

# UNITED STATES PATENT OFFICE

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## PROCESS FOR PREPARING ALKALI METAL GREASES

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This invention relates to novel alkali metal greases which are characterized by high dropping point and outstanding performance over a wide temperature range.

This application is a continuation-in-part of our copending application, Serial No. 192,376, filed October 26, 1950, and entitled Process for Preparing Alkali Metal Greases, wherein there is disclosed a novel procedure for preparing the wide temperature range alkali metal greases of this invention. The procedure disclosed in the afore-identified parent application involves saponification of a mixture of mineral oil, alkali metal hydroxide and soap-forming material, 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. This application involves the novel alkali metal greases prepared by the procedure disclosed in the parent application.

The novel alkali metal greases of this invention are prepared by digesting at a 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 a dehydrated reaction mixture comprising 15 to 25 per cent alkali metal soaps of a fatty material having an iodine number of at least 40, 60 to 80 per cent mineral oil and 1 to 3 per cent alkali metal hydroxide. Additives may comprise 1 to 10 per cent of the alkali metal greases of this invention and are added to the grease composition after the elevated temperature-air pressure digestion. 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.

The alkali metal greases of this invention are important additions to the field of commercial greases. The high dropping points and good low temperature torque properties of the alkali metal greases of this invention adapt them for use over a wide temperature range. The sodium and lithium greases of this invention are particularly useful commercial greases. Sodium base greases of the composition prescribed in this invention are buttery-type greases with dropping points over 500° F. The preparation of alkali metal greases characterized by the aforesaid properties represents a significant advance in the art of grease making.

Naphthene base oils or paraffin base oils can be employed to prepare novel alkali metal greases.

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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 0.25 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 novel alkali metal greases 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 mineral oil content of the novel greases of this invention comprise 60 to 80 per cent of the total calculated grease composition. Advantageously, the mineral oil content comprises approximately 65 to 75 per cent of the total grease composition.

The alkali metal greases of the invention can be prepared from 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 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 which are commercially known as "Snodotte acids." A 3 to 1 menhaden oil-Snodotte acid mixture has proven particularly useful as a soap-forming stock. Commercially available "Snodotte acids" have approximately the following stated composition:

	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 preparation of greases of this invention. Advantageously, the soap-forming material has an iodine number higher than 90.

The soap-forming material of this invention is ordinarily employed in such amounts that the alkali metal soap content of the final grease composition comprises approximately 15 to 25 per cent of the total grease composition. Ordinarily the soap content of the grease is within the range of 18 to 22 per cent.

The excess alkali metal hydroxide content of the alkali metal greases of this invention amounts to approximately 1 to 3 per cent of the final calculated composition of the grease. Advantageously, the stoichiometric quantity of caustic required to neutralize the soap-forming material 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. As disclosed in the above-identified parent application, the preferred procedure involves the addition of the stoichiometric caustic plus more than half, and preferably 70 to 90 per cent, of the excess caustic prior to saponification; remaining excess caustic is added after the high temperature-air pressure digestion. Alkali metal hydroxide is advantageously added to the reaction mixture in the form of a saturated aqueous solution.

The novel greases of this invention may be prepared from all alkali metal hydroxides and the resulting greases are characterized by wide temperature range properties; the sodium and lithium base greases possess exceptionally high dropping points and good low temperature torque properties.

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 during the cooling of the grease to impart water resistance.

The saponification procedure employed in manufacturing the greases of 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 material 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 may be added to-

gether 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 20 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 250 and 330° 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 manufacture of the greases of this invention is illustrated in Examples I and II wherein sodium base and lithium base greases are prepared.

#### Example I

A mixture of 578 pounds of SAE grade 20 paraffinic mineral lubricating oil fraction, 28 pounds of a pale oil solution containing 30.5 weight per cent sodium petroleum mahogany sulfonate and 387 pounds of a 3 to 1 mixture of menhaden oil-Snodotte acids were charged to a kettle. This mixture was heated to 150° F. At 150° F. 185 pounds of 49.7 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

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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. at which time 797 pounds more of paraffinic SAE 20 lube oil were added 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 110 pounds per square inch. The reaction mixture was stirred in the pressure kettle at a temperature of 340 to 365° F. and under an air pressure of 70 to 110 pounds per square inch for approximately 18 hours. At the end of this time the air pressure was shut off, the head removed from the kettle and 100 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, 11.8 pounds of 49.7 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.; 20 pounds of diphenylamine 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.....	68.7
Aluminum stearate, per cent.....	5.0
Sodium petroleum mahogany sulfonate, per cent.....	1.4
Diphenylamine, per cent.....	1.0
Aniline yellow dye.....	0.004

The properties of the grease thus prepared are as follows:

Appearance.....	Orange glossy, short fiber.
Dropping point, ° F.....	500+.
Unworked pene.....	286.
Worked pene.....	277.
Low temp. torque:	
Sec./rev. at—	Cw.—Ccw.
0° F.....	2.0—1.4.
-10° F.....	6.6—4.0.
-20° F.....	15.8—19.6.
-30° F.....	62.4—45.2.
-40° F.....	>120—>120.
Dynamic water resistance, per cent loss.....	21—42.
Norma Hoffman oxidation, lb./drop in 500 hr.....	12—12.
Working stability AN-G-25—penetration after 100,000 strokes.....	354.
Grease breakdown room to 300° F.:	
Lubrication.....	Channeled to 250° F. then fed in.
Texture.....	No change.
AN-G-25 Cu corrosion.....	Passes.
Mean Hertz load.....	24.
High temperature performance—hours to failure at 250° F.....	1200.

#### Example II

A mixture of 16 pounds of a paraffinic mineral lubricating oil fraction of an SAE 20 grade, 0.9 pound of sodium petroleum mahogany sulfonate, and 11.6 pounds of a 3/1 mixture of menhaden

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oil-Snodotte acids, 20.5 lbs. of a 10.2% solution of lithium hydroxide and 6 grams of a methyl silicone (Dow Corning Anti-Foam A) were charged to a kettle. The reaction mixture was stirred in the kettle at a temperature of 150–200° F. for approximately 1 hour with the resulting saponification of the soap-forming materials present in the reaction mass. The reaction mixture was then slowly raised to a temperature of 300–330° F., in order to dehydrate the reaction mixture, at which time 25.9 pounds more of paraffinic SAE 20 lube oil were added. 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 70–80 pounds per square inch. The reaction mixture was stirred in the pressure kettle at a temperature of 340–350° F. and under an air pressure of 70–80 pounds per square inch for approximately 15 hours. At the end of this period the air pressure was shut off, the head removed from the kettle and 2.84 pounds 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 1.6 pounds of 10.2% lithium hydroxide solution were added to the reaction mixture at a temperature of approximately 300° F. 0.57 pounds of diphenylamine dissolved in 0.79 pound of SAE 20 grade paraffinic mineral lubricating oil was added at 250° F. The grease was then drawn from the kettle at 200° F. and pumped through 3–60 mesh screens into containers. The lithium grease thus prepared had the following calculated composition:

Li 3:1 menhaden oil-per cent Snodotte acid soap.....	20.2
Excess alkali in charge.....	1.9
Added later.....	0.3
Glycerin.....	1.5
Paraffinic mineral oil SAE.....	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:

Appearance.....	Brown, glossy, short fiber.
Dropping point, ° F.....	488–500+.
Unworked pene.....	119.
Worked pene.....	172.
Low temp. torque:	
Sec./rev. at—	0° F.....
0° F.....	3.3—3.4.
-10° F.....	10.5—8.0.
-20° F.....	52.7—22.5.
-30° F.....	>120—>120.
-40° F.....	.....
Dynamic water resistance, percent loss.....	0.2—2.5.
Norma Hoffman oxidation, lb./drop in 100 hr.....	20—23.
Working stability AN-G-25—penetration after 100,000 strokes.....	191.
Grease breakdown room to 300° F.:	
Lubrication.....	Channeled throughout test.
Texture.....	No change.

The foregoing examples illustrate the excellent wide temperature range ball and roller bearing alkali metal greases of this invention. The high dropping points and the good low temperature torque properties are particularly significant. The wide temperature range ball and roller bearing alkali metal greases of this invention find a wide variety of uses because of their excellent properties.

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. Lubricating greases comprising mainly a dehydrated mixture of 15 to 25 per cent alkali metal soaps of a soap-forming material having an iodine number of at least 40, 60 to 80 per cent mineral oil and 1 to 3 per cent alkali metal hydroxide, said mixture having been subjected to digestion at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch for at least 5 hours.

2. Lubricating greases of the type described in claim 1 wherein the dehydrated mixture is subjected to digestion at a temperature of 340 to 350° F. and an air pressure of 70 to 90 pounds per square inch for a period of at least 5 hours.

3. Lubricating greases comprising a dehydrated mixture of 15 to 25 per cent alkali metal soaps of a soap-forming material having an iodine number of at least 40, 60 to 80 per cent mineral oil, 1 to 3 per cent alkali metal hydroxide and 1 to 10 per cent additives, said mixture of said alkali metal soaps, said mineral oil and said metal hydroxide having been subjected to digestion at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch for a period of at least 5 hours, and said additives having been incorporated in said grease after said digestion.

4. A grease of the type described in claim 3 wherein sodium soaps are employed.

5. A grease of the type described in claim 3 wherein lithium soaps are employed.

6. Lubricating greases comprising mainly a dehydrated mixture of 15 to 25 per cent alkali metal soaps of a soap-forming material having an iodine number of at least 90, 60 to 80 per cent paraffinic base mineral oil, 0.5 to 3 per cent petroleum mahogany sulfonate salt and 1 to 3 per cent alkali metal hydroxides, said dehydrated mixture having been subjected to digestion at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch for a period of at least 5 hours.

7. A grease of the type described in claim 6 wherein the soap-forming material comprises a 3 to 1 mixture of menhaden oil and hydrogenated fish oil fatty acids.

8. Lubricating greases comprising mainly a dehydrated mixture of 15 to 25 per cent alkali metal soaps of a soap-forming material having an iodine number of at least 90, 60 to 80 per cent paraffinic base mineral oil, 0.5 to 3 per cent petroleum mahogany sulfonate salt, 1 to 3 per cent alkali metal hydroxide and 1 to 10 per cent additives, said mixture of alkali metal soaps, paraffinic mineral oil, petroleum mahogany sulfonate salt and alkali metal hydroxide having been sub-

jected to digestion at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch for a period of at least 5 hours and said additives having been incorporated in said grease after said digestion.

9. A grease of the type described in claim 8 wherein the additives are diphenylamine and aluminum stearate.

10. Lubricating greases comprising a dehydrated mixture of 15 to 25 per cent sodium soaps of a 3 to 1 mixture of menhaden oil and hydrogenated fish oil fatty acids, 60 to 80 per cent SAE grade 20 paraffinic mineral oil, 0.5 to 3 per cent sodium petroleum mahogany sulfonate, 1 to 3 per cent sodium hydroxide, 3 to 7 per cent aluminum stearate and 0.5 to 2 per cent diphenylamine, said mixture of sodium soap, mineral oil, sodium petroleum mahogany sulfonate and a major portion of said sodium hydroxide having been subjected to digestion at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch for at least 5 hours, and said diphenylamine, aluminum stearate and a minor portion of sodium hydroxide having been incorporated in said grease after said digestion.

11. A grease of the type described in claim 10 in which approximately 85 per cent of the sodium hydroxide was added prior to digestion.

12. Lubricating greases comprising a dehydrated mixture of 15 to 25 per cent lithium soaps of a 3 to 1 mixture of menhaden oil and hydrogenated fish oil fatty acids, 60 to 80 per cent SAE grade 20 paraffinic mineral oil, 0.5 to 3.0 per cent sodium petroleum mahogany sulfonate, 1 to 3 per cent lithium hydroxide, 3 to 7 per cent aluminum stearate and 0.5 to 2.0 per cent diphenylamine, said mixture of lithium soap, mineral oil, sodium petroleum mahogany sulfonate and a major portion of said lithium hydroxide having been subjected to digestion at a temperature of 300 to 390° F. and at an air pressure of 50 to 120 pounds per square inch for about 18 hours, and said diphenylamine, aluminum stearate and a minor portion of lithium hydroxide having been incorporated in said grease after said digestion.

13. A grease of the type described in claim 12 in which approximately 85 per cent of the excess lithium hydroxide was added prior to digestion.

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