

2,712,527

IMPROVED LUBRICATING GREASES CONTAINING DIHYDROXY STEARIC ACID SOAP

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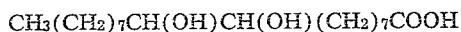
The present invention relates to improved lubricating greases and methods of preparing the same. More specifically, the invention pertains to lubricating greases containing as a grease thickener a complex soap of dihydroxy-stearic acid and a low molecular weight aliphatic carboxylic acid having not more than 5 carbon atoms per molecule.

Prior to the present invention it has been found that high molecular weight hydroxy fatty acids are desirable starting materials for the production of suitable water-insoluble soaps useful as grease thickeners. A typical example is 12-hydroxy-stearic acid and, more particularly, its lithium soap. However, attempts to produce satisfactory water-insoluble greases on the basis of other hydroxy-stearic acids particularly dihydroxy-stearic acid as the basis for the grease thickener have not been too successful.

When the lithium soap of dihydroxy-stearic acid is incorporated in grease making proportion into mineral or synthetic ester-type lubricating oils, the resultant greases while exhibiting some structure are soft and tend to separate oil readily. On application of mechanical stresses, these products break down to soft fluid masses. The present invention overcomes this disadvantage.

It has now been found that dihydroxy-stearic acid may be converted into soaps of excellent thickening properties imparting to the grease highest structural stability under mechanical stresses, by co-neutralization of the dihydroxy-stearic acid and a low molecular weight aliphatic carboxylic acid with a suitable soap-forming metal base.

Dihydroxy-stearic acid has the formula



Some of the hydroxyl groups may be in other than 9 and 10 positions but the 9,10 isomers unquestionably predominate. Acids of this type which are suitable for the purposes of the invention may be prepared in any conventional manner, for example by oxidation of unsaturated acids with alkaline potassium permanganate; treatment of unsaturated acids with HOCl ; etc.

However, in accordance with a preferred embodiment of the invention the dihydroxy-stearic acid is prepared by a condensation reaction with hydrogen peroxide. This reaction may be carried out in the presence of a low molecular weight aliphatic carboxylic acid to form an ester acid which may be readily converted into the desired complex soap as will appear more clearly hereinafter. Normally the dihydroxy-stearic acid and the low molecular weight acid are neutralized in equimolecular proportions. However, the low molecular weight acid may be present in smaller and larger proportions, mol ratios in the range of 1:1 to 3:1 of low to high molecular weight acids being preferred.

The low molecular weight acids to be combined with dihydroxy-stearic acid to form the complex soap thickener of the invention may be any aliphatic carboxylic acid having 1-5 carbon atoms per molecule, such as formic, acetic, propionic, butyric, valeric, furoic, acrylic acids, etc. The preferred low molecular weight acids

are formic and acetic acids. These acids may be obtained in any conventional manner. However, these acids are usually present in the process in which the dihydroxy acid is formed and they can be utilized as such at a considerable cost saving.

Metal bases suitable for the formation of complex soaps in accordance with the invention include the hydroxides of alkali, alkaline earth and certain other metals, such as lithium, sodium, potassium, calcium, barium and aluminum. However, lithium hydroxide which forms complex soaps of satisfactory water solubility, greatest stability and high dropping point is the preferred neutralizing agent of the invention.

Regarding suitable lubricating oil bases for greases containing the complex soap thickener of the invention, mineral as well as synthetic lubricating oils may be used including diesters, complex esters and hydrocarbon polymers having lubricating oil characteristics. It has been found that the solubility and recrystallization characteristics of the complex soaps of dihydroxy-stearic acid and low molecular weight fatty acids are particularly satisfactory in polar solvents, such as the synthetic oils of the di-ester type of which di-2-ethylhexyl sebacate is an outstanding example. Other synthetic lubricating oils of the polar type and similar utility for the purposes of the invention include complex esters prepared from dibasic acids, glycols and monobasic acids, such as those described in U. S. Patent Nos. 2,575,195 and 2,575,196 of Paul V. Smith, Jr. Polar synthetic lubricating oils of this general type are the preferred dispersing agents for the grease thickeners of the present invention.

Although non-polar oils, such as most mineral oils, and hydrocarbon polymers have inferior solvent power for complex soaps of dihydroxy-stearic acid and low molecular weight fatty acids they may serve as lubricating oil bases for greases in accordance with the invention. It has been found that excellent greases having good structural stability may be prepared from these non-polar oils with the complex soaps of the invention provided the thickener contains, in addition to the complex soap, a simple soap of a high molecular weight fatty acid, particularly of stearic acid. Lithium stearate is preferred for this purpose. The ratio of simple soap to complex soap may be about 0.5:1 to about 3:1 and is preferably about 1:1 to 2:1.

Greases in accordance with the invention are normally prepared by preforming the complex soap thickener and incorporating the same in the lubricating oil in grease making proportions of about 10-40 wt. per cent. For this purpose, the dihydroxy-stearic acid may be melted in water at temperatures of about 130°-180° F. The low molecular weight acid may then be added to the liquid mass. The combined acids may be co-neutralized with a boiling aqueous solution of metal hydroxide. Usually a slight excess of the metal base, say about 0.25-2.0% over that theoretically required for complete neutralization is employed. The soap formed is dried at temperatures below the fusion point of the soap, say about 180°-250° F.

As indicated above, the complex soaps of the invention may also be made from ester acids obtained in the preparation of the dihydroxy-stearic acid from oleic acid. When employing this preferred procedure, oleic acid is condensed with hydrogen peroxide in a solution of the low molecular weight acid desired. The hydrogen peroxide is added slowly in small increments which prevents the temperature from rising above about 120° F. The mixture is heated for 1-5 hours at about 100°-120° F. At these conditions the oleic acid is converted into a monoester of dihydroxy-stearic acid with the low molecular weight acid used. A small portion of the oleic acid remains unchanged and another small portion

is converted into by-product acids of unknown composition. The presence of these acids does not interfere with the utility of the product for grease making purposes, particularly when the grease is heated to temperatures of about 480°–550° F. after the soap addition.

The total reaction product may be freed of excess low molecular weight acid by extraction with ether and water washing of the extract. Instead of extracting the reaction product with ether, it is often more convenient and more economical to remove the excess of low molecular weight acid from the reaction mixture by topping under reduced pressure. The residual material may then be used in the grease making process. The isolated monoester acid is hydrolyzed and neutralized with a metal base at temperatures of about 150°–250° F. and an amount of metal base sufficient to neutralize the high molecular and low molecular weight acids formed. Preferably a slight excess of the metal base is employed.

In accordance with a modification of this embodiment of the invention, diesters of the dihydroxy-stearic acid-low molecular weight acids as obtained in the hydroxylation reaction, may be converted into complex soaps by simply reacting the ester with sufficient metal hydroxide to hydrolyze the ester and to react with the low molecular weight acid and the dihydroxy-stearic acid, thus forming the combined soaps.

While preforming of the complex soap is the preferred procedure, it is noted that the complex soaps may also be formed in the lubricating oil base in situ, particularly when non-saponifiable oils, such as mineral oils or non-hydrolyzable synthetic oils are used. For this purpose, the ester of the dihydroxy-stearic acid is dissolved in a portion of the mineral oil (or synthetic oil base) and reacted at 200° F. with an aqueous solution of the metal hydroxide. When saponification is complete, the balance of the lubricating oil fluid is added and the soaps formed are dispersed.

Other conventional grease additives, such as anti-oxidants, particularly amino compounds, extreme pressure agents containing sulfur, halogen and/or phosphorus, etc., may be added to the grease in any conventional manner.

The invention will be further illustrated by the following experiments.

PREPARATION OF MONO-FORMIC ESTER OF DIHYDROXY-STEARIC ACID

A 3-way flask equipped with a stirrer, a return condenser and a thermometer, was charged with 400 gms. of oleic acid (technical), and 800 cc. of formic acid. The mixture was heated to 40° F., whereupon 70 gms. of 90% hydrogen peroxide was added drop by drop by means of a dropping funnel. Considerable amount of heat was evolved so that external cooling had to be applied from time to time in order to keep the reaction temperature below 120° F. The mixture was then heated at 100°–120° F. for 3 hours. At the end of the reaction the product consisted of two layers. Without any attempt to separate the two layers, the reaction product was treated with three volumes of water and was then extracted with ether. The ether extract was washed several times with water in order to remove the excess of formic acid, and was finally dried over sodium sulfate. On removal of the ether from the extract, an almost colorless oil was obtained which solidified partly on standing at room temperature. This crude material (Product A) weighed 480 gms. The combining weight of the crude material was found to be 155.7 mg. KOH/gm., which compares favorably with the calculated combining weight of 172 for the mono-formic ester of dihydroxy-stearic acid.

PREPARATION OF DIHYDROXY-STEARIC ACID

The unpurified mono-formic ester of dihydroxy-stearic acid obtained as described above was hydrolyzed by

treating with alcoholic potassium hydroxide and the products were acidified in order to free the acids. The crude acids obtained in this manner weighed 431 grams. They were extracted twice with ethyl ether. The ether-insoluble dihydroxy-stearic acid (Product B) thus obtained melted at 194° F. and weighed 202 grams.

The ether mother liquors obtained in the dihydroxy-stearic acid purification were evaporated to dryness. The residue consisted of a semi-solid light colored product almost completely insoluble in petroleum ether. This crude by-product (Product C) comprised a major proportion of unknown organic acid and a minor proportion of dihydroxy-stearic acid.

The methods and products described above were used in the preparation of greases in accordance with the invention as illustrated in the following specific examples.

Example I

A lithium dihydroxy-stearate grease was prepared in a synthetic oil base stock using the following ingredients:

	Wt. per cent
Lithium soap of dihydroxy-stearate	20.0
Di-2-ethylhexyl sebacate	80.0

PREPARATION

The lithium dihydroxy-stearate was prepared by mixing 200 gms. of dihydroxy-stearic acid (Product B) dispersed in 400 gms. water with 26 gms. lithium hydroxide mono-hydrate (10% aqueous solution) and heating to 200° F. The wet solid soap formed was then dried on the steam bath and the dry soap ground to a fine powder.

The dry preformed soap was mixed with the ester lubricating oil and heated, while mixing, to 400° F. A portion of the molten grease was cooled rapidly in shallow pans, while the other portion was cooled rather slowly within a time of about 4 hours. On cooling, both greases were very soft and, on stirring, readily broke down to semi-fluid products with appreciable separation of fluid.

Example II

A grease was prepared using as thickener the complex lithium soap of acetic acid and of the by-product acid (Product C) obtained in the treatment of oleic acid with hydrogen peroxide. The lubricating oil base stock employed was the synthetic oil di-2-ethylhexyl sebacate. The soap was prepared from the following ingredients.

	Wt. per cent
By-product acid (Product C)	60.00
Glacial acetic acid	30.00
LiOH—H ₂ O	10.00

The by-product acid was charged to a small grease making kettle and heated to 150° F. in 2 volumes of water. When the acid was completely melted, the glacial acetic acid was added and the combined acids co-neutralized with a boiling water solution of the lithium hydroxide (10%). The soap formed was dried out, and the final small quantity of moisture was removed on a steam bath to prevent fusing.

GREASE PREPARATION

Ingredients:	Weight per cent
Above complex soap	10.0
Di-2-ethylhexyl sebacate	89.0
Phenyl alpha-naphthylamine	1.0

The dry soap and ester were stirred together in the grease kettle first without heating. The mixed soap-ester slurry was then heated, while stirring, to 480° F. The fluid product was hazy. The grease was cooled in two portions. One portion was cooled rapidly in a thin layer. The cooled product was soft and fluid, and no solid grease structure was formed. The other portion was cooled slowly and the product had a semi-fluid structure of little stability.

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The above batch was repeated, heating the grease to 520° F. At this temperature most of the haziness in the fluid molten grease was removed. The inhibitor was added and the grease slowly cooled. Excellent firm structure resulted after cooling. The smoothness of the grease was further considerably improved by subsequent homogenization. After milling in the Morehouse mill, the grease was of excellent uniform appearance.

Properties:

Penetrations, 77° F. mm./10—	
Unworked	285
Worked 60 strokes.....	310
Worked 80,000 strokes.....	315
Dropping point, °F.....	456
Water solubility.....	(1)
Norma-Hoffman oxidation—	
5 p. s. i. drop in oxygen pressure.....	395
10 p. s. i. drop in oxygen pressure, hours>	510

¹ Insoluble in cold water up to 175° F. water temperature.

Example III

A grease was prepared using as thickener a complex lithium soap derived from the mono-formic ester of dihydroxy-stearic acid. In the preparation of the soap, the ester hydrolyzed giving formic acid and dihydroxy-stearic acid, and these were co-neutralized giving the complex lithium formate-lithium dihydroxy-stearate soap. The unpurified mono-formic ester described earlier as Product A was employed in making the soap, using the following quantities of ester and saponifying agent:

	Wt. per cent
Monoformate ester of dihydroxy-stearic acid (acid No. 395 mg. KOH per gram).....	77
Lithium hydroxide monohydrate.....	23

The mono-ester was melted in 500 c.c. of hot water and, while stirring, a 10% aqueous solution of the lithium hydroxide was added. The resulting complex soap curds out on forming. The material was partially dehydrated by heating in a small fire-heated grease kettle and completely dehydrated on the steam bath. Free alkalinity as NaOH was 0.95% on the finished dry soap.

A grease was prepared as described in Example II from the following ingredients.

Complex Li dihydroxy-stearate—Li formate soap	weight per cent..	10.0
Di-2-ethylhexyl sebacate.....	do.....	89.0
Phenyl alpha-naphthylamine.....	do.....	1.0

Properties:

Penetrations, 77° F. mm./10—	
Unworked	285
Worked 60 strokes.....	290
Worked 100,000 strokes.....	360
Dropping point, °F.....	350
Water washing test, per cent loss.....	None
Norma-Hoffman bomb oxidation—5 p. s. i.	
drop in oxygen pressure, hours.....	425

Example IV

As pointed out above, attempts to thicken mineral oil with the soap of the invention alone were not entirely successful, due to only partial solubility of the soap. However, excellent greases having good structural stability are obtained when only a portion of the thickener consists of the complex soap, the balance of the thickener consisting of lithium stearate. This is demonstrated by the following data.

	Wt. per cent
Complex lithium dihydroxy-stearate-lithium formate in 1:1 mol ratio.....	5.0
Lithium stearate.....	10.0
Naphthenic lubricating oil blend having a viscosity of 40 SSU at 210° F.....	84.0
Phenyl alpha-naphthylamine.....	1.0

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PREPARATION

The complex lithium soaps of dihydroxy-stearic acid and formic acid prepared as described in Example II and the simple soap, separately preformed lithium stearate, were combined and slurried in the lubricating oil and heated, while stirring, to 450° F. Phenyl alpha-naphthylamine was added and the grease drawn into pans for cooling. On cooling the grease was returned to the kettle and stirred to a homogeneous product. This grease may be homogenized or milled before packaging, if desired.

Properties:

Appearance	(1)
Dropping point, °F.....	385
Penetrations, 77° F. mm./10—	
Unworked after homogenization.....	265
Worked 60 strokes.....	270
Structural stability, mm./10—(worked 100,000 strokes fine hole worker 270— $\frac{1}{16}$ " hole plates)	345
Water washing test, per cent loss (AN-G-15 Method)	None
Norma-Hoffman oxidation—5 p. s. i. drop in oxygen pressure, hrs.....	245

¹ Excellent, smooth, buttery grease.

The above test results show this grease to have excellent properties.

The present invention is not limited to any theory of the process of grease making or soap production nor to the specific examples set forth above. The relative proportions of the grease constituents may be varied within the limits indicated to obtain greases of different consistency and varying characteristics.

What is claimed is:

1. A lubricating grease comprising a major proportion of a lubricating oil and a minor grease making proportion of a grease thickener containing a metal soap of dihydroxy stearic acid and a metal salt of low molecular weight aliphatic carboxylic acid having not more than 5 carbon atoms, said soap and salt being present in the form of a soap-salt complex and in a mol ratio within the range of about 1 to 3 mols of said low molecular weight aliphatic carboxylic acid salt for each mol of said dihydroxy-stearic acid soap.
2. A grease according to claim 1 in which said low molecular weight acid is formic acid.
3. A grease according to claim 1 in which said low molecular weight acid is acetic acid.
4. A grease according to claim 1 in which said metal is selected from the group consisting of sodium, potassium, calcium, barium and aluminum.
5. A grease according to claim 1 in which said metal is lithium.
6. A lubricating grease comprising a major proportion of a lubricating oil and a minor grease making proportion of a grease thickener containing the coneutralization product of a mixture of dihydroxy-stearic acid and a low molecular weight aliphatic carboxylic acid having not more than 5 carbon atoms, which contains about 1 to 3 mols of said low molecular weight aliphatic carboxylic acid for each mol of dihydroxy-stearic acid.
7. A lubricating grease comprising a major proportion of a polar synthetic lubricating oil and a minor grease making proportion of a grease thickener containing a metal soap metal salt complex formed by coneutralization of dihydroxy-stearic acid and a low molecular weight aliphatic carboxylic acid in a mol ratio ranging from about 1 to 3 mols of said low molecular weight aliphatic carboxylic acid for each mol of said dihydroxy-stearic acid having not more than 5 carbon atoms.
8. A grease according to claim 7 in which said oil comprises a complex ester of a glycol with a mono-basic and a di-basic acid.
9. A lubricating grease comprising a major proportion of a non-polar lubricating oil and a minor proportion of

a grease thickener containing a soap of a high molecular weight fatty acid and a substantial proportion of a metal soap metal salt complex formed by coneutralization of dihydroxy-stearic acid and a low molecular weight aliphatic carboxylic acid, in a mol ratio ranging from 1 to 3 mols of said low molecular weight aliphatic carboxylic acid for each mol of said dihydroxy-stearic acid, and about 0.5 to 3 mols of said high molecular weight fatty acid soap for each mol of said soap-salt complex having not more than 5 carbon atoms.

10. A grease according to claim 9 in which said high molecular weight fatty acid soap is lithium stearate.

11. The process of preparing lubricating greases which comprises melting dihydroxy-stearic acid in water at temperatures of about 130°-180° F., adding to the melt about 1-3 mols of a low molecular weight aliphatic carboxylic acid having not more than 5 carbon atoms for each mol of said dihydroxy-stearic acid, co-neutralizing the combined acids with a boiling aqueous solution of metal hydroxide to form a soap-salt complex and incorporating the latter in grease-making proportions into a lubricating oil.

12. The process of preparing lubricating greases which comprises reacting a mixture of oleic acid and a low molecular weight aliphatic carboxylic acid having not more than 5 carbon atoms with an oxidizing agent to form a reaction mixture containing an ester of dihydroxy-stearic acid with said low molecular weight acid, hydrolyzing said ester, neutralizing the mixture of acids formed with a metal base to form a metal soap metal salt complex and incorporating said complex into a lubricating oil in grease-making proportions.

13. The process of claim 12 in which said reaction mixture contains in addition to said ester unconverted oleic acid and by-product acids and wherein said hydrolization and neutralization are carried out in the presence of said unconverted oleic acid and by-product acids, sufficient metal base being used substantially to neutralize said unconverted oleic acid and by-product acids to form addi-

tional soaps, said additional soaps being incorporated into said lubricating oil together with said complex.

14. The process of claim 13 in which a low molecular weight acid is added to said reaction mixture after said hydrolization and prior to said neutralization.

15. The process of claim 13 in which said grease containing said complex and additional soaps is heated to temperatures of about 480°-550° F.

16. The process of claim 12 in which said hydrolization and neutralization are carried out in the presence of at least a portion of said lubricating oil.

17. The process of claim 12 in which said ester comprises a mono-ester of dihydroxy-stearic acid with said low molecular weight acid.

18. The process of claim 12 in which said ester comprises a di-ester of dihydroxy-stearic acid with said low molecular weight acid.

19. The process of claim 12 in which said oxidizing agent is hydrogen peroxide.

20. The process of claim 12 in which unreacted low molecular weight acid is removed from said reaction mixture prior to said neutralization.

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