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MANUFACTURE OF LITHIUM HYDROXY CARBOXYLIC ACID SOAP GREASES

George V. Browning, Schenectady, N. Y., Lawrence C. Brunstrum, Flossmoor, Ill., and Wilbur L. Hayne, Jr., Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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The present invention relates to improvements in the manufacture of lithium soap greases. More particularly, it relates to improvements in the manufacture of greases comprising lithium 12-hydroxy stearate or the lithium soap of hydrogenated castor oil and a lubricant base such as a mineral lubricating oil or the like.

Lithium 12-hydroxy stearate greases are ordinarily prepared commercially by heating a mixture of the soap and oil to above about 400° F., e. g. 425° F., in order to melt the soap and obtain a high degree of dispersion of soap in oil following which the mix is cooled from the melting temperature and milled either during the cooling or thereafter, if for example, shock chilling is employed. Heating the soap-oil mixture to such a temperature incurs certain difficulties, particularly when the grease is intended for use at very low temperatures at which the oleaginous vehicle, e. g. a mineral oil, must of necessity be of low viscosity and relatively high volatility. Equipment requirements pose a problem when operating at such temperatures because it is necessary to employ special heat exchange equipment, safety devices to guard against the fire hazard which is present with volatile oils, etc. Such high temperatures likewise have a deleterious effect on the oxidation stability of the greases. The prior art, of course, does suggest methods for the manufacture of lithium hydroxy stearate greases at temperatures below the melting point of the soap but these have generally been unsatisfactory in various respects. Such greases have had low yields (i. e. high soap contents), poor worked and unworked consistency and usually have not been mechanically stable. It is an object of the present invention to provide an improved method of preparing lubricant greases comprising lithium soaps of long chain hydroxy fatty acids. A further object of the present invention is to provide an improved low temperature process for the manufacture of semi-solid to solid lubricant greases comprising lithium 12-hydroxy stearate or the lithium soap of hydrogenated castor oil.

Another object of the invention is to provide a method of preparing superior yields of such lithium soap greases at steam kettle temperatures. A still further object of the present invention is to provide a method for the manufacture of lithium 12-hydroxy stearate greases and the like whereby uniformity of product from one batch to another can be consistently obtained. Another object is to provide a method of preparing semi-solid to solid greases of high consistency which are suitable for low temperature use. These and additional objects and advantages will be apparent from the following description of our invention.

In a preferred embodiment of the present invention a lubricant grease is prepared by charging a mixture of 12-hydroxy stearic acid, lithium hydroxide hydrate, water, and an oleaginous vehicle, preferably a solvent extracted mineral oil, to a jacketed pressure vessel having a stirring mechanism therein. After having charged the vessel with the above named constituents, the vessel is sealed and the contents are heated by introducing steam to the vessel jacket under sufficient pressure to raise the temperature of the mix in the vessel to at least about 275° F. The water in the mixture is vaporized at such temperatures and develops a pressure within the vessel approximately equal to the pressure in the jacket. It is preferred to operate at a temperature in the range of from about 300° F. to about 330° F. which is obtainable with steam at a pressure of from about 50 to 95

pounds per square inch. The mixture within the vessel is continuously agitated while it is being heated in this manner. When the temperature of the batch reaches the desired point it is preferably held at such temperature for a relatively short time, e. g. from about 10 minutes to about an hour or longer, after which the steam is vented in order to relieve the pressure. The venting of steam may be begun the moment the temperature reaches the desired level but as a practical matter it is desirable to hold the batch at such temperature for a short period of time. It is critical, when venting the steam, that the temperature of the batch be held at substantially the same temperature to which it had been heated, i. e. there should be no more than about 10° drop in batch temperature during the removal of steam. Rapid agitation should be continued during the release of steam. The introduction of steam to the vessel jacket at somewhat higher pressure results in the heat necessary to drive off the steam without causing a drop in the temperature of the batch itself. When the steam is flashed from the vessel without regard to reduction in temperature of the batch, although a somewhat improved product is obtained as compared to merely heating the mixture to such a temperature at atmospheric pressure, a softer grease having much poorer consistency results. When the vessel is opened, after the pressure is relieved, the contents often appear lumpy and somewhat grainy but can readily be smoothed to the desired consistency by milling the same, e. g. in a colloid mill. The resulting grease possesses excellent mechanical and oxidation stability and low leakage characteristics.

By the term "yield" as employed herein is meant the relationship between the amount of soap employed and the amount of oleaginous vehicle employed to produce a given quantity of grease of desired properties. Thus, the smaller the amount of soap employed to obtain a given quantity of grease of a particular consistency, the higher is said to be the "yield."

The yields of grease which are obtainable by the present method are a substantial improvement over those obtained by prior art methods employing temperatures below the melting point of lithium 12-hydroxy stearate or the lithium soap of hydrogenated castor oil. Thus, by our novel process, greases having excellent penetration values and fiber dispersement are obtainable with soap contents as low as about 3 to about 15 per cent. When oil and such relatively low amounts of soap constituents are heated to the temperatures employed in accordance herewith in an open kettle (without pressure) a fluid slurry, rather than a grease, results. Higher percentages of soap, for example 15 to 30 per cent or even more, may of course be employed if desired. Greases prepared in accordance with the present invention have been found to be equivalent in every way, if not superior, to greases prepared by high temperature prior art methods.

In accordance with the present invention, it is essential that the batch, before heating, constitute at least about 1 per cent of water by weight, preferably at least about 1½ per cent. Larger amounts of water may be employed, but more than about 5 per cent appears to be unnecessary since it does not contribute to any substantial improvement but must nevertheless be vented without reducing batch temperature which obviously would be a waste of heat. The continued presence of water in such an amount during the heating step contributes, in large measure, to achievement of the various objects of the invention.

The method of the present invention is described with particular reference to lithium soap prepared from 12-hydroxy stearic acid but it should be understood that lithium soap of hydrogenated castor oil may be employed with equally advantageous results. The soap constituents of the grease may, if desired, comprise part lithium 12-hydroxy stearate and part the lithium soap of hydrogenated castor oil. Acyclic acids containing 12 or more carbon atoms and one or more hydroxyl groups separated from the carboxyl group by at least 1 carbon atom may be advantageously employed in accordance herewith.

Oleaginous vehicles which may be employed in accordance herewith are for example mineral oils in the lubri-

cating oil viscosity range, i. e. about 80 S. S. U. at 100° F. to about 300 S. S. U. at 210° F., preferably solvent extracted oils in said range, i. e., oils from which a substantial portion of the aromatics have been removed such as by extraction with phenol, furfural, B,B'-dichlorodimethylether (Chlorex), liquid SO₂, nitrobenzene, etc. are particularly desirable and preferred for use in accordance with the present invention. Synthetic lubricating oils resulting from polymerization of unsaturated hydrocarbons or other oleaginous compounds within the lubricating oil viscosity range such as the high molecular weight ethers e. g. normal hexyl ether, etc. may be employed. Because of the temperatures employed the present invention is applicable to the manufacture of low temperature greases prepared from low viscosity, high volatility oils, preferably solvent extracted, having a viscosity in the range of about 40 to 80 S. S. U. at 100° F.

Whereas the present invention offers a particularly advantageous method whereby all of the desired constituents may be added at the outset, it is not necessary to charge the total amount of the oleaginous vehicle to the pressure vessel initially. Thus, it may be desirable to charge the soap constituents, water, and a relatively small percentage of the amount of vehicle ultimately employed in order to make optimum use of available autoclave capacity and produce a large batch of high soap content material which may then be mixed hot with the rest of the oleaginous vehicle and milled to give the relatively low-soap content final product.

The preferred embodiment of the present invention has been described with reference to the addition of lithium hydroxide-monohydrate and 12-hydroxy stearic acid to the reaction vessel with the formation of the soap taking place in situ; it should be understood that the soap may be prepared outside of the vessel and charged thereto in the desired amount without departing from the spirit of the present invention. As a practical matter it is usually more expedient to prepare the soap in situ and eliminate the separate soap making step. Furthermore, although lithium hydroxide-monohydrate is taught as the preferred neutralizing agent, the anhydrous lithium hydroxide may likewise be employed. Inasmuch as greases may be produced in accordance herewith by starting with either a previously prepared soap, e. g. lithium 12-hydroxystearate, etc., or by using the soap reactants and saponifying in situ during the preparation of the grease, the term "lithium hydroxy soap constituents" as employed in the appended claims shall include both a previously prepared soap and the reactants which upon being subjected to the process of the present invention will saponify in situ to produce such a soap.

The pressure within the vessel increases as the temperature is increased by introduction of a heat exchange medium such as high pressure steam to the vessel jacket. One of the particular advantages of this invention is that such excellent yields of grease may be prepared at high pressure steam temperatures but other heating mediums may be employed. The pressure within the vessel itself is ordinarily at some point below the pressure of the steam employed as heating medium. Greases may be prepared in accordance herewith at temperatures as low as about 275° F. It is preferred, however, to operate at a temperature of from about 300° F. to about 330° F. A gradual increase in yield and overall improvement in grease properties are observed for products produced at temperatures up to about 340° F. but little if any improvement has been observed when operating at a temperature thereabove.

The following operating examples are included to specifically illustrate the present invention without the intention of unnecessarily limiting the same. The tests set forth in these examples were carried out in a mechanically stirred, jacketed autoclave having a capacity of 210 gallons.

EXAMPLE 1

600 pounds of a mixture, comprising 89.6 percent of a phenol extracted SAE 40 lubricating oil, 9.8 percent 12-hydroxy stearic acid, 1.6 percent lithium hydroxide monohydrate and 2 percent of an amine type oxidation inhibitor marketed by DuPont under the designation PSF-34 or Ortholcum 300 (a mixture of substituted aromatic amines), was charged to the autoclave. To this mixture was added 30 pounds of water and the autoclave was sealed. By introducing high pressure steam to the jacket

of the autoclave the mixture was then heated with agitation to 300° F. at which temperature an internal pressure of 75 pounds per square inch was developed. The batch was held at 330° F. for about 45 minutes after which the steam was vented rapidly with a substantial drop in batch temperature. A relatively soft grease having an unworked penetration at 77° of 337 and a worked penetration of 342 was obtained by milling a sample of the batch in a colloid mill. Electron photomicrographs of the sample indicate relatively poor dispersion of soap fibers and a poor L/D ratio.

EXAMPLE 2

The batch prepared in Example 1, was reheated to a temperature of 330° F. in the autoclave after having added 25 pounds of water thereto. A pressure of 75 pounds per square inch was developed in the autoclave. The batch was held at such temperature for approximately 30 minutes. The pressure was then relieved by venting the steam while being careful to maintain the batch temperature at 330° F. by the introduction of additional amounts of high pressure steam to the jacket and stirring the mix at full speed. A heavier more fibrous product was obtained which upon removing a sample and milling it in a colloid mill gave a smooth grease having an unworked penetration of 276 and a worked penetration of 278. The dropping point of this grease was 390° F. + and electron photomicrographs indicated that the fibers were well dispersed with a good L/D ratio.

EXAMPLE 3

The same batch which had been initially prepared in accordance with the method set forth in Example 1 and then reheated in accordance with the method set forth in Example 2 was reheated for a third time after having added 25 pounds of water thereto. After holding the mix at a temperature of 330° F. and 75 pounds per square inch for a short time the valve was opened and the pressure was relieved rapidly (over a period of 5 to 10 minutes) without regard to maintaining the temperature of the batch at 330° F. A sharp drop of about 25° F. in the temperature of the batch occurred. A sample of the resulting product was milled in a colloid mill to give a somewhat softer product having an unworked penetration of 294 and a worked penetration of 293. Electron photomicrographs of this grease indicate poorer dispersion of soap fibers than that prepared in accordance with Example 2.

EXAMPLE 4

The batch from Example 3 was reheated to a temperature of 330° F. and a pressure of about 75 pounds per square inch after adding 25 pounds of water. The batch was maintained under those conditions for 3 hours after which the pressure was relieved slowly while agitating the batch rapidly with no temperature drop. A sample of the batch was then milled and a grease having an unworked penetration of 265 and a worked penetration of 266 was obtained. Electron photomicrographs of this grease indicated no large fibers and slightly better dispersion than that obtained in any of the first three examples.

EXAMPLE 5

Another grease prepared in accordance with the method of Example 1 was heated with 25 pounds of water but this time a pressure of only 30 to 39 pounds per square inch and a top temperature of about 275° F. was reached. After holding the batch at such temperature for 3½ hours the pressure was vented off without loss of temperature and after milling a sample thereof resulted in a grease having an unworked penetration somewhat over 400.

EXAMPLE 6

The batch from Example 5 was reheated with an added 25 pounds of water to a temperature of 320° F. and a pressure of 70 to 75 pounds per square inch and held at such temperature and pressure for 1 hour. The pressure was relieved without loss in batch temperature and a grease prepared by milling a sample of the mix had a heavy structure and milled into a bright grease having an excellent appearance. The unworked penetration of the grease was 264 and after 60 strokes it was 274. Electron photomicrographs indicate excellent dispersion of soap fibers and good L/D ratio.

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EXAMPLE 7

The batch prepared in Example 6 was reheated with an added 25 pounds of water to a temperature of 330° F. and a pressure of 80 to 84 pounds per square inch for about 50 minutes. The steam was vented without loss in temperature. The resulting grease obtained by milling a sample thereof was not as bright in appearance but was somewhat heavier than that of Example 6 and gave an unworked penetration of 255 and a worked penetration of 267.

EXAMPLE 8

The batch of Example 7 was again heated with 25 pounds of water to a temperature of 335° F. and a pressure of 90 pounds per square inch. The pressure was slowly relieved without loss in batch temperature and a grease was obtained after milling a sample of this material which had an unworked penetration of 254 and a worked penetration of 278.

EXAMPLE 9

20 pounds of water were added to the batch from Example 8 and the mixture was heated to a temperature of 335° F. and a pressure of 90 pounds per square inch. The high pressure steam was then shut off and water was introduced to the jacket of the autoclave to condense the steam within the vessel. After the pressure was completely reduced the vessel was opened and the water was boiled off. A sample was removed, milled and tested for consistency. An unworked penetration of 339 and a worked penetration of 354 was obtained. Electron photomicrographs indicate considerable break down and lack of continuity between fibers.

EXAMPLE 10

600 pounds of a mix comprising 88.6 percent of a phenol-extracted SAE 40 lubricating oil, 10.2 percent of hydrogenated castor oil, 1.6 percent of lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$), 0.2 percent of an amine type oxidation inhibitor marketed by DuPont under the designation PSF-34, and 25 pounds of water were charged to the autoclave. The temperature of the batch was raised to 320° F. and a pressure of 68 pounds per square inch was developed in the vessel. After venting the pressure without loss in batch temperature a sample was removed and milled in the colloid mill to give an unworked penetration of 262 and a worked penetration of 260. The penetration of the grease at 500 strokes was 260 and at 95,000 it was 286. The dropping point was 388° F. and electron photomicrographs indicate excellent dispersion and L/D ratio. Negligible leakage was encountered in tests on this grease.

EXAMPLE 11

405.7 pounds of a mix comprising 9.7 percent 12-hydroxy stearic acid 1.6 percent lithium hydroxide hydrate and the remainder phenol extracted SAE 40 lubricating oil was heated to 300° F., without sealing the autoclave, and was maintained at that temperature for about 30 minutes. A slurry resulted which comprised 10.5 percent soap.

To the slurry of Example 11, which obviously was unsatisfactory as a grease were added varying amounts of water (as set forth in Table I) and the batch was heated after each addition to 300° F. under pressure. The pressure was vented without loss in batch temperature, a sample was taken and tested for consistency and then the next larger amount of water was added, heated, etc. Thus, as may readily be seen from the following table, the use of pressure technique in accordance with the present invention with even slight amounts of water greatly improves the yield of grease. In accordance with the present invention, therefore, at least about 1 percent water by weight should be added to the mix, and preferably at least about 1½ to about 2 percent water. As indicated hereinabove, considerably more water may be used without departing from the spirit of the present invention but more than about 5 percent does not give an apparent improvement and merely makes it necessary to vent the additional amounts of steam before the milling operation can begin.

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Table I

	H ₂ O (pounds)	Percent H ₂ O*	Penetration**
2	-----	0.49	437
3	-----	0.74	363
4	-----	0.98	345
5	-----	1.22	297
6	-----	1.46	281
25	-----	5.82	263

*By weight based on total mix.

**Unworked penetration.

EXAMPLE 12

400 pounds of a mix consisting of phenol extracted SAE 40 lubricating oil and sufficient 12-hydroxy stearic acid and lithium hydroxide monohydrate to give 7½ percent soap concentration was prepared by heating the mix with 12 pounds of water to a temperature of 300° F. at which a pressure of 70 pounds per square inch was developed. The batch was held at this temperature for a short time and the steam was then vented without loss in temperature. The vessel was opened after the pressure was released while maintaining the batch at 300° F. and 0.1 percent of an amine type oxidation inhibitor marketed by DuPont under the designation PSF-34 or Ortholeum 300 (a mixture of substituted aromatic amines), was added thereto. The A. S. T. M. oxidation test was then conducted on a sample of the batch which has been milled in a colloid mill. In this test a 5 pound per square inch drop in oxygen pressure in 100 hours is considered failure for most greases. Set forth below are the results of this test.

Time (hours):	Oxygen pressure (p. s. i.)
0	110
24	109
118	108.2
190	107.8
382	106.0
454	104.0

Although the present invention has been described with particular reference to batch operation it is not limited thereto and may be carried out continuously or semi-continuously in known commercial equipment. A simple expedient which is particularly economical and yet highly advantageous is to employ two or more autoclaves and one or more colloid mills so that a batch may be milled while another batch is being heated, etc.

Various antioxidants, other than the product set forth in the above examples, may of course be used. A particularly desirable antioxidant is phenyl alpha-naphthylamine which may be added in proportions of about 0.01 to about 1 per cent by weight, based upon the finished grease. In addition we may add fillers such as talc or asbestos, solid lubricants, such as graphite, dyes, odorant materials, metal deactivators, corrosion inhibiting compounds, etc.

The pressures given hereinabove and in the appended claims are gauge pressures. Percentages given are by weight unless otherwise specified.

The greases prepared in accordance with the present invention are of the anhydrous type hence it should be understood that essentially all of the water is removed as steam during the venting operation. Obviously the moisture content of the grease could be readily adjusted to any level if for any reason it were found desirable to have a certain amount of water in the finished product.

While we have described our invention with particular reference to certain preferred embodiments thereof, it is to be understood that these are by way of illustration and not by way of limitation.

We claim:

1. A method of producing a grease comprising a lubricant base and a lithium soap of an organic acid substance selected from the group consisting of hydrogenated castor oil and hydroxy fatty acids of at least 12 carbon atoms wherein the hydroxyl group is separated from the carboxyl group by at least one carbon atom, which method comprises subjecting a mixture comprising lubricant base, lithium hydroxy soap constituents and at least about 1 percent of water to a temperature of at least about 275° F. and superatmospheric pressure, agitating said mixture, relieving the pressure after the

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mixture has reached said temperature by venting the steam therefrom, and maintaining said mixture at substantially said temperature while venting said steam.

2. The method of claim 1 wherein the lubricant base is a solvent extracted petroleum oil in the lubricating oil viscosity range.

3. A method of producing a grease comprising a lubricant base and a lithium soap of a hydroxy fatty acid having at least 12 carbon atoms wherein the hydroxyl group is separated from the carboxyl group by at least one carbon atom which method comprises subjecting a mixture comprising lubricant base, lithium hydroxy soap constituents and at least about 1 percent of water to a temperature in the range of at least about 275° F. and superatmospheric pressure, agitating said mixture, relieving the pressure after the mixture has reached said temperature by venting the steam therefrom, maintaining said mixture at substantially said temperature while venting said steam and milling the resulting product.

4. The method of claim 3 wherein the lubricant base is a solvent extracted petroleum oil in the lubricating oil viscosity range.

5. The method of claim 3 wherein the mixture is subjected to a temperature in the range of from about 300° F. to about 340° F. and water is present in amount of about 1½ percent to about 5 percent.

6. The method of claim 3 wherein the lithium hydroxy soap constituents comprise an amount of from about 3 percent to about 30 percent of the mixture.

7. The method of claim 3 wherein the lithium hydroxy soap constituents comprise lithium 12-hydroxy stearate.

8. A method of producing a grease comprising a lubricant base and a lithium soap of a hydrogenated castor oil which method comprises subjecting a mixture comprising lubricant base, lithium hydrogenated castor oil soap constituents and at least about 1 percent of water to a temperature of at least about 275° F. and superatmospheric pressure, agitating said mixture, relieving the pressure after the mixture has reached said temperature by venting the steam therefrom, maintaining said mixture at substantially said temperature while venting said steam and milling the resulting product.

9. The method of claim 8 wherein the lubricant base comprises a solvent extracted petroleum oil in the lubricating oil viscosity range.

10. The method of claim 8 wherein the mixture is subjected to a temperature in the range of from about 300° F. to about 340° F. and water is present in an amount of about 1½ percent to about 5 percent.

11. The method of claim 8 wherein the lithium hydrogenated castor oil soap constituents comprise an amount of from about 3 percent to about 30 percent of the mixture.

12. The method of claim 8 wherein the lithium hydrogenated castor oil soap constituents comprises lithium soap of hydrogenated castor oil.

13. A method of producing a grease comprising a solvent extracted petroleum oil lubricant base and lithium 12-hydroxy stearate which method comprises subjecting a mixture comprising lubricant base, lithium 12-hydroxy stearate constituents and at least about 1 percent of water to a temperature in the range of from about 300° F. to about 340° F. and a pressure of at least about 50 pounds per square inch, agitating said mixture, relieving the pressure after the mixture has reached said temperature by venting the steam therefrom, maintaining said mixture at substantially said temperature while venting said steam and milling the resulting product.

14. A method of producing a grease comprising a solvent extracted petroleum oil lubricant base and the lithium soap of hydrogenated castor oil which method comprises subjecting a mixture comprising lubricant base, lithium hydrogenated castor oil soap constituents and at least about 1 percent of water to a temperature in the range of from about 300° F. to about 340° F. and a pressure of at least about 50 pounds per square inch, agitating said mixture, relieving the pressure after the mixture has reached said temperature by venting the steam therefrom, maintaining said mixture at substantially said temperature while venting said steam and milling the resulting product.

15. The method of claim 14 which includes the step of adding an antioxidant to said mixture.

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