METHOD OF PREPARING MIXED-SALT CONTAINING LUBRICANTS

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This invention relates to an improved process for preparing mixed-salt containing lubricants. Particularly, this invention relates to an improved method of preparing lubricating compositions containing metal salts of intermediate and/or high molecular weight carboxylic acids with metal salts of low molecular weight fatty acids.

Lubricants containing the mixed-salts of high and/or intermediate molecular weight fatty acids with salts of low molecular weight fatty acids have been finding increasing applications in industry because of their excellent load-carrying and anti-wear properties. For example, fluid lubricants of this type have been found to be particularly useful in the lubrication of the upper cylinders of marine diesel engines; whereas the solid grease type lubricants are useful for a variety of industrial applications. Previously, this type of lubricant had been commercially prepared by neutralizing with a metal base, an oil dispersion of the low molecular weight fatty acid and the higher fatty acids. However, lubricants prepared by simple mixing and heating of the components, using lime as the metal base and acetic acid as the low molecular weight acid, contain an undesirable abrasive grit. The use of anhydrous calcium barium hydroxide, strontium hydroxide or magnesium hydroxide with acetic acid can also result in grit formation. Several methods have been suggested for overcoming the grit problem. For example one method is by highly agitating an oil-lime-higher fatty acid slurry as the acetic acid is added; another is by circulating the oils in a higher fatty acid slurry and then very slowly adding the acetic acid. However, a new method of forming these lubricants has been found, which does not require a high degree of agitation or circulating equipment, in order to form grit-free lubricants. In this new method acetic anhydride is utilized in place of acetic acid. Furthermore, by using acetic anhydride, a much simpler process for forming the lubricant may be employed because of the higher heat of reaction of the acetic anhydride as compared to the acetic acid and also because of the lesser amount of water that is formed during the reaction. Also, the acetic anhydride forms a superior fluid lubricant in that it has a lower viscosity for the same ash content. Similar lubricants may be prepared by using the anhydrides of acrylic acid and propionic acid, which will have many of the advantages of the acetic anhydride.

The compositions of the lubricant will comprise lubricating oil and about 4 to 30, e.g. 8 to 24, weight percent of the mixed-salt material. When a grease is desired, generally about 12 to 24 weight percent of the total composition will be the mixed-salt, while 8 to 16 weight percent of the mixed-salt material will be generally present in fluid type lubricants. The mixed-salt in turn will comprise in a molar ratio about 5 to 40, e.g. 5 to 12 moles of alkaline earth metal salt of a C10 to C26 fatty acid anhydride per mole of alkaline earth metal salt of the higher fatty acids. The higher fatty acids may consist entirely of intermediate molecular weight fatty acid or entirely of high molecular weight fatty acid or blends of these two types of fatty acids in any proportion. The fluid lubricants are best prepared by heating the mixed-salt material to temperatures of about 300 to 350° F., while the greases are best prepared by heating to about 430 to 700° F., where true complexing occurs. However, the fluid lubricants can also be prepared at these higher temperatures, i.e. 450° F. and above, while the greases may also be prepared at the lower temperatures, i.e. less than 430° F.

The high molecular weight carboxylic acids contemplated in this invention include the saturated and unsaturated grease-making fatty acids that are commonly known in the art. In general, these fatty acids have from 12 to about 30 carbon atoms, preferably about 14 to 22 carbon atoms per molecule, having saponification values of from about 300 to 150. Suitable fatty acids include myristic acid, palmitic acid, stearic acid, the various hydroxy stearic acids, oleic acid, arachidic acid, behenic acid and the like. Naturally occurring fatty acids such as fish oil acids, tallow acid, etc. may also be utilized directly or after hydrogenation to decrease, or desirably high degree of unsaturation. Mixtures of these high molecular weight fatty acids, e.g. hydrogenated fish oil acids with oleic acid, in any proportions, are also operable, as are fractions obtained by distillation, extraction or crystallization.

Intermediate molecular weight fatty acids operable for the salt formation include those aliphatic, saturated or unsaturated, unsaturated, monokarboxylic acids containing 7 to 12 carbon atoms per molecule, e.g. capric, caprylic, nonanoic acids, etc.

The metal components of the mixed-salt thickeners of this invention may be an alkaline earth metal such as calcium, strontium, barium and magnesium. Mixtures of the grease-forming metals may be employed if desired. The metals are usually reacted with the acids in the form of metal bases, such as hydroxides or oxides. Calcium is preferred.

The lubricating oil used in the compositions of the invention may be either a mineral lubricating oil, or a synthetic lubricating oil, or both. Synthetic lubricating oils which may be used include esters of monobasic acids (e.g. C10 Oxo alcohol esters of C18 Oxo acid), esters of dibasic acids (e.g. diethyl benzyl sebacate), esters of glycols (e.g. C12 Oxo acid diester of tetraethylene glycol), complex esters, esters of phosphoric acid, halocarbon oils, sulfite esters, silicone oils, carbonates, polyglycol-type synthetic oils, etc., or any mixture thereof.

Various other additives may also be added to the lubricating composition in amounts of about 0.1 to 10.0 weight percent, based on the total weight of the composition. For example, detergents such as calcium petroleum sulfonate; oxidation inhibitors such as phenyl alpha naphthylamine; corrosion inhibitors such as sorbitan monooleate; pour depressants; dyes; other grease thickeners and the like may be added.

The fluid lubricant compositions of this invention can be prepared by blending together the higher fatty acid (or the preformed higher fatty acid salt) and anhydride. A neutralizing amount of the dry metal base is dispersed in a portion of the lubricating oil to form a slurry which may be slightly warmed to a temperature of about 90 to 120° F. The mixed acids are then added to the slurry. Alternatively, the higher fatty acid may be incorporated in the metal base-oil slurry and then the acid anhydride is added. In either case, the heat of reaction will usually be sufficient such that a finishing temperature is reached, say about 300 to 350° F., e.g. 310 to 340° F. This method may be conducted batchwise or preferably in continuous equipment.

The compositions for solid high temperature greases can best be prepared in pressure equipment. Here, both
the acid anhydride and the slurried metal base portion are separately preheated to temperatures of about 200 to 325°F. e.g., 200 to 350°F. External heating may be applied, but generally will not be necessary due to the heat of reaction of the acid anhydride with the metal base. In this way, considerable mixed-salt thickeners requiring high temperatures can be formed without the use of the more costly fire heated, Dowtherm heated, or other high temperature kettles. Formation of the thickeners in a pressure system is particularly preferred, as it conserves heat and retins the water of reaction as steam which aids in obtaining a more complete reaction.

After the completion of the reaction, additional oil, if any, is added along with any additive material. The mixture may then be homogenized by passing through a Gaulin homogenizer or a Charlotte mill, followed by subsequent cooling to room temperature. However, while a batch or open kettle system may be used in preparing either the fluid or grease lubricants, the acid anhydride composition adapts itself well to a simple continuous or semi-continuous pressure system which can be carried out as follows:

Recalling, referring to the drawing, which represents a preferred method of carrying out the invention, the metal base and a portion of the lubricating oil (for example, one-third to one-sixth of the total oil used) are slurried together and heated to about 200 to 325°F. in a mixer 10. This slurry can be pumped through line 11 at a measured rate through a metering pump 12, to a mixer 13 (e.g., a centrifugal pump). At the same time, a measured rate of acid anhydride is pumped from the storage tank 14 through the line 15 by means of the pump 16 into the mixer 13, where the two streams are intimately mingled and the reaction begins. The resulting mixture may then pass through the line 17 into the bottom of a pressure reactor 18 which holds the mixture for about 1 to 10 minutes and will operate at temperatures of about 300 and higher (about 435 to 580°F. when greases are made), the heat being supplied by the reaction of the acid anhydride with the metal base, and the exact temperature depending on the proportion of ingredients and the amount of oil used. The reaction product is drawn off from the top of the reactor 18 through line 19. Additional lubricating oil, which may also contain additive materials, supplied from the storage tank 20 by means of the pump 21, also passes into the line 19 to dilute the above-mentioned reaction mixture. This diluted mixture then passes through the control valve 22 in the line 19 into a dehydrator 23, such as a Cornell homogenizer, or other vacuum chamber where the grease is subjected to vacuums of about 15 to 29 inches of mercury, such that the water is flashed off as steam. The grease then passes out of the dehydrator 23, through line 24 and is ready for packaging or further finishing. A pump is usually required to lift the grease out of the vacuum, although the Cornell homogenizer does this by centrifugal force. The invention will be further understood by the following examples which include preferred embodiments of the invention.

EXAMPLE I(A)

A base composition was prepared as follows: 30 grams of dry hydrated lime (i.e., Ca(OH)\(_2\)); 10 grams of hydrogenated fish oil acids having an iodine value of 2.0 and 10 grams of hydrogenated castor oil comprising the glycerides of 12-hydroxystearic acid and having an iodine value of 3.5; were dissolved in about 68 grams of a mineral oil having a viscosity of about 600 SUS at 100°F. This mixture was heated up to 220°F. to dissolve the acids, then cooled and 342 grams of the same oil were added. 40 grams of acetic acid were then mixed into the base composition and the temperature increase due to the heat of reaction was measured. Upon cooling the material was inspected.

EXAMPLE I(B)

Example I(A) was repeated except that 35.3 grams of acetic anhydride were used in place of the 40 grams of acetic acid.

Results of these tests are summarized in the following table.

<table>
<thead>
<tr>
<th>Example</th>
<th>I(A)</th>
<th>I(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams of Base</td>
<td>460</td>
<td>460</td>
</tr>
<tr>
<td>Grams of Acetic Acid</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>Temperature Rise</td>
<td>60°F</td>
<td>63.3°F</td>
</tr>
<tr>
<td>Condition at End</td>
<td>35°F</td>
<td>35°F</td>
</tr>
<tr>
<td>Smoothness</td>
<td>Slightly Gritty</td>
<td>Slightly Grit-Free</td>
</tr>
</tbody>
</table>

As seen from the above examples, the acetic anhydride formed a grit-free lubricant while the acetic acid formed grit. The gel of Example I(A) was due to a high water content of 2.4%, while Example I(B) with 1.2% water was already half dehydrated and correspondingly fluid. The difference of 43°F. in temperature rise indicates the amount of cooking time to be saved in an open batch process, to which may be added the time saved by not having to evaporate 1.2% of water.

However, the greatest savings are gained in the formation of lubricants containing a mixed-salt complex formed at above 435°F. particularly in the process, which process may be either batch or continuous. Using acetic anhydride as an example, if the initial mixture containing one-sixth of the oil is reacted, the temperature increase due to the heat of reaction becomes 335°F. At an initial temperature of 220°F. of the oil-fatty acid-acetic anhydride slurry, the resulting reaction mixture (after addition of dry Ca(OH)\(_2\)) has a temperature of 255°F., well above the minimum of 435°F. for complex formation. On the other hand, acetic acid will yield a final temperature of only 430°F. under these conditions. By thus using acetic anhydride, the entire operation then becomes self-cooking except for the initial preparation of the base at 220°F., which requires only exhaust steam heat thereby avoiding the use of fire, electric or Dowtherm heat. After this, water may be removed and the batch cooled by bleeding off steam, before or after oiling with the remaining five-sixths of the oil.

The following example illustrates both a continuous system of forming the mixed-salt concentrate, and the use of the acetic anhydride in forming a fluid type lubricant.

EXAMPLE II

An acid feed at 77°F. consisting of 3000 grams (78 weight percent) of acetic anhydride and 860 grams (22 weight percent) of Wecoline AAC acid (28 weight percent caprylic, 56 weight percent capric, and 16 weight percent lauric acid) was fed under pressure at the rate of 21 grams a minute into a mixer (a Gould centrifugal pump with a three inch open rotor operating at 1750 r.p.m.). Simultaneously, a slurry feed (77°F.) consisting of 2,625 grams (20 weight percent dry hydrated lime and 10,500 grams (80 weight percent) mineral lubricating oil having a viscosity of 80 SUS at 210°F. was also fed under pressure into the mixer at an average rate of 71.4 grams per minute. Flow through the centrifugal pump was the reverse of normal so as to maximize throughput. The outlet ranged from 305°F. and 357°F. and averaged about 327°F. The product issued from the mixer through a pressure control valve set at 80 p.s.i.g., which
permitted flashing most of the water of reaction into steam. A temperature rise of up to 280° F. was due to the heat of reaction, except for a small amount of heat due to mixing energy. Approximately 4.9 grams of water per minute were thus flashed off, leaving an output of 86.5 grams per minute of the remaining reaction mixture. This nearly dry reaction product was then passed into a steam kettle and accumulated. When all the reaction product had accumulated in the kettle, it was then heated to 250° F. for about 4 hours to reduce the water content from 0.6 to 0.4 weight percent after which a total of 67,067 additional grams of oil were added along with 135 grams of phenyl alpha naphthylamine to form the finished lubricant. The product was then milled twice by passing through an ND-1 Charlotte mill and finally cooled to room temperature.

The above experiment was repeated using acetic acid in place of the acetic anhydride (the number of moles of acetic acid being used being equal to the number of moles of acetic anhydride originally used). The critical results of this experiment are summarized in Table II which follows.

<table>
<thead>
<tr>
<th>Table II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Anhydride</td>
</tr>
<tr>
<td>Mixx Outlet Temperature, °F.:</td>
</tr>
<tr>
<td>Maximum</td>
</tr>
<tr>
<td>Average</td>
</tr>
<tr>
<td>Viscosity at 100° F., SSU</td>
</tr>
<tr>
<td>Viscosity at 210° F., SSU</td>
</tr>
<tr>
<td>Sediment by Centrifuge (4 Hrs.) @ 1500 r.p.m.</td>
</tr>
<tr>
<td>%</td>
</tr>
<tr>
<td>Free Alkalinity as NaOH</td>
</tr>
<tr>
<td>Water Content</td>
</tr>
</tbody>
</table>

As seen from the above table, the use of the acetic anhydride gave a much larger temperature rise in the mixer (i.e. reactor), thus substantially reducing the time and amount of heat required in the steam kettle to obtain the desired degree of dehydration. Also, the use of the acetic anhydride resulted in a more fluid lubricant having a lower viscosity and yet having the same metal content as that prepared from the acetic acid.

What is claimed is:

1. A method of preparing a lubricating oil composition containing 4 to 30 weight percent of a mixed-salt material comprising alkaline earth metal salt of a C6 to C30 fatty acid and alkaline earth metal salt of a C2 to C4 fatty acid, in a molar ratio of about 5 to 40 moles of said C6 to C30 fatty acid salt per mole of said C2 to C4 fatty acid salt, which comprises, reacting with an alkaline earth metal base in a lubricating oil menstrum, said C6 to C30 fatty acid and a C2 to C4 fatty acid anhydride.

2. A method according to claim 1, wherein said reaction mixture is heated to temperatures of about 300° F. to 700° F.

3. A method according to claim 1, wherein said fatty acid anhydride is acetic acid anhydride.

4. A method according to claim 3, wherein said alkaline earth metal is calcium.

5. A method of forming a fluid lubricant comprising lubricating oil and about 8 to 16 weight percent of a mixed-salt material comprising alkaline earth metal salt of a C7 to C30 fatty acid and alkaline earth metal salt of a C2 to C4 fatty acid, in a molar ratio of about 5 to 40 moles of said C7 to C30 fatty acid salt per mole of said C2 to C4 fatty acid salt, which comprises forming a slurry of a portion of the lubricating oil, alkaline earth metal base, and a material selected from the group consisting of C7 to C30 fatty acid and alkaline earth metal salt of C7 to C30 fatty acid, mixing a C2 to C4 fatty acid anhydride into said slurry, the proportion of lubricating oil and other ingredients being such that a finishing temperature of about 300 to 350° F. is obtained by the heat of reaction, adding the remainder of said oil and then cooling to form said lubricant.

6. A method according to claim 5, wherein said alkaline earth metal is calcium, and said acid anhydride is acetic acid anhydride.

7. A method of forming a lubricating oil containing 4 to 30 weight percent of a mixed-salt material comprising alkaline earth metal salt of a C7 to C30 fatty acid and alkaline earth metal salt of a C2 to C4 fatty acid, in a molar ratio of about 5 to 40 moles of said C7 to C30 fatty acid salt per mole of said C2 to C4 fatty acid salt, which comprises forming a slurry of: about one-third to one-sixth of the lubricating oil, the C7 to C30 fatty acid and an alkaline earth metal base; preheating said slurry to about 200 to 325° F., mixing with said preheated slurry a C2 to C4 fatty acid anhydride whereby the heat of reaction raises the temperature of the reaction mixture to 430° F. to 700° F., adding the remainder of the lubricating oil and dehydrating to form said lubricant.

8. A method according to claim 7, wherein said reaction is carried out in a pressure system.

9. A method according to claim 7, wherein said lubricating oil is mineral oil.

10. A method according to claim 9, wherein said alkaline earth metal is calcium, and said fatty acid anhydride is acetic acid anhydride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,417,428 McLennan Mar. 18, 1947
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,909,485

Alan Beerbower et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 52, for "C₆" read -- C₇ --.

Signed and sealed this 25th day of April 1961.

(SEAL)
Attest:
ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents