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SHEAR-RESISTANT GREASE

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This invention relates to improved lubricating grease compositions and particularly to texture-stable grease compositions in which a synthetic oleaginous compound comprises part or all of the oil component.

Recent developments in the production of lubricating greases and particularly those designed for specialty equipment employing sealed bearings and operating over wide temperature ranges, have lead to the use of a number of organic chemical compounds as substitutes for the conventional mineral lubricating oils. These oleaginous compounds offer a marked advantage over the mineral oils in that they possess a comparatively uniform viscosity over a wide temperature range and are not as susceptible to evaporation loss as a comparable viscosity mineral oil. These features are particularly desirable and have been used to advantage in the production of greases used in sealed life-time bearing installations and low temperature greases used in aircraft controls and the like. However, one undesirable characteristic of these so-called synthetic greases is their lack of resistance to shear. Under conditions of operation where high shearing stresses are involved, such as in ball and roller-bearing lubrication, the structure of these greases gradually breaks down and their consistency falls off until they become liquid or semi-liquid. At this point the greases no longer adhere to the lubricating surfaces and bearing failures result.

In accordance with the present invention it has been found possible to produce a synthetic grease composition which possesses not only the desirable characteristics imparted by the oleaginous compounds, but is also resistant to shear. The synthetic greases previously proposed and accepted by the industry have been prepared from the metal soaps of the conventional fatty acid sources, such as stearic acid and other soap-forming fatty acids or their glycerides. It has been discovered that the acid component of the metal soap is an important factor in the production of synthetic greases and that synthetic greases produced from metal soaps of soap-forming hydroxy fatty acids or their glycerides possess exceptional texture-stability and maintain their structure with little change in consistency even after extensive working at either high or low temperatures.

This unusual characteristic of the metal soaps of hydroxy fatty acids is applicable to those grease compositions in which a synthetic oleaginous compound comprises part or all of the oil component. The term "synthetic oleaginous compound" as used herein embraces those organic

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compounds or mixtures thereof which possess lubricating qualities and may be substituted in whole or in part for the conventional mineral lubricating oils. The choice of the particular

5 compounds used in the preparation of the synthetic grease depends upon the type of lubrication and the temperature range within which the grease is intended to be operated. In general, these compounds are adapted to specialized lubrication outside the conventional lubricating temperature ranges, such as ultra low temperature operation found in refrigeration systems and arctic service lubrication, or to general purpose lubrication over a wide lubricating temperature range which was previously unattainable through the use of a single mineral lubricating oil due to their high viscosity change over such wide temperature ranges.

As a general proposition, certain factors are prerequisite in the compounds falling within the category of synthetic oleaginous compounds. These compounds are necessarily chemically and physically stable liquids at the temperatures of operation and possess a minimum viscosity of 0.5 centistoke within the lubricating temperature range. Furthermore, the vapor pressure of these compounds in the lubricating temperature range are substantially negligible, although under conditions of flooded lubrication, where evaporation loss is not too critical, compounds of measurable vapor pressure may be used.

Inasmuch as the primary requisites of the oleaginous compounds are physical in nature, they cannot be conclusively defined in terms of their chemical structure. However, the majority of these compounds are polar compounds with oxygen as the principal type of polar constituent. Another general observation is that, in the compounds of a given chemical classification, those of comparatively high molecular weight possess the least change in viscosity per change in temperature. The types of compounds which are recognized or have been proposed as synthetic oleaginous compounds include the aliphatic ethers, aromatic acid esters, aliphatic mono- and di-carboxylic acid esters, phosphorus acid esters, and halogenated aromatic compounds. For the purposes of the present invention and as illustrative of the synthetic oleaginous compounds contemplated by the invention, those compounds falling within the category of aliphatic dicarboxylic acid esters are preferred. The compounds within this particular class are the esters of such acids as sebacic, adipic, pimelic, azelaic, alkenylsuccinic, alkylmaleic, etc. The esters thereof are

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preferably the aliphatic esters and particularly the branched chain aliphatic esters. Specific examples of the preferred oleaginous compounds are di-2-ethylhexyl sebacate, di-sec-amyl sebacate, di-2-ethylhexyl alkenylsuccinate, di-2-ethoxyethyl sebacate, di-2-(2'-methoxyethoxy) ethyl sebacate (di-methylcarbitol sebacate), di-2-(2'-ethylbutoxy) ethyl sebacate, di-2-butoxyethyl azelate (di-butylcellosolve azelate), di-2-(2'-butoxyethoxy) ethyl alkenyl succinate (di-butylcarbitol alkenylsuccinate), triethylidene sorbitol, di-2-butoxyethyl alkenyl succinate (di-butylcellosolve alkenylsuccinate), etc.

These oleaginous compounds may be used as the sole oil component of the greases or they may be blended with a mineral lubricating oil as desired. In some instances where the soap component is to be formed in situ it is desirable to conduct the saponification in the presence of mineral oil which is inert to the reaction and then add the oleaginous compound. This would result in the combination of mineral oil and oleaginous compound as the oil component of the finished grease. Furthermore, various addition agents may be incorporated with the oleaginous compounds to impart other desirable characteristics. Thus, an extreme pressure agent may be incorporated to improve the anti-wear characteristics of the compound or an antioxidant may be incorporated to improve the antioxidant properties of the compound and/or the finished grease.

The metal soaps which have been found to contribute to the desirable attributes of the synthetic greases are those in which a soap-forming hydroxy fatty acid constitutes at least part of the acid component. The soap-forming hydroxy fatty acids contemplated herein are those containing at least 12 carbon atoms in the molecule and one or more hydroxyl groups separated from the carboxyl group by at least one carbon atom, as well as mixtures thereof. These hydroxy fatty acids may be obtained from natural sources, such as castor oil, or may be prepared by the classical synthetic methods, such as oxidation of unsaturated fatty acids or catalytic oxidation of petroleum oils and waxes with extraction and fractionation to the desired molecular range. In the practice of the invention, as described herein, 12-hydroxy stearic acid and hydrogenated castor oil will be used as the representative types of hydroxy fatty acids and their glycerides. These acids are preferred because of their advantage of availability and cost which renders them competitive to the conventional fats and fatty acids.

The soap-forming hydroxy fatty acids may be used as the sole acidic component of the metal soaps or they may be blended or combined with the conventional fats or fatty acids in such proportions that at least 50% of the total acidic component is comprised of the hydroxy fatty acids. The choice of fats or fatty acids and the specific proportion thereof which may be blended or combined with the hydroxy fatty acids depends upon the particular metallic constituent and the type of service for which the synthetic grease is intended. In general, any of the recognized fatty acid materials normally used in grease manufacture may be used providing they are essentially saturated in character. These fats and fatty acids include mixtures of fatty acid glycerides found in naturally-occurring fats and oils, together with fractionated components thereof. The fatty acids may be a mixture of acids split

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off from these fats or prepared from hydrogenation of fish oils, etc., or the individual acids themselves.

The metallic constituent of the soaps of hydroxy fatty acids may be any of the metals normally used in the production of thickening agents for lubricating oils, such as Na, Li, Ca, Ba, Al, etc., as well as mixtures thereof. In many respects, the choice of the metallic constituent is dependent upon the physical properties desired in the finished grease, such as dropping point, water resistance, texture, etc. For the purpose of the present invention the metals preferred are the alkali metals, sodium and lithium.

The choice of the particular methods of manufacture applicable to the production of the synthetic greases of the invention will depend upon the type of oleaginous compound used and whether or not mineral oil is to be used as part of the oil component. The conventional method of preparing synthetic greases is the gelling method in which the preformed metal soap and the oleaginous compound are heated to a homogeneous solution and rapidly cooled to form the grease gel. This method of preparation possesses certain disadvantages in that it requires a preformed metal soap which in and of itself raises the cost of the grease because of the separate saponification step required and extensive milling equipment to work the grease gel to a homogeneous consistency. However, in preparing the greases of the invention other methods of manufacture, conventional to the grease industry, may be used. A particular advantage in the use of metal soaps of hydroxy fatty acids is the fact that the high temperatures required by the conventional gelling methods may be avoided and the preparation conducted at temperatures around 300° F. or at least those attained in a steam-heated kettle and the finished grease drawn from the kettle without requiring homogenization. Furthermore, saponification in situ is possible either in the presence of mineral oil or a synthetic oleaginous compound which is inert to the saponification reaction.

The following examples are presented as illustrating the preparation of representative synthetic greases falling within the scope of the present invention. It is to be understood, however, that these examples are merely illustrative and not definitive of the invention and as such may be modified within the scope of the invention as previously defined in accordance with the skill of the art.

Example I

A steam-heated kettle equipped with stirring mechanism was charged with 16.8 pounds of 10.4% lithium hydroxide solution and 9.0 pounds of water. Stirring was started at 35 R. P. M. and the lithium hydroxide solution heated to 180° F. 16.2 pounds of hydrogenated castor oil (Titer—74.6° C., Sap. No.—183, hydroxyl value—165) and 22.6 pounds of a mildly refined mineral oil were then added. The kettle contents were held at 170–190° F. for four hours and 5.52 pounds of triple pressed stearic acid were added. The temperature was then maintained at 186–190° F. for an additional hour and the kettle shut down over night. After standing over night stirring at 35 R. P. M. was begun and the saponification mixture dehydrated at 290–312° F. for four hours. At this point the soap had a very light tan color. The heat was then reduced and 12.2 pounds of mineral oil were added. The physical tests on the

mineral oil and synthetic oleaginous compound are as follows:

	Mineral Oil	Di-2-Ethylhexyl Sebacate
Flash, COC ° F	300	418
Fire, COC ° F	325	500
Viscosity Kinematic at 100° F. cs.	7.73	12.26, 12.74
Viscosity Kinematic at 210° F. cs.	2.08	3.24, 3.30
Viscosity Index	63	153, 155

At 236° F. 160 grams of triple-pressed stearic acid were added to render the grease slightly acidic. 26 pounds of di-2-ethylhexyl sebacate were then added slowly. At approximately 190° F. 36.60 pounds of additional di-2-ethylhexyl sebacate were added and during the addition of the ester 196.3 grams of phenyl alpha naphthylamine were added simultaneously. At this point the grease contained approximately 15% soap and possessed an ASTM penetration at 77° F. of 301-303 unworked and 317-324 worked. 5 pounds of a blend of 28% mineral oil and 72% sebacate ester and 23 grams of phenyl alpha naphthylamine were then added. The grease was finally drawn at a temperature of 166° F. and pumped through three 60 mesh screens. The product was a light cream-colored buttery grease having the following calculated composition:

	Per cent
Lithium soap (75% hydroxy stearic acid, 25% stearic acid)	13.6
Glycerine	1.0
Mineral oil	23.8
Di-2-ethylhexyl sebacate	60.9
Phenyl alpha naphthylamine	0.5
Free fatty acid	0.2

The foregoing synthetic grease was subjected to a dynamic shear test which was conducted in an apparatus consisting of a perforated piston reciprocating within a closed cylinder maintained at a constant temperature. In the test the grease was charged to the cylinder at a temperature of 225° F., and the piston then reciprocated at 49 strokes per minute for a period of eight hours. At the conclusion of the run the grease was removed and miniature penetrations taken. These miniature penetrations were then compared with the miniature penetrations of the grease taken before the test to determine the effect of the shearing action on the grease structure. The results obtained on the subject grease showed an original miniature penetration of 89 and a final miniature penetration of 113.

A lubricating grease comprising a high molecular weight aliphatic dicarboxylic acid ester as the lubricating base, together with sufficient lithium soap of a soap-forming hydroxy fatty acid or glyceride to thicken said base, and more specifically the grease of the foregoing example, is disclosed and claimed in our co-pending application, Serial No. 615,074, filed September 7, 1945.

Example II

A grease base consisting of the lithium soaps of the combination of 75% hydrogenated castor oil and 25% triple-pressed stearic acid and mineral oil was prepared in accordance with the procedure of Example I. This grease base possessed the following calculated composition:

	Per cent
Lithium soap	47.2
Glycerine	3.5
Mineral oil	49.3

750 grams of the grease base were charged to a kettle and heated with stirring at 234° F. The heat was then reduced and 1020 grams of a dimethyl silicone polymer possessing a flash point above 600° F., with a kinematic viscosity of 82 cs. at 100° F. and 32 cs. at 210° F. were slowly added over a period of six and one-half hours. At this point the temperature was 147° F. and the ASTM control penetration at 77 was 203-210 unworked and 221-223 worked. 1000 grams of additional dimethyl silicone polymer were then added slowly until a control worked penetration of 345 at 78° F. was obtained. The batch was then drawn at a temperature of 176° F. The product was a smooth, light-colored, buttery grease having the following calculated composition:

	Percent
Lithium soap	12.8
Glycerine	0.9
Mineral oil	13.4
Dimethyl silicone polymer	72.9

The subject grease was tested in a so-called grease-breakdown machine wherein a No. 204 anti-friction bearing was packed with the grease and mounted on a motor-driven shaft operating at 3450 R. P. M. and surrounded by a heating jacket. The test was started at room temperature and the bearing gradually heated, while running at a constant speed, until the temperature reached 300° F. During the period of the test the lubricating performance was noted. At the conclusion of the test the grease was removed from the bearing and examined as to change in texture and consistency. The results obtained on the subject grease indicated excellent lubrication, with no appreciable change in texture or consistency of the grease at the conclusion of the test.

In comparison therewith a commercial dimethyl silicone grease was also tested and, although supplying excellent lubrication, the grease became semi-fluid toward the end of the test and drained from the bearing when the test was stopped.

A lubricating grease comprising a liquid silicone polymer within the lubricating viscosity range as the lubricant base, together with sufficient metal soap of a soap-forming hydroxy fatty acid or glyceride, and more specifically the grease of the foregoing example, is disclosed and claimed in our co-pending application, Serial No. 20,606, filed April 12, 1948.

Example III

100 grams of lithium 12-hydroxy stearate and 900 grams of di-2-ethylhexyl sebacate were mixed and heated with stirring. At 350° F. the soap began to dissolve in the ester and at 390° F. was completely in solution. The solution was heated to 400° F. and poured in a thin layer on the bottom of a grease pan, taking care that no thick spots were formed. After cooling, a smooth, buttery gel was formed which showed no signs of separation. The ASTM control worked penetration of the grease gel was 240 at 77° F. The product possessed the following calculated composition:

	Percent
Lithium 12-hydroxy stearate	10
Di-2-ethylhexyl sebacate	90

This grease was tested in the dynamic shear test described in Example I in comparison with a 10% lithium stearate grease containing di-2-

ethyihexyl sebacate as the sole oil component and the results obtained are as follows:

Miniature Penetration	Lithium Hydroxy Stearate	Lithium Stearate
Original.....	126, 130	181.
Final.....	268, 270	Semi-fluid.

Example IV

The kettle was charged with 225 grams of hydrogenated castor oil, 200 grams of mineral oil whose characteristics are set forth in Example I, and 200 grams of water. The mixture was then heated with stirring to 210° F. 88.8 grams of a 45.9% sodium hydroxide solution were then added over a period of one-half hour. At this point the saponification mixture in the kettle was a white, soft dough. Stirring was continued for an additional hour at 186-192° F. and 75 grams of triple-pressed stearic acid added. After stirring for one and one-quarter hours the heat was turned on to dehydrate the soap base at 308° F. and a white, tough, fibrous base was formed. This base was held at 280-308° F. for one-half hour. The heat was then turned off and 142 grams of mineral oil added over a period of one-half hour. When the temperature reached 206° F. 7.8 grams of phenyl alpha naphthylamine and 3.1 grams of triple-pressed stearic acid were added. Thereafter, 877 grams of di-2-ethylhexyl sebacate were added slowly. After the addition of the sebacate ester control ASTM penetrations indicated an unworked penetration of 112 and a worked penetration of 102. 1050 grams of a blend of 71.7% sebacate ester, 27.8% mineral oil and 0.5% phenyl alpha naphthylamine were then added slowly, and at 194° F. a control worked penetration of 376 at 770° F. was obtained. The batch was then drawn and the product obtained was a smooth, buttery, glossy grease of a light color. The calculated composition of the resulting grease was as follows:

	Percent
Sodium soap	12.1
Glycerine	0.8
Mineral oil	24.2
Di-2-ethylhexyl sebacate	62.4
Phenyl alpha naphthylamine	0.5

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 lubricating grease composition comprising as the essential and at least major portion of the lubricating base a high molecular weight high boiling liquid aliphatic dicarboxylic acid ester within the lubricating oil viscosity range and

possessing lubricating properties, and sufficient metal soap of a soap-forming fatty material selected from the group consisting of hydroxy fatty acids and hydroxy fatty acid glycerides to thicken said lubricating base, said grease composition being texture-stable under high shearing stress.

2. A lubricating grease composition according to claim 1, wherein the said aliphatic dicarboxylic acid ester is a branched chain aliphatic diester.

3. A lubricating grease composition according to claim 2, wherein the said diester is a branched chain aliphatic sebacate.

4. A lubricating grease composition according to claim 3, wherein the said ester is di-2-ethylhexyl sebacate.

5. A lubricating grease composition according to claim 1, wherein the metal soap is a sodium soap.

6. A lubricating grease composition comprising essentially a lubricating base consisting of at least a major proportion of an oil-soluble high molecular weight high boiling liquid aliphatic dicarboxylic acid ester within the lubricating oil viscosity range and possessing lubricating properties and not more than a minor proportion of mineral lubricating oil, sufficient metal soap of a soap-forming fatty material containing at least 50% by weight on the basis of the fatty material of hydrogenated castor oil to thicken said lubricating base, glycerine, and a small amount of an oxidation inhibitor.

7. A lubricating grease composition comprising essentially a lubricating base consisting of a major proportion of di-2-ethylhexyl sebacate and a minor proportion of mineral lubricating oil, sufficient metal soap of hydrogenated castor oil to thicken said lubricating base, glycerine, and a small proportion of an oxidation inhibitor.

8. A lubricating grease composition according to claim 7, wherein said metal soap is a sodium soap, and said oxidation inhibitor is phenyl alpha naphthylamine.

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HARRY V. ASHBURN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 40, Example IV, for "770° F." read 77° F.;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of January, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.