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HIGH-TEMPERATURE LUBRICATING
GREASE MANUFACTURE

Arnold J. Morway, Clark, and John J. Kolfenbach, Somerville, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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The present invention relates to the manufacture of high temperature lubricating greases and relates particularly to a manufacturing process by which a product of superior properties is obtained through a process which includes, among other things, an application of the Cannizzaro reaction to certain organic aldehydes such as furfural and related materials. The present application is a continuation-in-part of application Serial No. 60,615 filed November 17, 1948, now Patent No. 2,516,137.

In the above-mentioned patent application, there is described in some detail a process for converting furfural or other aldehydes to the corresponding alkali metal salts and alcohols through the well-known Cannizzaro reaction. In general, the salts so obtained remain in the grease and combine with the normal soap of long chain fatty acids to thicken the product to the desired consistency and to give it a grease structure. The salts obtained through the Cannizzaro reaction improve substantially the high temperature performance of the grease. Products so prepared have been found to have outstanding properties for the long life lubrication of anti-friction bearings and for other uses where high quality and long life performance are required. While the products described in the aforesaid application were very good, difficulties have been encountered in larger scale operations. Furfural type greases made in small laboratory batches have excellent dispersion of the complex thickener but this has been found difficult to duplicate in larger scale manufacture. Other difficulties have also been encountered.

In the manufacture of anti-friction bearings, for example ball and roller bearings, it is frequently desired by the bearing manufacturers to provide them with a lubricant which will operate satisfactorily, even at relatively high temperatures, e. g., 300° F. Furthermore, such lubrication is expected to last a long time, often as long as the bearing is expected to be in service. For such lubrication, it is, of course, essential that the product have a high degree of structure stability as well as good resistance to oxidation and to any other type of deterioration. It is desirable also that such a product be of reasonably firm consistency so that it will not readily be lost from the bearing. At the same time, it must be sufficiently soft to provide effective lubrication. Anti-friction bearing manufacturers prefer a product having an A. S. T. M. penetration ranging from 190 to 260 mm./10.

On the other hand, greases used in mechanical dispensers, as in automotive service stations and in other power operated grease handling equipment, should not be too hard in consistency. It

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is highly desirable, in such applications, to have a lubricant which is fairly soft and which feeds readily into the pressure dispenser equipment but which also hardens because of the shear to which it is subjected in the dispenser. The products of the present invention may readily be made of such soft consistency and with the self-hardening feature just referred to. The subsection of greases of the complex salt-soap, especially those in which the salt is formed in situ through the Cannizzaro reaction, to the action of vigorous or drastic homogenizing equipment such as the Manton-Gaulin homogenizer, constitutes an important aspect of this invention.

In order to prepare lubricating greases, for example soda base greases having the desired consistency, and to obtain satisfactory and complete dispersion of the salt produced in the Cannizzaro reaction, it is necessary either to cook the product to fairly high temperatures over a substantial period of time or to devise an alternative procedure by which the desired consistency may be obtained without high temperature cooking. Cooking at high temperatures involves certain hazards due to the release of volatile and relatively explosive alcohols in the Cannizzaro reaction. Standard grease manufacture equipment commonly includes steam jacketed kettles for cooking, but such kettles are limited in their temperature range to a maximum of about 340° F. due to limitation on the steam pressure employed. Such temperatures are not adequate for securing the firm and stable greases which the anti-friction bearing manufacturers require without some variation in the method of preparation.

Apparently, the consistency and structural stability of greases of this character are, at least partly, functions of the degree to which the thickeners (e. g. sodium furoate and soap) are dispersed in the lubricating oil. When high cooking temperatures, e. g. 450° to 500° F., are employed, dispersion is facilitated, but such temperatures are somewhat hazardous per se and especially where they involve the use of fire-heated kettles. In such kettles, there is always danger of heating the kettle in spots or local areas to temperatures sufficient to ignite the furfuryl alcohol or other alcohol released in the Cannizzaro reaction, with danger of explosion.

While it is possible to use special heat exchange media that permit heating greases up to 400° to 500° F. with direct fire heating, such equipment is expensive for commercial scale operations. Steam-heated kettles, with an upper temperature limit of about 340° F., because of limitations on allowable steam pressures, do not

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permit cooking with a satisfactory degree of dispersion of the soap and salt in the oil.

It is, therefore, an object of the present invention to modify the prior processes to obtain a satisfactory dispersion of soap and salt at safe temperatures which can be obtained in standard steam jacketed grease kettles.

A further feature of the present invention resides in the use of a relatively light mineral base lubricating oil for formation of a salt-soap complex concentrate, this concentrate being subsequently blended with additional oil of similar or preferably more viscous grade to obtain the desired final product. By using a light oil for the initial dispersion operations, a smoother, more homogeneous product is obtained. In general, not more than half the total oil is used for making the concentrate. The additional oil is preferably worked into the relatively dry concentrate in small increments. The grease so blended should have an A. S. T. M. penetration value of not less than about 200 and not more than about 360 mm./10, subject to further hardening (decrease in penetration value) upon vigorous mechanical homogenization.

According to the present invention, conventional steam jacketed kettles may be used notwithstanding their relatively low maximum cooking temperatures by a variation in the manner in which the ingredients are compounded, the process being supplemented by vigorously milling or homogenizing the grease product after cooking has been completed in the steam jacketed equipment.

In the present invention, fatty acids which are to be saponified, as in conventional grease manufacture, are first mixed with part of the lubricating oil, preferably a mineral base oil, in a cold kettle and thereafter a saponifying agent is added to form the soap. Instead of using theoretical quantities, a substantial excess of the saponifying agent, for example alkali metal hydroxide, is added for a purpose presently to be described. The fatty acids, which are preferably substantially saturated and which are normally within the range of 12 to 22 carbon atoms per molecule preferably averaging nearly 18, or a little more or less, are neutralized or saponified by the alkali metal hydroxide with some rise in temperature. The saponification reaction, which is exothermic, may raise the temperature from normal ambient temperature to about 100° F. more or less. This is not objectionable.

After the saponification has been completed or has progressed substantially toward completion, an aldehyde capable of undergoing the Cannizzaro reaction, and of molecular weight substantially lower than that of the fatty acids, is charged to the kettle. Thereupon, the Cannizzaro reaction takes place spontaneously resulting in the formation of the alkali metal salt which corresponds to the aldehyde and the release of the corresponding alcohol. For example, when furfural is used, which is the preferred aldehyde, sodium furoate is formed by the employment of NaOH as the saponification agent. Furfuryl alcohol is released and it remains in the composition at ordinary temperatures. As the temperature is raised in subsequent operations, the furfuryl alcohol may be largely evaporated although a small part of it may be polymerized or otherwise combined in the product and remain in the grease composition.

While the proportions of ingredients may be varied considerably, it is preferred to use 1 to 5 parts by weight of fatty acid, preferably substan-

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tially saturated, of between 12 and 22 carbon atoms per molecule, and 3 to 10, preferably 5 to 10, parts of mineral base lubricating oil of desired consistency as initial ingredients. A light oil of 35 to 50 S. S. U. viscosity at 210° F. is preferable although somewhat heavier oils may be used if necessary. These ingredients are well mixed, the saponifying base is added, preferably NaOH, and saponification proceeds without external heat but preferably with stirring.

After saponification, one-fourth to 2 parts by weight of the aldehyde are added. As pointed out in the copending parent application, Serial No. 60,615, various aldehydes, ranging from formaldehyde to the cyclic, heterocyclic and aromatic aldehydes, may be used but the cyclic aldehydes such as benzaldehyde and furfural are preferred, especially the latter and the closely related heterocyclic aldehydes.

After sufficient time has been given to substantially complete the Cannizzaro reaction, for example about one to two hours for small batches and a longer time for larger batches, the kettle is heated by passing steam through the steam jacket and the product is cooked. The temperature is first raised to about 210° F. to 230° F. for a period of time sufficient to evaporate nearly all the water of saponification and most of the alcohol which is released in the Cannizzaro reaction. After these have been substantially eliminated, the temperature rises further to about 325° to 340° F., the maximum obtainable with ordinary steam pressures available at oil refineries and the grease plants (about 125 p. s. i. steam).

In the process so far described, only a small part, for example one-fourth to one-half, of the total lubricating oil is used and a concentrated mass of soap, salt and oil is produced which becomes relatively dry and heavy. Thereafter, the remainder of the lubricating oil, of the same or of heavier viscosity, is added gradually and worked slowly into the grease. The maximum cooking temperature which the steam supply permits should be maintained during the addition and working of the residual oil, although a minor reduction in temperature is not objectionable. In the preparation of an experimental 300 pound batch, for example, the oil was added in increments of 5 pounds and each increment was thoroughly worked into the mass before more was added.

After all the oil has been added and worked into the grease as described above, it is desirable to add a conventional anti-oxidant such as phenyl alpha naphthylamine. Thereafter, the grease may be cooked a little longer, if desired, and it should then be cooled with continued mixing. This may be accomplished in the jacketed kettle by passing cold water through the jacket while stirring is continued. Conventional pan-cooling may be used but more rapid cooling is preferable.

Products prepared as above are relatively soft greases at first, having an A. S. T. M. penetration between about 300 to 350 mm./10. When such greases are milled on a paint mill or passed through a Lancaster disperser, a Manton-Gaulin homogenizer or an equivalent homogenizer, they harden considerably. The degree of hardening approximates 100 to 150 mm./10, giving a final product having the desired penetration range of about 200 mm./10.

An important aspect of the present invention is the superior dispersion of the relatively oil-insoluble salt which results from the Cannizzaro reaction. While the exact mechanism is not

clearly understood, it is believed that when the oil-soluble furfural reacts with the strong base in the presence of soap, the soap forms a protective colloid about the aldehyde salt. This prevents the formation of relatively large and poorly dispersed particles of salt. A fine dispersion results and this produces a grease of maximum consistency (low penetration number) for the quantity of soap and Cannizzaro reaction salt employed.

When viewed through a microscope, greases prepared by carrying out the Cannizzaro reaction first, or prepared by attempting to combine oil containing the salt in suspension with a grease containing soap, is seen to have relatively large brown particles of the salt. These do not adversely affect the general lubricating properties of the grease but they represent a relative waste of thickeners. Such greases lack the desirable homogeneous and transparent appearance of simple soap greases.

On the other hand, greases prepared according to the present invention are relatively free of large particles of salt or salt-soap complex. They are smooth and homogeneous in appearance. They possess the firm and stable physical structure required for long-life lubrication of anti-friction bearings.

The invention will be more fully understood by reference to the following specific example:

EXAMPLE

A lubricating grease was prepared by blending approximately equal quantities of hydrogenated fish oil acids, having approximately the average chain length of stearic acid and being substantially saturated, and mineral base lubricating oil of about 40 S. S. U. viscosity at 210° F. An excess of an aqueous solution of sodium hydroxide was added, sufficient to completely saponify the fatty acids and also to carry out the Cannizzaro reaction, to be described below. These operations were carried out at approximately room temperature although the temperature rose somewhat due to the exothermic saponification reaction.

After saponification was substantially complete, the mixture having been stirred for about one hour in the unheated grease kettle, furfural was added, about $\frac{2}{3}$ as much furfural being used as fatty acids, on a weight basis. The sodium hydroxide readily converted the furfural to sodium furoate with the release of furfuryl alcohol. This reaction proceeded without heating and the temperature of the ingredients rose somewhat above 100° F. Steam was introduced into the jacket of the kettle and the contents were heated with continued stirring to a temperature sufficient to boil off the water and to evaporate most of the alcohol. The time required varies with the size of the batch, being 4 to 6 hours for a 300 pound batch, for example.

The dried product was a stiff concentrate to which were added small increments of mineral lubricating oil of about 70-80 S. S. U. viscosity at 210° F. The total quantity of mineral oil represented about 80% of the total composition, with about 15% soap and 5% sodium furoate by weight. Stirring was continued with continued heating to raise the temperature to the maximum obtainable with the plant steam supply, about 315° to 330° F. The grease was then cooled to 110° F. by passing cold water through the kettle jacket with continued stirring.

The grease of the example showed no parti-

cles of undispersed sodium furoate upon microscopic examination although some lumps of the undispersed heavy grease, as prepared in the concentrated form, were observed. This process appears to have a distinct advantage over the prior process in the superior dispersion of sodium furoate obtained. Carrying out the Cannizzaro reaction in the presence of a soap previously formed gives a definitely superior dispersion. Upon passage of the grease of the example through a homogenizer, the lumps of heavy grease disappeared and a smooth uniform product was obtained.

Upon examination in a 100-power microscope, the product of the example showed no distinct particles whereas the product of the earlier process by steam kettle manufacture, where the Cannizzaro reaction is carried out before the soap is made in the oil, showed a large quantity of particles of 5 to 200 microns in diameter.

The grease of the example was a very soft product prior to passage through the homogenizer. It showed an initial penetration of 335 mm./10 and a penetration after 60 strokes in the A. S. T. M. grease worked of 262 mm./10. After homogenization, the grease was much harder, having a penetration value of approximately 200.

In the first pilot plant batch of grease prepared (Batch No. 1), the maximum manufacturing temperature attained was 330° F. The total batch was then cooled to 110° F. while stirring and passing cold water through the kettle jacket. The grease after this treatment was very soft (penetration of 335 mm./10 and a 60-stroke penetration of 262 mm./10). Batch No. 2 after completion of the cooking cycle (maximum temperature 325° F.) was divided into two portions, one-third being drawn at 325° F. and pan-cooled, the balance being worked while cooling in the kettle to 110° F. Penetration values obtained on the pan-cooled grease were 227 and 242 mm./10 unworked and worked 60 strokes, respectively. The portion of the grease cooled to 110° F. was quite soft, having unworked and worked penetrations of 334 and 300 mm./10, respectively. Batch No. 3, prepared at a maximum manufacturing temperature of 328° F., was also divided into two portions, 25 pounds being drawn at 328° F. and pan-cooled. The balance was cooled to 200° F. and drawn into 25 and 100-pound containers. Penetrations of 215 and 225 mm./10 unworked and worked, respectively, were obtained on the portion drawn hot, while penetrations of 228 and 227 mm./10 were obtained on the grease cooled to 200° F. and drawn into the 25-pound pail. It thus appears that cooling conditions have some bearing on grease consistency but the method of preparing the salt and soap in the oil seems to have a more fundamental effect.

Cooking at lower temperatures results in even softer products. A batch prepared with a maximum cooking temperature of 315° F. was soft, even though drawn hot, having an unworked penetration of 349 m./10, and a worked penetration of 309 mm./10. This increase in consistency or hardness with working, which is not common in most greases, is characteristic of the furoic acid salt greases. Mechanical working, especially in a highly effective homogenizer, improved their consistency to a marked degree. Such treatment has, furthermore, the important advantages of eliminating lumps of undispersed soap-oil concentrate.

As suggested above, pilot plant batches of grease had unworked penetrations at 77° F. of

335 and 334 mm./10 and worked (60 strokes) penetrations of 262 and 300 mm./10, respectively. After milling these greases on the laboratory three-roll paint mill (one passage through the mill), the penetration values were decreased to 212 and 245 mm./10 unworked and 251 and 272 mm./10 worked. Cooling the grease (Batch No. 3) to 200° F. resulted in penetrations of 288 and 227 mm./10 unworked and worked, respectively. Milling this grease decreased the unworked and worked penetrations to 177 and 203 mm./10. Milling of a 400-pound batch decreased the unworked and worked penetrations from 349 and 309 mm./10 to 239 and 262 mm./10, respectively. Milling the grease drawn at the elevated temperatures with the exception of the 400-pound batch resulted in some decrease in the unworked penetrations, but apparently the worked penetrations of the milled greases approached the values obtained on the unmilled greases after working. In addition, milling greatly improved the appearance of all the greases whether drawn hot or kettle cooled. Observation of samples of the milled product after short storage showed no indication of oil separation.

Passage of one of the greases (Batch No. 2) drawn at 110° F. through a "Balcrank" commercial type air operated grease gun also hardened the grease considerably, penetration values being reduced from 334 and 300 mm./10 unworked and worked to 182 and 206 mm./10, respectively. Homogenization by this means also reduced the unworked and worked penetration values on the 400-pound batch drawn at 315° F. from 349 and 309 mm./10 to 216 and 247 mm./10, respectively. Similar improvement in appearance to that obtained on milling was also noted.

All of the greases described above whether drawn hot or cooled from the grease kettle had very high dropping points, above 500° F. in all cases. Furthermore, they showed excellent resistance to water-washing up to a water temperature of 125° F. They showed good structural stability in mechanical working. In all cases, the penetration values were less than 360 mm./10 after working 60,000 strokes with the fine-hole worker plate. In the 10,000 R. P. M. spindle test operating at a temperature of 300° F., a milled sample corresponding to the example showed a test life of 590 hours.

EVALUATION TESTS ON PILOT PLANT BATCHES

Batch No.	1	2	3	4	5	6
Drawing Temperature, °F.	110	325	110	328	200	315
Tests:						
Dropping Point, °F.	500+	500+	500+	500+	500+	500+
Water Washing Test, Percent Loss (125° F. Water Temp.)	0	0	0	0	0	0
Structural Stability to Mechanical Working Penetration After 60,000 Strokes, mm./10	352	356	356	335	340	356
After Homogenization in Manton-Gaulin Apparatus at 3,000 p. s. i. Pressure	312					352
Microscopic Examination	(¹)	(¹)	(¹)	(¹)	(¹)	(¹)
10,000 R. P. M. Spindle Test at 300° F., Hours	590	500				
Percent Free Alkalinity as NaOH	0.26	0.28		0.26		0.23
Norma-Hoffman Bomb Oxidation Test at 210° F., 5 p. s. i. Drop in Oxygen Pressure, Hours	534	768		500+		500+

¹ No noticeable soap particles on milled grease.

The above data indicate that the greases prepared in the steam jacketed pilot plant kettle

retain all the excellent properties previously shown for furfural type grease. In addition, they have the superior dispersion and consequent improvement in consistency and stability referred to above.

The usual oxidation inhibitors may be added to greases prepared as described above, along with other conventional modifiers such as metal deactivators, extreme pressure agents, tackiness agents, viscosity index improvers, etc. The major part of the lubricating oil, added after the chemical reactions have been substantially completed, may be either of mineral oil base or may be a synthetic oil such as the aliphatic esters of polybasic acids (e. g. di-2-ethyl hexyl sebacate or adipate), or polyglycols and ether derivatives. The mineral oils are preferred and should be used in any case where the saponification and/or Cannizzaro reactions are taking place in situ.

What is claimed is:

1. The process of preparing a lubricating grease which comprises mixing about 1 to 5 parts by weight of a saponifiable fatty acid having between about 12 and 22 carbon atoms with about 3 to 10 parts of a mineral base lubricating oil, adding a strong metal base in excess to saponify said fatty acid, adding about one-fourth to 2 parts of an aldehyde of molecular weight less than C₁₂ fatty acids and capable of undergoing the Cannizzaro reaction in the presence of said base to form the corresponding salt in the presence of said lubricating oil and saponified fatty acid, heating to above 210° F. but not above about 340° F. with mixing to remove water and to substantially evaporate alcohol released in said Cannizzaro reaction, and further cooking and blending in additional lubricating oil to form a grease of the desired consistency.

2. Process in accordance to claim 1, wherein the grease is cooled and passed through a homogenizer to make it uniform in texture and firm in consistency.

3. Process according to claim 1, wherein the quantity of fatty acid soap is between 5 and 25%, based on the weight of the total composition.

4. The process which comprises combining about 1 to 5 parts by weight of fatty acids of the C₁₂ to C₂₂ range with 3 to 10 parts of mineral base lubricating oil, adding an excess of alkali metal base to saponify said acids and leave a substantial amount of said base, adding ¼ to 2 parts of a low molecular weight aldehyde capable of undergoing the Cannizzaro reaction to form the alkali metal salt of acid corresponding to said aldehyde in the presence of said saponified acids, cooking to a temperature of not more than about 340° F. to remove volatile ingredients, blending in lubricating oil to obtain a product of the desired consistency, and thereafter homogenizing the product to further disperse the salt and soap in said oils and to harden the grease to firmer consistency.

5. Process according to claim 4 wherein the aldehyde is a cyclic aldehyde.

6. Process according to claim 4 wherein the aldehyde is a heterocyclic aldehyde.

7. Process according to claim 4 wherein the aldehyde is furfural.

8. Process according to claim 4 wherein the first mentioned lubricating oil is of light viscosity and the additional oil is of heavier viscosity.

9. Process which comprises preparing a concentrate of sodium soap of the C₁₂ to C₂₂ fatty acid range in light mineral base oil, using an excess of sodium hydroxide as saponifying agent,

adding about two-thirds as much weight of
furfural as fatty acids used to make said soap
to react with said excess, heating the reaction
products to a temperature range between 210°
and 340° F. to drive off volatile ingredients and
form a dry soap-salt concentrate in said oil,
thereafter blending in additional mineral oil in
small increments, until a grease of desired con-
sistency between 200 and 360 mm./10, and of
at least twice the oil content of the concentrate
is obtained, and thereafter subjecting the grease
to vigorous mechanical homogenization to further

disperse the soap-salt complex thickener and to
increase the hardness of said grease.

ARNOLD J. MORWAY.
JOHN J. KOLFENBACH.

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file of this patent:

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