump which supplies the major portion of the energy required to accomplish the shearing within plug cock 29 and also the recycling of the soap—oil mixture via line 21. The temperature T3 is maintained and controlled by injection from line 20 into line 21 of oil, for example, a 750 SSU at 100° F. pale oil, such as is used to prepare the initial slurry concentrate. The injection oil in line 25 is supplied thereto via line 23 from a high pressure positive displacement type pump 29; the oil is heated by passing through heat exchanger 30 wherein the temperature of the injection oil emerging therefrom is maintained and/or controlled by suitable temperature control devices actuated by a selected temperature T5 in line 19 to control the amount of heat exchange fluid entering and leaving said heat exchanger 30 via lines 31 and 33, respectively.

A portion of the quenched, sheared soap—oil admixture from line 18 passes into a high capacity forced—film type of heat exchanger (Votator type) 32 which is supplied with a suitable coolant, such as water. The cooled grease emerges from heat exchanger 32 at some reduced temperature, for instance, in the neighborhood of 100° F., and is ready for packaging or for any other processing which may be desired.

In order to determine and demonstrate the critical influence of the various temperatures, such as the solution temperature, T1, and the quenched oil—soap temperature, T2, upon the finished grease, a number of experiments were performed wherein various temperatures for T1 and T2 were employed. Additionally, to demonstrate the effect of varying amounts of work (shearing) performed upon the grease during quenching as well as the influence of recycle ratio, R, thereupon, e.g., the weight ratio of the recycle stream to the product stream to cooler 22, a number of experiments were carried out wherein these factors were varied.

Specifically, the experiments consisted of basing a concentrated slurry of gelling agent and additives (about 12% by weight of the total composition) in a mineral oil (750 SSU at 100° F., pale oil), said slurry having been obtained by saponifying hardened castor oil glycerides with lithium hydroxide to obtain a lithium hydroxy—oleate type of soap which is supplied with a suitable coolant, such as water. The cooled grease emerges from heat exchanger 32, wherein it is rapidly cooled (quenched) by contact with a relatively cool recycle dilute soap—oil stream from line 21 to some temperature, T2, in the neighborhood of 330—340° F., about 45° F. below temperature T1.

While the soap—oil admixture is quenched within line 19, work is being performed upon it by forcing it through a shearing device 25, such as a plug cock. Although any number of shearing devices are suitable, a plug cock is selected because of its simplicity, flexibility, low cost, etc. Furthermore, by adjusting the size of the opening in the plug cock a wide range of pressure drop, ΔP, across the same is possible. A relatively large portion of the quenched, sheared soap—oil admixture at a temperature T2 is withdrawn via line 16 by line 24 which leads to a high pressure positive displacement type pump 26, such as a gear pump which supplies the major portion of the energy required to accomplish the shearing within plug cock 29 and also the recycling of the soap—oil mixture via line 21. The temperature T3 is maintained and controlled by injection from line 20 into line 21 of oil, for example, a 750 SSU at 100° F. pale oil, such as is used to prepare the initial slurry concentrate. The injection oil in line 25 is supplied thereto via line 23 from a high pressure positive displacement type pump 29; the oil is heated by passing through heat exchanger 30 wherein the temperature of the injection oil emerging therefrom is maintained and/or controlled by suitable temperature control devices actuated by a selected temperature T5 in line 19 to control the amount of heat exchange fluid entering and leaving said heat exchanger 30 via lines 31 and 33, respectively.

A portion of the quenched, sheared soap—oil admixture from line 18 passes into a high capacity forced—film type of heat exchanger (Votator type) 32 which is supplied with a suitable coolant, such as water. The cooled grease emerges from heat exchanger 32 at some reduced temperature, for instance, in the neighborhood of 100° F., and is ready for packaging or for any other processing which may be desired.
fect upon the finished grease were considered and determined:

1. Temperature, \( T_1 \), to which the slurry-concentrate was heated in the heating-Votator.
2. Temperature, \( T_s \), of the quenched-sheared soap-oil admixture after passing through plug cock.
3. Pressure drop \( \Delta P \) across the recycle pump which is the sum of the pressure drop, \( \Delta P_s \), across the plug valve plus the pressure drop, \( \Delta P_i \), in the recycle line, excluding the plug valve.
4. Recycle ratio, i.e., weight ratio of soap-oil admixture passing through recycle pump to weight of grease taken off as product per unit of time.

**Effect of concentrate temperature, \( T_1 \)**

The temperature \( T_1 \) to which the concentrate was heated in the heating-Votator varied between 300° and 420° F. while the recycle stream temperature \( T_2 \) was maintained at 325° F. and the pressure drop \( \Delta P \) across the recycle pump, and the recycle ratio, \( R \), were maintained at 50 p. s. i. and 15.5, respectively. A number of runs were made under the above conditions and the consistencies (penetration) of the resulting greases were determined. The results of these tests are graphically presented in Figure II.

Figure II is a graphical presentation of the influence of final soap-oil temperature, \( T_1 \), (before quenching and shearing) upon consistency of a lithium 12-hydroxydecanoate mineral oil un-homogenized grease as evidenced by penetration values of the finished grease. As can be seen from Figure II, the temperature \( T_1 \) for maximum "yield" (i.e., high "yield" is represented by a grease having a low penetration for a given amount of gelling agent therein) is about 380° F. whereas "yield" rapidly decreases as the temperature \( T_1 \) is increased or decreased beyond this value.

The physical significance of this temperature (380° F.) can be readily understood from the results of a differential thermal analysis of the subject lithium hydroxydecanoate grease. Thermal analysis studies indicate the presence of two transition temperatures; the lower temperature, about 330° F., can be considered as the "frozen" temperature and the higher temperature, about 380° F., can be considered as the solution temperature.

Within this transition range heating causes loosening of the soap structure and increasing solubility. Substantially complete solution occurs at the solution temperature.

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 two 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 a substantial amount of the gelling agent therein is present as molecular aggregates (crystal nuclei) or at least discrete molecules approximating colloidal dimensions in size. Solution 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.

As indicated hereinafter, the state of aggregation materially affects the physical properties of the grease, thus any difference in the dispersion of the soap fibers contained therein will correspondingly affect the yield. Accordingly, as \( T_1 \) approaches 380° F., the soap fiber bundles more easily disrupted and dismembered for a given amount of shearing, a higher degree of dispersion with accompanying increase in "yield" results.

When \( T_1 \) is 380° F., a large portion of the soap fibers break down, disappear and dissolve (depending upon the residence time in the heating-Votator) leaving a multitude of molecular aggregates (crystal nuclei) as sites for recrystallization. Recrystallization takes place when the relatively hot soap-oil admixture originating from the heating-Votator is rapidly cooled (quenched) by admixture with the relatively cold recycle stream, causing a high degree of supersaturation which in turn causes the formation of many fine soap crystals (fibers) which can be easily dispersed by working.

When \( T_1 \) is greater than 380° F., especially greater than 380° F. (the solution temperature), the molecular aggregates (crystal nuclei) are destroyed, decreasing the number of crystallization sites and thereby causing an increase in the particle size of the soap fibers upon quenching. Since large coarse fibers are not conducive to high "yields," therefore, as a general rule, increasing \( T_1 \) above the solution temperature for its system results in a decreasing "yield." This effect, however, may be minimized by increasing the shearing stress or work performed upon the quenched grease.

However, it has been found, for example, in batch experiments, that if \( T_1 \) is increased beyond the solution temperature for its particular system, an excellent grease of high "yield" may still be obtained by addition thereto immediately prior to quenching of a small amount of preferred grease or soap to supply the crystal sites needed for recrystallization of the fine soap crystals (fibers). It is also possible for the recycle stream, the quenching agent in the hereinafter-described continuous process, to act as a "seeding agent" to supply the crystal sites.

The solution temperature of a gelling agent in liquid carrier varies with the type of gelling agent and liquid carrier employed (usually a liquid organic compound such as mineral oil). Thus, the solution temperature of lithium 12-hydroxydecanoate in a mineral oil varies according to the viscosity and/or average molecular weight of the mineral oil, solution temperature increasing with increasing viscosity. The data in Table I illustrate the effect of increasing mineral oil viscosity on the solution temperature of lithium 12-hydroxydecanoate therein. The mineral oil in each case was a refined solvent extracted raffinate fraction.

**TABLE I**

<table>
<thead>
<tr>
<th>Viscosity SS at 100° F.</th>
<th>Solution Temperature, ° F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>375</td>
</tr>
<tr>
<td>170</td>
<td>385</td>
</tr>
<tr>
<td>490</td>
<td>388</td>
</tr>
<tr>
<td>750</td>
<td>385</td>
</tr>
<tr>
<td>1,500</td>
<td>388</td>
</tr>
<tr>
<td>3,599</td>
<td></td>
</tr>
</tbody>
</table>

Additionally, in order to determine the effect of the upstream-downstream temperature gradient of the grease on passing through the cooling-Votator, a sample of grease was withdrawn after
quenching and shearing but before the rapid chilling in the cooling-Votator, and permitted to cool slowly. Upon comparison of this grease with another grease sample which had been chilled in the cooling-Votator, no appreciable difference could be found. Also, a slurry soap-oil concentrate containing a greater percentage of weight lithium 12-hydroxystearate soap in mineral oil was easily processed and no significant difference could be discerned in the finished product.

**Effect of recycle temperature $T_s$**

In order to determine the effect of recycle temperature upon the consistency (penetration) of the grease, a number of experiments was performed wherein the temperature $T_s$ of the quenched-sheared grease was varied between 365° and 340° F., while the temperature $T_i$ of the soap-oil suspension upon emergence from the heating-Votator was maintained at 380° F. and the pressure drop $\Delta P$ across the recycle pump and the grease recycle ratio $R$ were maintained at 50 p.s.i. and 19.5, respectively. The results of these experiments are presented graphically in Figure III.

Figure III is a graphical presentation of the influence of the recycle temperature $T_s$ (grease temperature after being quenched and worked) upon consistency of the grease, as evidenced by the penetration values obtained.

The influence of recycle temperature $T_s$ upon the physical properties of the finished grease is complicated by two variables which are dependent on the recycle temperature, viz.: (a) the temperature at which the grease is worked (sheared) and (b) the quencher temperature differential (i.e., $T_i$ minus $T_s$) which controls the fiber size of the soap in the finished grease.

From the standpoint of (a) a maximum temperature differential is desirable, as pointed out hereinbefore, but from the standpoint of the consideration (a), shearing at temperatures below the "frozen" point requires a considerably greater expenditure of energy to achieve a given state of aggregation. Thus, Figure III indicates that shearing below 320° F. has a more deleterious effect on the "yield" than is gained from the higher degree of superstabilization and the accompanying increased rate of cooling.

Conversely, above 340° F. the quencher temperature differential diminishes, leading to greater soap fiber size and/or coarser grease. This, in addition to the possibility of soap fiber (crystal) reaggregation upon leaving the recycle line, leads to a poorer "yield." A relationship between optimum recycle temperature corresponding to maximum yield and the temperature (frozen) transition is thus indicated, the optimum recycle temperature, $T_s$, being 335° F.

A suitable method of reducing the amount of aggregation after quenching is to quench a more dilute soap-oil concentrate.

**Effect of shearing (working)**

In order to determine the effect of shearing upon the consistency (penetration) of the grease a number of experiments was performed wherein the temperatures $T_i$ and $T_s$ were maintained at 385° F. and 325° F., respectively, and the recycle ratio $R$ and the pressure drop $\Delta P$ across the recycle pump were varied over a rather wide range of values. The above conditions were obtained by adjusting the valve core and by the use of a variable speed drive on the recycle pump (gear pump). The results of these experiments are graphically presented in Figures IV and V.

Figure IV is a graphical presentation of the relationship between the pressure drop $\Delta P$ across the plug cock and the recycle ratio $R$ with respect to various soap-oil concentrate containing a lithium 12-hydroxystearate grease. Figure V is a graphical presentation of the relationship between consistency (penetration) of a lithium 12-hydroxystearate grease and the amount of shearing (work) performed thereupon.

Referring now to Figure V wherein are plotted lines of constant penetration, the family of curves indicates some relationship to the laws of constant energy input, i.e., the product of recycle ratio and the pressure drop across the plug valve. Expressing the above in terms of unit rate of feed gives units of power per unit rate of finished grease output or, if time is cancelled from the expression, in work per unit mass of finished grease (W/m).

Referring now to Figure V, the best correlation between shearing work performed per unit mass of finished grease (W/m) and consistency (penetration) is obtained when the pressure drop employed to determine the rate of energy expended in shearing the grease is taken as the sum of pressure drop across the plug valve (\(\Delta P\)) plus one-tenth (0.1) of the value of the recycle line pressure drop $\Delta P$, excluding the plug valve. This relationship is shown in Figure V using the log scale for the value of W/m merely for convenience of illustration. As indicated by Figure V, the degree of shearing should be at least about 4000 ft. pounds per pound of finished grease, while the optimum amount of shearing is in the neighborhood of about 4500 ft. lbs. per lb. of finished grease, preferably about 6,500 ft. lbs. of work per lb. of finished grease.

Since only a small portion of the work expended on the grease results in an increase in potential energy, the rest going to thermal energy, the method and/or means of expending this energy may be of importance. Thus, as indicated by Figure V, the energy absorbed by line friction is only one-tenth (0.1) as effective in hardening the grease as the energy expended in shearing the grease through the plug cock.

All the above experiments were performed in a continuous process in accordance with the preferred practice of the invention. That is, forming a slurry of gelling agent and liquid lubricant carrier and continuously heating said slurry to solution temperature, adding additional liquid carrier, if required, to bring the components thereof to desired proportions, and continuously shearing, recycling and cooling to produce a finished grease. It is also possible to adapt the process of the invention to the so-called batch-type operation. In this type of batch operation an amount of gelling agent and liquid carrier therefor is heated to solution temperature $T_i$ in a kettle. The resulting solution is then drawn off and enters a recycle line where it is cooled to the quenched temperature $T_s$ by the addition of liquid carrier thereto and sheared, as by passing through a plug cock, drawing a portion as product and recycling the remainder. If preferred, instead of adding the remaining liquid carrier required to bring the soap content of the finished grease to the desired value, a mixture containing gelling agent and liquid carrier in the proportions to be found in the finished grease may be prepared in the solution kettle.
and quenching accomplished by means of a heat exchanger while shearing.

In the above-described modified batch-type process the effect of Ti and Ts on consistency displayed the same trends as were found in the continuous process. In general, the yields obtained were inferior to those from the continuous process at solution temperature in the solution kettle for a prolonged period, resulting in complete solution of the soap and the destruction of the crystallization sites (molecular aggregates for crystal nuclei). Higher yields, however, were obtained by this modified batch process over the conventional batch process, i.e., less soap was required to achieve a given penetration value.

Tabulated data below show the advantages of the preferred continuous process over the batch process. Greases, specifically lithium 12-hydroxy steareic mineral oil greases, manufactured according to the continuous process of the invention require less soap, usually about 1% to about 2% by weight of the total grease composition, to achieve a given penetration value as compared with a similar grease manufactured by the batch process. This result is in a saving of about 25% of the soap required.

<table>
<thead>
<tr>
<th>Soap, Percent Wt.</th>
<th>Batch</th>
<th>Continuous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration</td>
<td>4.0</td>
<td>7.8</td>
</tr>
<tr>
<td>Separated, 90 strokes</td>
<td>285</td>
<td>395</td>
</tr>
<tr>
<td>Homogenized, 60 strokes</td>
<td>290</td>
<td>290</td>
</tr>
</tbody>
</table>

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-hydroxy steareic as the gelling agent (soap), the invention is applicable to other combinations of soaps, or mixtures thereof, and oils. The invention, exemplified by its application to a lithium hydroxy steareic-mineral oil grease, was not intended to be limited thereby but has been fully described therewith as illustrative of the advantages to be achieved.

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 having from 10 to 32 carbon atoms and may be saturated, unsaturated or polar substituted fatty acids, such as capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, myristoleic, oleic, linoleic, ricinoleic, erucic 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; acids produced by oxidation of petroleum oil and waxes, rosin acids, tall oil acids, abiatic acids, including dihydroarotic acid and dihydroarotic acid; naphthenic acids, petroleum sulfonic acids and the like.

A particularly preferred class of saponifiable materials is the group of fatty acids and their glycerides, such as dimethyl hydroxy fatty acids, dimethyl hydroxy fatty acids, dimethyl hydroxy capries, dimethyl hydroxy重回oleic acid, ricinoleic acid, ricinoleic acid, 12-hydroxy steareic acid, 9,10-dihydroxy steareic acid, 4-hydroxy palmitic acid, linoleic acid, lauric acid, linolenic acid, acid, dihydroxy acid, dicyclohydroxy 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 20 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 holding the glicerides can be used such as castor oil or hydrogenated castor oil or mixtures of free hydroxy fatty acids and their glicerides 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 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 hydroxy stearate, lithium ricinoleate, lithium soap of hydrogenated fish-oil fatty acids, lithium soap of mixed stearic and hydroxy stearic acid, sodium stearate, sodium hydroxy stearate, sodium oleate, potassium oleate, potassium ricinoleate, calcium stearate, calcium hydroxy stearate, barium stearate, barium soap of mixed stearic and hydroxy stearic acid, lithium soap of mixed oleic and hydroxy stearic acid, sodium soap of mixed stearic and hydroxy stearic acid; barium soap of mixed stearic and oleic acid, lead ricinoleate; mixed soaps of lithium stearate and sodium stearate; mixed soaps of lithium hydroxy stearate and sodium stearate; mixed soaps of lithium hydroxy stearate 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, e.g., silicas 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 and may be as high as 50% or more. 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 8% to 8% by weight on 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 SUS at 140° F. to about 2000 SUS at 100° F. The viscosity index of the oil can vary from below zero to about 50 or higher and can have an average molecular weight ranging from about 250 to about 600. It may be highly refined and solvent treated if desired by known means. A preferred mineral oil is that which has a viscosity of 300 to 700 SUS 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 lubrificants may be substituted in part or wholly for the mineral oil. Among the synthetic lubricants which can be used are: polymeric olefins; polyalkylene glycols and
2,652,866 their partial or complete ethers and esters; or ganic esters, e.g., 2-ethyl-hexyl sebacate, dioctyl phthalate, tri-ethylhexyl phosphate; polymeric tetrahydrofuran; polyalkyl silicone polymers, e.g., dimethyl silicone polymers; alkylated aromatic materials such as waxy naphthenalene, 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 com positions of this invention.

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

$$\text{HO} \left(\begin{array}{c} \text{CH}_2 \text{CH}_2 \text{O} \\ \text{C}_n \text{H}_{2n+1} \end{array}\right) \text{OH}$$

wherein \(n\) and \(\alpha\) are the same or different integers in a given molecule and \(\alpha\) is an integer. Preferably the polymeric alkylene glycols as represented by the above general formula should be such that the product of the factor \(\alpha\) 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 weight.

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, may be incorporated into sodium soap greases as described above a minor amount of aluminum soap or alkali and alkaline earth metal naphthenates, acetates, hydroxybenzoate, alpha-hydroxyesterate, alpha-hydroxypropanoate, beta-hydroxypropanoate, gamma-hydroxyvalerate, Ca salt of an allylphenol- 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 paraphenylenediamine. Also effective as oxidation inhibitors are alpha or beta naphthylamine, phenyl-alpha or beta naphthylamine, alpha-alpha, beta-beta dinaphthylamine, diphenylamine, tetramethyl-diphenylmethane, petroleum alkyl phenols, and 2,4-ditettrary-butyl-6-methyl phenol.

Corrosion inhibitors which are particularly applicable with compositions of this invention are M-primary amines containing at least 6 up to 18 and more carbon atoms in the molecule such as hexylamine, octylamine, decylamine, dodecylamine, octadecylamine, heterocyclic nitrogen-containing organic compounds such as alkyl substituted oxazolines and oxazolines salts of fatty acids. Extreme pressure agents can be added to such grease and the preferred agents comprise esters of phosphorus acids such as triaryl-, alkylhydroxy-, alkyl-, alkylsulfuric acids, thiophosphates, phosphites, etc., neutral aromatic sul-

fur compounds such as diaryl sulfides and polysulfides, e.g., diphenyl sulfide, di cresol sulfide, dibenzyl sulfide, methyl butyl diphenyl sulfide, etc., diphenyl selenide and diselenide, di cresol selenide and polyselenide, etc., sulfurized fatty oils or esters of fatty acids and monohy drolic 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 phos phoric or phosphorus acids with hydroxy fatty acids, chlorinated hydrocarbons such as chlori nated 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, aliphathanes, car bazides, carbazones, etc.; or rubber, polyisobutylene, polyvinyl esters, etc.; viscosity index (V. I.) improveme rs such as polyisobutylene having a molecular weight above about 600, volatile paraffin wax, unsaturated polymerized esters of fatty acids and monohy drolic alcohols, etc.; oiliness agents such as stearic and oleic acids and pour point depressors such as chlorinated naphthenalene to further lower the pour point of the lubricant.

The amount of the 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 manufactured according to this invention are applicable for general automotive uses, and are excellent aircraft greases, industrial greases and the like.

We claim as our invention:

1. A process for the preparation of a lubricating grease which comprises heating a mixture of a lubricating oil and a gelling agent therefor to about solution temperature \(T_s\), quenching the heated mixture in a period of time less than about one minute to a lower temperature \(T_s\) between about 25° F. and 55° F. lower than said solution temperature \(T_s\); substantially all of the quenching being conducted before any substantial shearing of the mixture, and thereafter shearing said mixture at temperature \(T_s\), to form a grease, the amount of shearing performed upon said grease being at least 4,000 ft. lbs. per pound of finished grease.

2. The process of manufacturing a superior lubricating grease according to claim 1 wherein the liquid carrier lubricant is a mineral oil of lubricating viscosity.

3. The process of manufacturing a superior lubricating grease according to claim 1 wherein the gelling agent is a metal soap of a higher fatty acid.

4. The process of manufacturing a superior lubricating grease according to claim 1 wherein the gelling agent is a metal soap of a fatty acid and wherein the liquid carrier lubricant is a mineral oil of lubricating viscosity.

5. The process of manufacturing a superior lubricating grease according to claim 1 wherein the gelling agent is a lithium fatty acid soap.

6. The process of manufacturing a superior lubricating grease according to claim 1 wherein the gelling agent is lithium 12-hydroxy stearate.

7. The process of manufacturing a superior lu-
The lubricating grease according to claim 1 wherein the gelling agent is a sodium fatty acid soap.

9. A continuous process for the manufacture of a superior lubricating grease which comprises: continuously, rapidly heating an admixture of a mineral oil of lubricating viscosity and lithium 12-hydroxy stearate to about 380° F.; rapidly cooling the resulting solution to a temperature of about 330° F. by comminuting said resulting solution with a relatively cool recycle stream substantially all of said quenching being conducted before any substantial shearing of the mixture and thereafter shearing the commingled streams at about said latter temperature, the amount of shearing performed upon said commingled streams being at least about 4,000 ft. lbs. per pound mass of finished grease product; continuously withdrawing a portion of said commingled streams as product and continuously recycling and cooling the remainder of said commingled streams to provide said cool recycle stream.

10. A process for the preparation of a lubricating grease which comprises heating a mixture of a mineral lubricating oil and a grease-forming amount of lithium hydroxystearate to a temperature between the minimum solution temperature and about 3° F., at least the period of heating above about 265° F., being carried out in a forced film heat exchanger, quenching in a period of time less than about one minute to a temperature between about 45° F. and 55° F. below said solution temperature, substantially all of the quenching being conducted before any substantial shearing of the mixture, and thereafter shearing said mixture at about said temperature, the amount of shearing performed upon the grease so formed being at least 4,000 ft. lbs. per pound of finished grease.

11. A process according to claim 9 wherein the lithium hydroxystearate is lithium 12-hydroxy stearate.

12. A grease-forming process which comprises heating a mineral lubricating oil having a viscosity of between 100 and 1500 SSU at 100° F. and a gelling amount of lithium 12-hydroxy stearate to a temperature between the minimum solution temperature and about 5° F. therebelow, quenching said grease in a period of time less than about one minute to a temperature between about 45° F. and about 55° F. below said solution temperature, substantially all of the quenching being conducted before any substantial shearing of the mixture, by the addition of mineral oil to said mixture, and shearing the soap and oil to a grease structure at about said latter temperature, the amount of thereafter shearing performed upon said grease being between 4500 and 8000 ft. lbs. per pound of finished grease.

13. A grease-forming process which comprises rapidly heating a mixture of a lubricating oil and a gelling proportion of a grease-forming soap to a temperature between the minimum solution temperature and 5° F. therebelow; quenching said mixture to a temperature between about 25° F. and about 55° F. below said solution temperature by comminuting the mixture with a relatively cool recycle stream and added lubricating oil, substantially all of the quenching being carried out with substantially no shearing, and thereafter shearing the commingled mixture at about the minimum quench temperature, the amount of shearing performed on said commingled mixture being at least about 4,000 ft. lbs. per pound of finished grease product, withdrawing a portion of said product and cooling and recycling it to provide said cool recycle stream.

14. A grease-forming process which comprises rapidly heating a mixture of mineral lubricating oil having a viscosity of about 750 SSU at 100° F. and a gelling proportion of lithium-12-hydroxy stearate to a solution temperature of about 380° F., quenching said mixture to about 335° F. by comminuting the mixture with a relatively cool recycle stream and added lubricating oil, substantially all of the quenching being carried out with substantially no shearing, and thereafter shearing the commingled mixture at about 335° F., the amount of shearing being about 8000 ft. lbs. per pound of finished grease product, withdrawing a portion of said product and cooling and recycling it to provide said cool recycle stream, the weight ratio of recycle stream to weight of finished grease being at least about 19.5.

Robert C. Jones.
Robert J. Wall.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,943,806</td>
<td>Beckert et al.</td>
<td>Jan. 16, 1934</td>
</tr>
<tr>
<td>2,450,285</td>
<td>Puryear et al.</td>
<td>Sept. 28, 1948</td>
</tr>
<tr>
<td>2,461,276</td>
<td>Hetherington</td>
<td>Feb. 6, 1949</td>
</tr>
<tr>
<td>2,478,917</td>
<td>Hain</td>
<td>Aug. 1, 1949</td>
</tr>
<tr>
<td>2,480,847</td>
<td>Grud et al.</td>
<td>Aug. 30, 1949</td>
</tr>
<tr>
<td>2,483,282</td>
<td>Houton</td>
<td>Sept. 27, 1949</td>
</tr>
<tr>
<td>2,497,133</td>
<td>Morway et al.</td>
<td>Feb. 14, 1950</td>
</tr>
<tr>
<td>2,542,159</td>
<td>Stevens</td>
<td>Feb. 20, 1951</td>
</tr>
<tr>
<td>2,588,154</td>
<td>Bailey et al.</td>
<td>May 27, 1952</td>
</tr>
</tbody>
</table>