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## PROCESS FOR PREPARING ALKALI METAL GREASES

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This invention relates to a novel procedure for preparing alkali metal greases. More particularly, this invention relates to a procedure whereby alkali metal greases of high dropping point and of outstanding performance over a wide temperature range are prepared.

Alkali metal greases characterized by high dropping point and excellent performance characteristics over a wide temperature range are prepared by the novel process of this invention involving saponification of a mixture of mineral oil, alkali metal hydroxide and a soap-forming material which is either a soap-forming fatty acid, a soap-forming ester or a mixture of soap-forming fatty acids and esters, dehydration of the saponified mixture and digestion of the saponified, dehydrated reaction mixture in a pressure kettle under an air pressure of 50 to 120 pounds per square inch and at a temperature of 300 to 390° F. for a period of at least five hours. The reaction mixture contains excess alkali metal hydroxide over the stoichiometric amount required to saponify the soap-forming constituents of the reaction mass. The excess alkali metal hydroxide amounts to 1 to 3 per cent of the final composition of the grease. Digestion of the saponified, dehydrated reaction mixture in a pressure kettle under an air pressure of 50 to 120 pounds per square inch and a temperature of 300 to 390° F. results in partial oxidation of the reaction mixture to form acidic materials which are neutralized by the excess alkali present. The alkali metal greases produced by this invention are characterized by dropping points over 500° F. and possess good low temperature torque properties so that they are properly classified as wide temperature range ball and roller bearing greases.

It has been known in the grease making art to employ mineral oils and soap-forming materials which have been preoxidized either alone or in combination prior to the addition of caustic in the grease formulation. Greases prepared from pre-oxidized mineral oils and soap-forming materials are hard block-type greases which are known as driving journal greases. It has also been known to effect saponification of the grease making ingredients in a pressure kettle under air pressure. The process of this invention distinguishes from the prior known procedures for manufacturing grease in that a saponified and dehydrated reaction mixture is digested in a pressure kettle at an elevated temperature under super-atmospheric air pressure. Moreover, none of the procedures of the prior art involving pressure kettle treatment of one or more of the grease ingredients produces alkali metal greases which are characterized by very high dropping points and good low temperature torque properties. For example, a buttery-type sodium grease with a dropping point over 500° F. is prepared by the procedure of this invention. The preparation of alkali metal greases characterized by wide temperature range properties represents a significant advance in the art of grease making.

Naphthene base oils or paraffin base oils can be employed in the process of this invention to prepare novel alkali metal greases. With the paraffin base oils it is necessary to incorporate petroleum mahogany sulfonate salts as stabilizing agents in order to obtain suitable greases. Sodium petroleum mahogany sulfonate is ordinarily employed as the stabilizing agent. With paraffin base oils, the added petroleum mahogany sulfonate salt amounts to about 0.24 to 4 per cent of the final calculated grease composition. The sodium petroleum mahogany sulfonate is added to the reaction mixture together with the paraffin base oil and is present during saponification and dehydration of the reaction mixture.

When naphthene base oils, commonly known as pale oils, are employed in the process of this invention, it is not necessary to employ stabilizing agents such as petroleum mahogany sulfonate salts since greases of high stability are prepared without the use of a stabilizing agent.

The grease making process of the invention can be used with almost any type of soap-forming material, but best results are obtained with soap-forming acids, esters and mixtures thereof which contain a considerable olefin content. The presence of double bonds in soap-forming materials provides points of attack for the oxidation which occurs during the high temperature-pressure digestion of the saponified, dehydrated reaction mixture. Soap-forming fatty acids, soap-forming esters and mixtures thereof may all be employed in this invention with special emphasis being placed on the use of a soap-forming stock, which is olefinic in nature and has an iodine number higher than 40.

A particularly preferred soap-forming material comprises a mixture of menhaden oil and hydrogenated fish oil fatty acids commercially known as "Snodotte acids." A 3 to 1 menhaden oil-Snodotte acid mixture has proven particularly useful in the process of this invention. Commercially available "Snodotte acids" have approximately the following stated compositions:

| | Per cent |
|---|---|
| Myristic acid | 9 |
| Palmitic | 22 |
| Stearic | 27 |
| Arachidic | 22 |
| Behenic | 20 |

Typical tests on commercially available Snodotte acids are as follows:

| | |
|---|---|
| Sap. No. | 197 |
| Neut. No. | 193 |
| Iodine | 1 |
| Titer, °C. | 54.6 |

Other unsaturated soap-forming acids and esters such as castor oil, linoleic and linolenic acids are also useful in the process of this invention. Advantageously, the soap-forming material has an iodine number higher than 90.

The excess alkali metal hydroxide employed in procedures of this invention amounts to approximately 1 to 3 per cent of the final calculated composition of the grease. Advantageously, the stoichiometric quantities of caustic and a major portion of the excess caustic is added to the grease mixture prior to saponification and the remaining caustic solution constituting a minor portion of the excess alkali metal hydroxide is added after the elevated temperature-air pressure digestion of the saponified, dehydrated grease mixture. It is also possible to add the total caustic during the saponification of the grease mixture. In the preferred procedure, the stoichiometric caustic plus more than half, and preferably 70 to 90 per cent, of the excess caustic are added prior to saponification; remaining excess caustic is added after the high temperature-air pressure digestion.

All alkali metal greases may be prepared in accordance with the procedure of this invention, but the procedure is particularly adapted to sodium and lithium greases. Alkali metal hydroxide is advantageously added to the reaction mixture in the form of a saturated aqueous solution. The procedure of the invention constitutes the preparation of a buttery-type sodium base grease.

Various additives are blended into the grease after the digestion of the saponified, dehydrated mixture at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch. For example, diphenylamine, an oxidation inhibitor, may be blended into the grease at a temperature of about 250° F. and atmospheric conditions during the cooling of the grease after elevated temperature-pressure digestion. Aluminum stearate may also be added to the grease to impart water resistance during the cooling of the grease.

The saponification procedure employed in this invention is effected at conventional conditions. The mineral lubricating oil fraction and the soap-forming stock are heated with stirring to a temperature of approximately 125 to 160° F. to effect good distribution of the reagents. If a paraffin base mineral oil is employed, the stabilizing petroleum mahogany sulfonate salt is added to the mixture at this time. At approximately 150° F. the aqueous solution of alkali metal hydroxide is added to the reaction mixture. A small amount of silicone anti-foam agent is advantageously added together with the caustic solution to minimize foaming. The saponification is effected at a temperature between 150 and 200° F. in a period of about one hour.

Dehydration of the saponified reaction mixture is effected at a temperature between about 290 and 350° F. and ordinarily takes approximately 3 to 5 hours. The preferred temperature range for dehydrating the saponified reaction mass is 300 to 330° F.

Digestion of the saponified and dehydrated reaction mixture at superatmospheric pressure is effected in a closed vessel or autoclave which is equipped with efficient stirring means. It is recommended that the kettle wherein the reaction mixture is digested under air pressure be equipped with side wall scrapers.

The air pressure in the closed kettle is maintained between 50 and 120 pounds per square inch and advantageously at a pressure of 70 to 110 pounds per square inch. The temperature during pressurized digestion of the reaction mixture is maintained between 300 and 390° F. and preferably at a temperature of 340 to 365° F. The period of time required for the pressure kettle digestion of the reaction mixture varies with the temperature and pressure conditions employed during the oxidative digestion but ordinarily will be in the range of 5 to 15 hours.

The nature of the soap-forming material employed is a decisive factor in determining the temperature and pressure conditions to be employed and the length of time required to obtain the product of the desired characteristics. With highly olefinic stocks, temperatures and pressures in the lower portion of the prescribed range are employed and the duration of the pressurized digestion is also within the lower portion of the prescribed range. In contrast, when highly paraffinic soap-forming materials such as tallow are employed, higher temperatures and pressures within the prescribed ranges are employed and, in addition, pressurized digestion is continued for a longer time.

After the pressurized digestion, additives such as aluminum stearate and diphenylamine are added while the reaction mixture is hot. The additives are usually added at temperatures between 275 and 380° F. The remaining excess alkali is also added during the cooling procedure if split addition of excess alkali is employed. Addition of residual excess alkali is advantageously effected during cooling of the grease at a temperature of about 275 to 300° F.

The grease is drawn at a temperature of about 200° F. Advantageously it is screened through —60 mesh screens during the drawing operations.

The novel grease making process of this invention is illustrated in Examples I and II wherein sodium base and lithium base greases are prepared in accordance with the procedure of this invention.

### *Example I*

A mixture of 40.3 pounds of a paraffinic mineral lubricating oil fraction having an SAE viscosity of about 20, 0.9 pound of sodium petroleum mahogany sulfonate and 11.6 pounds of a 3 to 1 mixture of menhaden oil-Snodotte acids were charged to a kettle. This mixture was heated to 150° F. and 6 g. of a methyl silicone (Dow-Corning Anti-Foam A) were added. At 150° F. 5.54 pounds of 49.3 per cent solution of sodium hydroxide were added to the reaction mixture; the added caustic comprised the stoichiometric amount required to saponify the soap-forming constituents and in addition an excess of sodium hydroxide which calculated approximately 1.9 weight per cent of the final calculated grease composition. The reaction mixture was stirred in the kettle at a temperature of 150 to 200° F. for approximately 1 hour with the resulting saponification of the soap-forming materials present in the reaction mass. The reaction mixture was then raised to a temperature of 300 to 330° F. and maintained at this level for approximately 3 hours with the resulting dehydration of the reaction mixture. After dehydration the head was placed on the pressure kettle and the temperature raised to approximately 340° F. whereupon the pressure kettle was subjected to an air pressure of 70 to 90 pounds per square inch. The reaction mixture was stirred in the pressure kettle at a temperature of 340 to 350° F. and under an air pressure of 70 to 90 pounds per square inch for approximately 12 hours. At the end of this time the air pressure was shut off, the head removed from the kettle and 2.84 pounds of aluminum stearate added, whereafter the mixture was stirred for 30 minutes. The heat was then removed from the kettle and the reaction mixture cooled down to 200° F. with stirring. During the cooling period, 0.34 pound of 49.3 per cent caustic solution amounting, on the basis of sodium hydroxide added, to approximately 0.3 weight per cent of the final calculated grease composition, were added to the reaction mixture at a temperature of approximately 275 to 300° F.; 0.57 pound of diphenylamine dissolved in 0.79 pound of 20 grade paraffinic mineral lubricating oil was added at 250° F. The grease was drawn from the kettle at 200° F. and pumped through three —60 mesh screens into containers. The sodium grease thus prepared had the following calculated composition:

| | |
|---|---|
| Na 3:1 menhaden oil-Snodotte acid soap, per cent | 20.2 |
| Excess NaOH in charge, per cent | 1.9 |
| Added later | 0.3 |
| Glycerin (from fat), per cent | 1.5 |
| Paraffinic mineral oil, SAE 20, per cent | 68.6 |
| Aluminum stearate, per cent | 5.0 |
| Sodium petroleum mahogany sulfonate, per cent | 1.5 |
| Diphenylamine, per cent | 1.0 |
| D. C. Anti-Foam A, parts per million | 220 |

The properties of the grease thus prepared are as follows:

| | |
|---|---|
| Dropping point, ° F | 500+ |
| Unworked Pene | 245 |
| Worked Pene | 289 |
| Low Temp. torque, sec./rev. at 0° F | 1.2–1.2 |
| —10 | 3.2–3.6 |
| —20 | 14.4–12.0 |
| —30 | 91.6–98.2 |
| —40 | >120–>120 |
| Dynamic water resistance, per cent loss | 33 |
| Norma Hoffman oxidation, lb./drop in 500 hr | 26 |

*Example II*

A lithium base grease was prepared in accordance with the procedure set forth for sodium base grease in Example I. The proportions of reactants and the reaction conditions were exactly the same as those set forth in Example I. Neutralization of soap-forming constituents and excess alkali was supplied by 22.1 pounds of 10.2 per cent lithium hydroxide solution; 20.5 pounds were

added prior to saponification and 1.6 pounds during the cooling of the grease. The lithium grease thus prepared had the following calculated composition:

| | |
|---|---|
| Li 3:1 menhaden oil-Snodotte acid soap, per cent | 20.2 |
| Excess alkali in charge | 1.9 |
| Added later | 0.3 |
| Glycerin | 1.5 |
| Paraffinic mineral oil SAE 20 | 68.6 |
| Aluminum stearate | 5.0 |
| Sodium petroleum mahogany sulfonate | 1.5 |
| Diphenylamine | 1.0 |
| D. C. Anti-Foam A, parts per million | 220 |

The properties of the lithium base grease thus prepared are as follows:

| | |
|---|---|
| Dropping point, ° F | 488–500+ |
| Unworked Pene | 119 |
| Worked Pene | 172 |
| Low temp. torque, sec./rev. at 0° F | 3.3–3.4 |
| —10 | 10.5–8.0 |
| —20 | 52.7–22.5 |
| —30 | >120–>120 |
| —40 | ------ |
| Dynamic water resistance, per cent loss | 0.2–2.5 |
| Norma Hoffman oxidation lb./drop in 100 hr | 20–23 |

The foregoing examples illustrate the excellent wide temperature range ball and roller bearing alkali metal greases that can be prepared by the process of this invention. The high dropping points and the good low temperature torque properties are particularly significant. The process of the invention is an important step forward in the art of grease making since it provides for the first time a preparative procedure for alkali metal greases which can be classified as wide temperature range ball and roller bearing greases.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for preparing alkali metal greases which comprises saponifying a mixture of a mineral lubricating oil fraction, an aqueous solution of alkali metal hydroxide and a soap-forming material selected from the group consisting of soap-forming acids, soap-forming esters and mixtures thereof, said alkali metal hydroxide being in excess of the stoichiometric amount required for saponification of said soap-forming material, dehydrating said mixture and digesting said saponified and dehydrated reaction mass at an elevated temperature of 300 to 390° F., at an air pressure of 50 to 120 pounds per square inch for a period of at least five hours, cooling and drawing said reaction mixture.

2. A process according to claim 1 in which digestion of the saponified, dehydrated reaction mixture is effected at a temperature of 340 to 365° F.

3. A process according to claim 1 in which the digestion of the reaction mixture is effected at a pressure between 70 and 110 pounds per square inch.

4. A process according to claim 1 in which the soap-forming material has an iodine number of at least 40.

5. A process according to claim 1 in which a saturated aqueous solution of sodium hydroxide is employed.

6. A process according to claim 1 in which a saturated aqueous solution of lithium hydroxide is employed.

7. A process according to claim 1 in which the excess alkali metal hydroxide amounts to approximately 1 to 3 per cent of the final calculated grease composition.

8. A process for preparing alkali metal greases which comprises saponifying a mixture of a mineral lubricating oil fraction, an olefinic soap-forming material having an iodine number higher than 40 and selected from the group consisting of soap-forming acids, soap-forming esters and mixtures thereof, and an aqueous solution of alkali metal hydroxide, said alkali metal hydroxide being in excess of the stoichiometric amount required to saponify said soap-forming material, dehydrating said mixture and digesting said saponified and dehydrated reaction mass at an elevated temperature of 300 to 390° F. at an elevated pressure of 50 to 120 p. s. i. g. for a period of at least 5 hours, cooling and drawing said reaction mixture.

9. A process according to claim 8 in which digestion of the saponified dehydrated reaction mixture is effected at a temperature of 340 to 365° F.

10. A process according to claim 8 in which digestion of the reaction mixture is effected at a pressure between 70 and 110 p. s. i. g.

11. A process according to claim 8 in which said olefinic soap-forming material has an iodine number higher than 90.

12. A process according to claim 8 in which the excess alkali metal hydroxide is approximately 1 to 3 per cent of the final calculated grease composition.

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