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SYNTHETIC LUBRICATING OILS CONTAINING PARAFFINIC RESINS

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This invention relates to new and improved lubricating compositions. Particularly the invention relates to lubricating grease compositions having outstanding properties at high temperatures. More particularly the invention relates to a solid grease lubricant consisting of a blend of a synthetic lubricating oil of the complex ester type and a fluid resin obtained from certain paraffinic crude residuums by propane extraction thickened to a grease consistency with the lithium soap of a high molecular weight substantially saturated fatty acid.

In the lubrication of jet engine bearings which operate at very high temperatures the prior art greases have hitherto been lacking in some instances. In attempts to prepare greases, having the requisite high melting points and having a soap-dispersing fluid with requisite high flash point, grease formulations have been made from synthetic lubricating oils of the diester type exemplified by di-2-ethyl hexyl sebacate have been prepared. However, they have generally proven unsatisfactory for this high temperature use due to low dropping points and too high volatility. Attempts to prepare greases by thickening the complex ester type synthetic oils, such as a synthetic oil prepared by reacting two molar proportions of a half ester of a dibasic acid with one molar proportion of a glycol, have been generally unsuccessful.

It has now been found and forms the object of this invention that a lubricating grease composition having desirably high temperature characteristics may be prepared by blending with a synthetic oil of the diester or complex ester type a high molecular weight resin and thickening the blend with a lithium soap of a high molecular weight fatty acid.

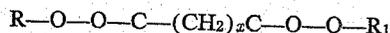
THE SYNTHETIC OIL

The synthetic esters operable in the preferred embodiment of this invention are those esters, distillable or not distillable, which are formed by the interaction of two or more of the following compounds:

1. Monohydric alcohols.
2. Monobasic acids.
3. Dibasic acids.
4. Glycols.
5. Polyhydric alcohols.
6. Polybasic acids.

When at least one polyfunctional alcohol and at least one polyfunctional acid are employed, the resulting ester is known to the art as a complex ester. Diesters of dibasic acids, or single esters of monobasic acids are referred to as simple esters.

Especially preferred among the simple esters are those esters having the formula



where R and R₁ are alkyl groups alike or different and contain from 1 to 20 carbon atoms in a straight or branched chain and where x is an integer from 2 to 10,

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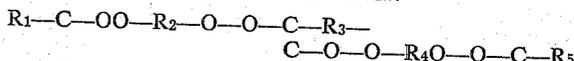
preferably 4 to 8. These esters include those prepared from the following acids:

- Succinic acid.
- Glutaric acid.
- Adipic acid.
- Pimelic acid.
- Suberic acid.
- Azelaic acid.
- Sebacic acid.
- Brassylic acid.
- Pentadecanedicarboxylic acid.
- Tetracosanedicarboxylic acid.

The C₄-C₂₄ alkenylsuccinic acids listed above are prepared by condensing olefins or mixtures of olefins with maleic anhydride.

The complex esters contemplated by this invention are grouped under the following types as follows:

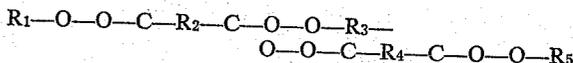
Type I.—Monobasic acid-glycol-dibasic acid-glycol-monobasic acid. This complex ester may be considered to have the following structural formula:



wherein R₁ and R₅ are the alkyl radicals of the monobasic acids; R₂ and R₄ are the alkyl radicals from the glycols; and R₃ is the alkyl radical from the dibasic acid.

The esters of this type are prepared by admixing the calculated amounts of the various compounds and carrying out a straightforward esterification reaction. The reaction conditions are continued with an occasional sample of the product being tested for acidity until the minimum acidity is attained.

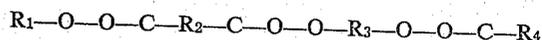
Type II.—Alcohol-dibasic acid-glycol-dibasic acid-alcohol. This material may be represented by the following formula:



wherein R₁ and R₅ are the combining radicals of the alcohol; R₂ and R₄ are the alkyl radicals of the dibasic acids; and R₃ is the alkyl radical of the glycol.

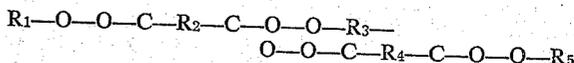
These esters are prepared in the manner similar to those of Type I.

Type III.—Alcohol-dibasic acid-glycol-monobasic acid. These esters are prepared by reacting a dibasic acid and a glycol under such conditions that one hydroxyl group of the glycol combines with one carboxyl group of the dibasic acid, in other words, so that a half ester is formed. This half ester is then reacted with a molar proportion each of an aliphatic alcohol and a monobasic acid. These materials may be said to have the general formula:



wherein R₁ is the combining radical of the aliphatic alcohol; R₂ the alkyl radical of the dibasic acid; R₃ the alkyl radical of the glycol; and R₄ the alkyl radicals of the monobasic acid.

Type IV.—Alcohol-dibasic acid-glycol-dibasic acid-alcohol. These materials may be said to have the type formula:



wherein R₁ and R₅ are the combining alkyl radicals of the alcohol; R₂ and R₄ the alkyl radicals of the dibasic acid; and R₃ is the alkyl radical of the glycol.

It will be noted that the esters of Type IV have the same structural formula as Type II. However, these complex esters are prepared by reacting an alcohol with a dibasic acid under such conditions that a half ester is formed and

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3. It raises the viscosity of the synthetic oils which are somewhat low in viscosity in the extreme temperature range.

4. It replaces the expensive synthetic oil with a material having a decided lower cost, resulting in an obvious economic advantage.

Other advantages will become apparent as the description proceeds.

Standard inspection data on the individual components and a blend in accordance with this invention are set out in the table below:

TABLE
Inspection of fluids

	Di-2-ethyl hexyl Sebacate	Complex Ester ¹	Lt. Resin	Blend, 30% Lt. Resin, 70% Complex Ester
Flash Point (° F.)	420	420	650	455
Vis./210° F. (SUS)	37.5	42.5	443.6	58.2
Vis./100° F. (SUS)	68.9	178		275.6
Viscosity Index	159	150	100	138
Pour Point (° F.)	<-75	<-75	50	0
Bulk Oil Evaporation Test, Percent Evaporation (2 hrs. at 302° F. blowing with N ₂ at rate of 5 liter/min.)	1.5	<0.5	<0.1	<0.1

¹ Made from: 1 mol of polyethylene glycol; 2 mols of sebacic acid; 2 moles of 2-ethyl-hexyl alcohol.

THE THICKENING SOAP

The blend of the synthetic oil and the resin is advantageously thickened with the lithium soap of a high molecular weight substantially saturated fatty acid. It is contemplated to use other alkali or alkaline metal soaps such as sodium, potassium, calcium, barium, strontium soaps of soap forming acids, however, the lithium soap is used in the preferred embodiment. Listed among those commonly used soap forming materials which are known to the art and which are operable to form the thickening agents of this invention are the hydrogenated fish oil acids, oleic acid, stearic acid, hydroxy stearic acids, beef fat, tallow, the saturated or unsaturated glycerides of various fatty acids, or mixtures of the above in any proportions although the fatty acids rather than the glycerides are preferred.

PROPORTIONS OF COMPONENTS

To form the lubricating oil base for the improved high temperature greases of this invention it is contemplated that a blend containing from about 20% to 50% by volume of the resin to about 80% to 50% of the synthetic oil chosen be used. Various factors will affect the component proportions used, of course, such as the type of synthetic oil used, the viscosity of the resin, the temperature at which the grease composition is to be used and the like. It is generally preferred, however, to blend with a synthetic lubricating oil of the ester type about 25% to 35% by volume of a resin having a viscosity in excess of about 300 SUS at 210° F.

The amount of soap that is used to thicken the blend into a finished grease formulation will also vary according to the desired product. Generally, it has been found advantageous to thicken the blends with from 10% to 25% by weight of the soap, with from 15% to 20% of the soap being preferred.

The procedure used in formulating the grease compositions of this invention is straightforward and presents no problems to those familiar with the art. Generally it is as follows:

The resin and the preformed soap are stirred together in a fire heated grease kettle and heated to a temperature of about 150°-300° F. The synthetic oil is then added and the mixture stirred and heated to a temperature of about 400°-430° F. is reached. The grease is then drawn into shallow pans and allowed to cool. After

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cooling it is homogenized by working. If desirable, inhibitors or other improving additions may be added to the grease after heat has been removed and before drawing.

If it is desired to form the soap in situ this may be done by adding the fatty acid to the kettle followed by the lithium, usually in the form of the hydroxide while only the resin is present. After complete neutralization and dehydration of the soap the complex ester is then added. By this method any hydrolysis of the ester is materially prevented.

To further describe the advantages of the grease compositions of instant invention the following examples are given:

Example I.—Di-2 ethylhexyl sebacate grease

About 50 parts by weight of a synthetic oil formed by esterifying sebacic acid with 2-ethyl hexanol was admixed with 20 parts by weight of lithium stearate in a fire heated grease kettle. The mixture was stirred while heating to about 150° F. At this temperature 29 parts of the synthetic oil was added and the temperature was raised to about 410° F. At that temperature heating was stopped and about 1 part by weight of an oxidation inhibitor was added. The formulation was then drawn into pans, cooled and homogenized by working. A clear homogeneous grease product resulted which had the following properties.

ASTM penetration (mm./10):

Unworked	240
Worked (60 strokes, fine hole worker plate)	265
Worked (100,000 strokes, fine hole worker plate)	310
Dropping point (° F.)	380
Aeration (60 minutes in a grease beater)	5%
Percent evaporation at 350° F.—24 hours	8.0

Example II.—Complex ester base grease

Using the procedure outlined in detail in Example I above attempts were made to prepare a lithium soap grease using as a base oil a blend of 65% of di-octyl sebacate with 35% of a complex ester prepared by reacting together two mols of a mono 2-ethyl hexanol ester of sebacic acid with one mol of a polyethylene glycol. This blend has a flash point of 420° F., and a viscosity at 210° F. of 42.5 SUS. The attempts were unsuccessful since a mushy, grainy product resulted indicating that the soap would not disperse in the ester.

Example III.—Grease compositions of invention

- A. 7.5% lithium hydroxy stearate.
7.5% lithium stearate.
1.0% oxidation inhibitor.
24.0% resin (vis. 210° F./444 SUS).
60.0% complex ester (same as in Example II).

The lithium soaps were mixed in the resin and dispersed at 350° F., when the complex ester was added and the mass heated while stirring to 420° F.; the inhibitor was added and the grease cooled in shallow trays.

ASTM inspections:

Penetration (mm./10)—	
Unworked	265
Worked (60 strokes)	267
Worked (100,000 strokes)	295
Dropping point (° F.)	395
Aeration (same condition as Example I)	5%
Percent evaporation at 350° F.—24 hours	1.0
B. 7.5% hydroxy stearic acid. 7.5% hydrogenated fish oil acids. 2.4% LiOH·H ₂ O. 1.0% oxidation inhibitor. 22.6% resin (vis. 210° F./444 SUS). 59.6% complex ester (same as in Example II).	

The hydroxy stearic acid, fish oil acids and the resin were charged to a fire heated grease kettle and warmed while stirring to 150° F., an aqueous solution of the lithium hydroxide was added and the soap formed dispersed and dehydrated while raising the temperature to 300° F. When dry the complex ester was slowly added while raising the temperature to 420° F. The grease was drawn into pans for cooling and when cold returned to the kettle and homogenized by stirring cold. Further homogenization may be accomplished by passage of the grease through a homogenizer.

ASTM inspections:

Penetration (mm./10)—	
Unworked	255
Worked (60 strokes)	270
Worked (100,000 strokes)	300
Dropping point (° F.)	395
Aeration (same condition as Ex. I)	less than 5%
Percent evaporation at 350° F.—24 hours	1.0

C. 20.0% lithium stearate.

- 1.0% oxidation inhibitor.
- 29.0% light resin (vis. 210° F./444 SUS).
- 50.0% di-2-ethyl hexyl sebacate.

The lithium soap was mixed in the resin and dispersed at 350° F., when the complex ester was added and the mass heated while stirring to 420° F.; the inhibitor was added and the grease cooled in shallow trays.

ASTM inspections:

Penetration (mm./10)—	
Unworked	265
Worked (60 strokes)	265
Worked (100,000 strokes)	285
Dropping point (° F.)	380
Aeration (beater test)	None
Percent evaporation at 350° F.—24 hours	less than 1.0

It is to be seen that the grease compositions of this invention have outstanding high temperature properties as shown by their structure stability and their high dropping points.

To summarize briefly, this invention relates to high temperature lubricating grease compositions useful for the lubrication of jet engine bearings. The grease compositions are prepared by thickening to a grease consistency a lubricating oil blend with a lithium soap of a high molecular weight substantially saturated fatty acid. The lubricating oil blend comprises a synthetic oil from 20% to 50% by volume of a resinous material extracted from a paraffinic crude residue by propane precipitation. The resinous materials operable have viscosities ranging from about 300 to 1500 SUS at 210° F. and have flash points in excess of about 500° F. The synthetic oils are preferably of the ester type, either a simple ester as exemplified by di-2-ethylhexyl sebacate, a complex ester, such as the reaction product of two moles of a dibasic acid half-ester with one mole of a polyglycol, or mixtures of these types.

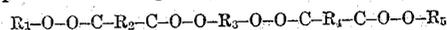
What is claimed is:

1. A lubricating grease composition having outstanding

high temperature properties which comprises 50 to 80% by volume of at least one synthetic lubricating oil selected from the group consisting of (a) a diester lubricating oil having the formula



wherein R and R₁ are alkyl groups having from 1 to 20 carbon atoms and x is an integer from 2 to 10, and (b) a complex ester having the formula



wherein R₁ and R₅ are monohydric alcohol alkyl radicals, R₂ and R₄ are dibasic acid alkyl radicals, and R₃ is a glycol alkyl radical, containing combined therein about 20 to 50% by volume of a propane precipitated paraffinic resin having a viscosity in excess of 300 SUS at 210° F. thickened to a grease consistency with a lithium soap of a high molecular weight saturated fatty acid.

2. The lubricating grease composition of claim 1 wherein said synthetic lubricating oil is said complex ester lubricating oil containing combined therein about 25 to 35% by volume of said propane precipitated paraffinic resin.

3. The lubricating grease composition of claim 2 wherein said lithium soap is present in an amount from 10 to 25% by weight.

4. A lubricating grease composition having outstanding high temperature properties which consists essentially of about 50 to 80% by volume of di-2-ethyl-hexyl sebacate containing combined therein about 20% to 50% by volume of a propane precipitated paraffinic resin having a viscosity in excess of 300 SUS at 210° F. thickened to a grease consistency with from 15% to 20% by weight of a lithium soap of a high molecular weight saturated fatty acid.

5. A lubricating grease composition having outstanding high temperature properties which consists essentially of 50 to 80% by volume of a synthetic lubricating oil consisting essentially 65% of di-octyl sebacate and 35% of the reaction product of 2 moles of sebacic acid, 2 moles of 2-ethyl-hexyl alcohol and 1 mole of a polyethylene glycol containing combined therein about 20% to 50% by volume of a propane precipitated paraffinic resin having a viscosity in excess of 300 SUS at 210° F. thickened to a grease consistency with from 15% to 20% by weight of a lithium soap of a high molecular weight saturated fatty acid.

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