United States Patent Office

2,908,645

Patented Oct. 13, 1959

1

2,908,645

BLENDED LITHIUM CALCIUM BASE GREASE

Arnold J. Morway, Clark, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Application April 28, 1955
Serial No. 504,659

5 Claims. (Cl. 252—40)

This invention relates to improved lubricating grease compositions having outstanding lubricating life and water resistance characteristics. More particularly, the invention pertains to blends of separate grease components to form greases having excellent water emulsion stability and long lubrication service.

In brief compass, the invention relates to lubricating grease compositions comprising a blend of two component greases, one component being a lubricating oil thickened to grease consistency with an organo-metallic soap-salt or mixed salt complex, having a high combined but active metal content, and the other component being a lithium soap thickened grease. These two component greases are made separately and then blended together by thorough mixing or by the use of a suitable homogenizer or grease mill.

The use of organo-metallic complexes having high metal content as grease thickeners has recently been suggested. In general, these complex thickeners have been prepared from the metal salts of low molecular weight carboxylic acids in combination with metal soaps of high molecular weight carboxylic acids, metal salts of intermediate molecular weight carboxylic acids, or metal salts of medium molecular weight carboxylic acids and metal soaps of high molecular weight carboxylic acids. The metal constituents of the complex thickeners have usually been selected from the divalent metals, especially the alkaline earth metals. Calcium is particularly preferred. Greases containing these complex thickeners have been found to have outstanding extreme pressure properties and long lubricating lives, but they tend to form fluid emulsions when water is churned into them.

The use of lithium soaps in grease-making is well known in the art. Such lithium soap type thickeners have been prepared from the conventional soap-forming high molecular weight carboxylic acids, including their hydroxy derivatives and esters thereof. Lithium-containing grease thickeners have also been prepared from mixtures of lithium and calcium soaps of high molecular weight fatty acids. Greases thickened with these lithium-containing soaps, such as the lithium soap of hydroxy stearic acid, have excellent water resistance but notably poor lubricating lives.

In U.S. Patent No. 2,397,956 Fraser teaches the preparation of a lubricating grease using a lithium soap of 12-hydroxy stearic acid or hydrogenated castor oil. The patent also discloses that the calcium soap of a high molecular weight fatty acid, preferably as a preformed calcium grease, may be combined with a lithium hydrogenated castor oil soap grease. This combination is, however, directed toward a specific grease composition, wherein the lithium grease is present in a predominate proportion.

It has now been found that a grease composition incorporating the desirable characteristics of the high metal

2

content organo-metallic complex thickened greases and the lithium soap thickened greases may be prepared by blending from about 20 to 60% of the lithium base grease with from about 40% to 80% of the complex thickened grease. The resulting grease compositions have good water emulsion stability, long lubrication lives as well as other desirable grease characteristics. The grease compositions of this invention are composed of two components. Component 1 is a divalent metal complex thickened grease, and component 2 is a lithium soap thickened grease.

As described above, component 1 is a grease containing an organo-metallic complex thickener, having a high combined but active metal content. Suitable complex thickeners include the following:

(*a*) The soap-salt complexes prepared from the metal salts of low molecular weight carboxylic acids having from 1 to 3 carbon atoms per molecule, and the metal soaps of high molecular weight carboxylic acids having from 12 to 30 carbon atoms per molecule, wherein the mol ratio of the low to high molecular weight acids is about 7:1 to 40:1, preferably about 8:1 to 25:1;

(*b*) The mixed salt complexes prepared from the metal salts of low molecular weight carboxylic acids having from 1 to 3 carbon atoms per molecule, and metal salts of intermediate molecular weight carboxylic acids having from 7 to 10 carbon atoms per molecule, wherein the mol ratio of low to intermediate weight acids is about 2:1 to 40:1, preferably about 4:1 to 25:1;

(*c*) The soap-salt complexes prepared from the metal salt of acetic acid, metal salts of medium molecular weight carboxylic acids having from 3 to 10 carbon atoms per molecule, and metal soaps of high molecular weight carboxylic acids having from 12 to 30 carbon atoms per molecule; wherein the mol ratio of acetic to the medium and high molecular weight acid is about 4:1 to 40:1, the mol ratio of medium to high molecular weight acids is about 0.5:1 to 10:1, and the difference in number of carbon atoms per molecule between the high and medium molecular weight carboxylic acid is at least 7, preferably about 7 to 15.

The high molecular weight carboxylic acids useful for preparing the complex thickeners described above are those saturated and unsaturated, grease-making fatty acids that are commonly known to the art. In general, these fatty acids have from about 12 to 30 carbon atoms, preferably about 16 to 22 carbon atoms per molecule, and include such fatty acids as myristic acid, palmitic acid, stearic acid, the various hydroxy stearic acids, oleic acid, arachidic acid, behenic acid and the like. Mixtures in any proportions of these high molecular weight fatty acids are also operable. Naturally occurring high molecular weight acids such as fish oil acids, tallow acids, castor oil acids, coconut oil acids may also be utilized either in their natural state or after partial or complete saturation by hydrogenation. Preferred acids are mixtures derived from natural sources such as hydrogenated fish oil acids, animal fatty acids and the like.

The intermediate molecular weight acids are those aliphatic monocarboxylic acids containing from about 7 to 10 carbon atoms, preferably about 8 to 9 carbon atoms, per molecule. Either saturated or unsaturated fatty acids may be utilized, though the saturated fatty acids are preferred. Straight chain or substantially straight chain acids are preferred in the preparation of relatively firm greases; while the branched chain acids are useful in the preparation of softer greases. Single or mixed intermediate weight acids having an average saponification value of from about 310 to 440, especially about 320 to 420, are preferred. Suitable acids include:

5-methyl-2-hexanoic
Heptanoic (enanthic)
Octanoic (caprylic)
2-ethyl hexanoic
C_8 Oxo acid
Nonanoic (pelargonic)
Decanoic (capric)
C_{10} Oxo acids

The Oxo acids are those formed by the well known Oxo process of synthesis with carbon monoxide, hydrogen and olefins, the latter being C_7 and C_9 polymers of propylene with or without some butylene, for making C_8 and C_{10} Oxo acids.

The medium molecular weight carboxylic acids, as designated for the purposes of this invention, include straight and branched chain saturated aliphatic carboxylic acids, hydroxy aliphatic mono- and poly-carboxylic acids, aromatic mono- and poly-carboxylic acids and anhydrides thereof, and heterocyclic acids containing from about 3 to 10, preferably 6 to 9, carbon atoms per molecule. Suitable carboxylic acids are as follows:

Pentanoic (valeric)	Glyceric
Hexanoic (caproic)	Lactic
Heptanoic (enanthic)	Citric
Octanoic (caprylic)	Benzoic
Nonanoic (pelargonic)	Hydroxy benzoic
Decanoic (capric)	Toluic
Isobutyric	o-Phthalic
C_5 Oxo acids	Phthalic anhydride
C_8 Oxo acids	Terephthalic
C_9 Oxo acids	Furoic
C_{10} Oxo acids	Thiophene carboxylic

Mixed as well as single medium molecular weight carboxylic acids may be employed in the preparation of these complex thickeners.

The low molecular weight carboxylic acids contemplated in this invention include saturated and unsaturated carboxylic acids having from about 1 to 3 carbon atoms, such as formic, acetic, propionic, acyclic and similar acids including their hydroxy derivatives, e.g. lactic acid. Monocarboxylic acids are particularly useful, and acetic acid is especially preferred. In general, the low molecular weight carboxylic acid employed should have a saponification value of above about 600, preferably about 750 to 1300. Mixed low molecular weight carboxylic acids, wherein the acids contain from about 1 to 3 carbon atoms, having saponification values above about 600 may also be employed. The acetic acid can be either glacial acetic acid or an aqueous solution of acetic acid. When the latter is employed, the concentration of acid in solution may vary from about 60 to 99.9 wt. percent, and is preferably about 80 wt. percent.

The metal component of the complexes described above is used in a form which can combine chemically with carboxylic acids to form salts or soaps. Ordinarily the metal hydroxide is used. The alkaline earth metal hydroxides or carbonates such as those of calcium, barium and strontium are particularly useful for the purposes of this invention. Calcium hydroxide is especially preferred. The alkaline earth metals differ in this respect from the alkali metals, i.e. sodium, potassium and lithium. Complexes having a high alkali metal content and which consist of the combinations of acids, mol ratios, etc. of the alkaline earth metal complexes of this invention yield greases with poor structural stability. It is preferred, therefore, to use metals having a valency of two. Metals such as magnesium and zinc are also useful for the purposes of this invention.

The soap-salt complex thickening agents may be utilized in combination with a wide variety of mineral as well as synthetic lubricating oils. Mineral base lubricating

oils ranging in viscosity from about 30 to 1000 SUS at 100° F. are preferably employed as the liquid phase of the grease composition within the range of about 50 to 95 wt. percent based on the total weight of the final grease composition. These naturally occurring mineral lubricating oils may be derived from any petroleum crude source, whether paraffinic or naphthenic in type, and may be refined by any of the well known refining techniques of the petroleum industry.

Suitable synthetic lubricating oils include the hydrocarbon, hydrocarbon polymer, ester, complex ester, formal, mercaptal, polyalkylene oxide, silicone and similar types. Synthetic oils such as di-2-ethylhexyl sebacate, di-C_8 Oxo azelate and other branched chain simple esters of dicarboxylic acids can be used, as well as complex esters prepared from glycols, dicarboxylic acids, and alcohols or monocarboxylic acids.

The high metal content soap-salt complex or salt complexes may be prepared by coneutralization of a mixture of the acids employed with suitable bases, particularly the hydroxides and/or carbonates of the metals desired. This coneutralization step may be carried out in situ in the liquid menstruum to which the complex is to be applied in actual use. For example, the mixed acids may be coneutralized in a portion or all of the lubricating oil forming the dispersant of a grease to be thickened by the soap-salt or salt complexes. The coneutralized material is heated to high temperatures of about 400° to 550° F. or higher prior to use in order to dehydrate the product and to promote the formation of the complex. When this heating step is carried out in a liquid dispersant, the latter should have a boiling point above the heating temperature or the heating should be carried out under pressure.

The high metal soap-salt or salt complexes may also be prepared by separately preforming at least a portion of the high molecular weight carboxylic acid soap, when employed, and/or the low and intermediate molecular weight carboxylic acid salts. This method is particularly useful when different metals are employed as bases.

Soap-salt or salt complex proportions of about 5–30 wt. percent, preferably about 10–20 wt. percent, based on the total grease composition may be employed in preparing the greases constituting component 1 of this invention.

The constitution and chemical structure of the soap-salt and mixed salt complexes are not fully understood. X-ray diffraction spectra obtained from various soap-salt and salt complexes do show, however, patterns definitely inconsistent with those of physical mixtures of the soap and salt or mixtures of salts. Moreover, the spectra show that the temperature to which the complex components are heated or reacted is important. Patterns obtained from heating complex components to a temperature within the range of about 400° to 550° F. and at lower temperatures clearly differ from each other indicating different products. Accordingly, for the purposes of this invention as well as for consistency with terminology already established by the art, the products obtained by heating mixtures of high molecular weight carboxylic acid soap with lower molecular weight carboxylic acid salt; low and intermediate molecular weight carboxylic acid salts; or low and medium molecular weight acid salts with high molecular weight carboxylic acid soaps within the aforementioned temperature range are designated as complexes. It is almost certain that these complexes are not ordinary chemical compounds, but rather some sort of Werner complex with coordinated valences.

Component 2 is a lithium base grease, i.e. a lubricating oil thickened to grease consistency with lithium soaps of high molecular weight carboxylic acids. Mixtures of lithium and strontium or lithium and calcium soaps may also be employed to prepare these greases.

The grease-forming fats or high molecular weight fatty acids listed above are also suitable for preparing the component 2 grease. Thus, the grease can be made from a lithium soap of 12-hydroxy stearic acid produced from hydrogenated castor oil or from hydrogenated castor oil fatty acids or esters thereof prepared with low molecular weight alcohols such as methyl, ethyl alcohols, etc.

The lubricating oils into which the lithium soaps or the mixture of lithium with calcium or strontium soaps are incorporated may be either mineral or synthetic lubricating oils having viscosities of from 30 to 1000 SUS at 100° F., as described above.

The conventional methods of grease manufacture such as cooking in a fire heated kettle followed by drawing into thin pans or deep cakes for cooling may be employed in preparing the lithium soap thickened greases. They may also be prepared in steam heated kettles followed by cooling with stirring while running cold water through the kettle jacket or by a continuous method of manufacture.

U.S. Patent 2,641,577 contains a detailed description of the composition and preparation of a lithium-calcium lubricating grease composition suitable for use as component 2 of this invention. As disclosed in this patent, the mol ratios of the lithium soap to the calcium soap may vary between about 2:1 to 8:1, the preferred ratio being about 3:1 to 6:1.

U.S. Patent 2,397,956 discloses the preparation of greases containing a lithium soap of 12-hydroxy stearic or the lithium soap of hydrogenated castor oil as a thickener. The lithium soaps are present in amounts up to 50%, preferably 8 to 40%, of the total weight of the grease. In addition, these greases are preferably prepared at temperatures of between about 400° to 425° F.

In preparing greases containing a lithium soap any suitable lithium compound may be used such as lithium hydroxide, lithium carbonate, lithium oxide and the like. Preferably, however, the lithium compound used is lithium monohydrate which contains from 53 to 55% of lithium hydroxide.

In blending the grease components of this invention, operable proportions include from about 20 to 80% of component 1 and from about 20 to 80% of component 2. Preferred proportions, however, are from about 40 to 80% of component 1 and from about 20 to 60% of component 2. The temperatures of blending are within the range of about 100° to 300° F., preferably about 180° to 225° F. The maximum temperature range may be just below the phase change in the lithium grease, i.e. when the grease changes in structure from a rubbery fibrous product to a smooth homogeneous product. As described above, the two grease components are blended together by thorough mixing or by being passed through a Gaulin homogenizer or Morehouse mill at a temperature sufficient to give an outlet temperature below the phase change of the lithium soap thickened grease component.

The invention will be more fully understood by reference to the following example illustrating various modifications of the invention.

EXAMPLE

Grease A

A grease was prepared from the following ingredients:

7.2% glacial acetic acid
1.8% Hydrofol Acid 51
1.8% hydrogenated castor oil
5.4% hydrated lime
0.4% phenyl alpha naphthylamine
83.4% mineral lubricating oil, 55 SUS/210° F.

The hydrogenated castor oil, the Hydrofol Acid 51 (hydrogenated fish oil acids corresponding to commercial stearic acid in degree of saturation), hydrated lime and all of the mineral oil were charged to a fire heated kettle equipped with agitating means, and the mixture was heated to about 130° F. The acetic acid was then added. Heating was continued and the temperature was raised to 500° F., at which time heating was discontinued and the grease was cooled to 200° F. while stirring. Thereafter, the grease was homogenized in a Gaulin homogenizer. The ratio of the acetic to the higher acids was about 10:1.

Grease B

A grease was prepared from the following ingredients:

8.4% animal fatty acid
0.48% hydrated lime
1.01% lithium monohydrate
90.11% mineral lubricating oil, 70 SUS/210° F.

The fatty acid and about one half of the mineral oil were added to steam kettle, and the calcium hydroxide was stirred in at a temperature of about 155° F. Heating and stirring were continued, and the lithium hydroxide added as a 10% aqueous solution at a temperature of 198° F. The grease batch was then heated to a temperature of about 290° F. to effect dehydration. During this period the viscosity of the mass was cut down by the addition of small amounts of oil. Thereafter the heat was shut off, and the balance of the mineral oil added while stirring over a period of about 1 to 2 hours. The grease was finished by being passed through a Morehouse mill at an inlet temperature of about 90° F. and an outlet temperature of about 118° F.

Greases C, D, E and F

These greases were prepared by blending Greases A and B, separately prepared as described above, in accordance with formulations listed in the table below at a temperature of 125° F.

Grease G

A grease was prepared from the following ingredients:

15.0% glacial acetic acid
3.6% caprylic acid
11.1% hydrated lime
0.5% phenyl alpha naphthylamine
69.8% mineral lubricating oil, 55 SUS/210° F.

The hydrated lime and all of the mineral lubricating oil were charged to a fire heated grease kettle. The temperature of the kettle was then raised to about 135° F. with stirring. When this temperature was reached, the mixture of acetic acid and caprylic acid was charged to the kettle, and the temperature raised with stirring to about 480° F. At this temperature, heating was discontinued and the mixture cooled to about 250° F. with stirring. Phenyl alpha naphthylamine was then added, and cooling continued to a temperature of about 200° F. The resulting grease composition was milled through a Gaulin homogenizer and filtered.

Grease H

A grease was prepared from the following ingredients:

12.00% methyl 12-hydroxy stearate
1.68% lithium monohydrate
0.50% phenyl alpha naphthylamine
85.82% mineral lubricating oil, 55 SUS/210° F.

The methyl 12-hydroxy stearate and the mineral oil were charged to a fire heated kettle and warmed while mixing to 150° F. A 20% aqueous boiling water solution of the lithium monohydrate was then added and the grease heated to 400° F. The fluid grease was cooled while stirring to 350° F. where the grease was just starting to solidify. The phenyl alpha naphthylamine was then added, and the grease drawn into pans for cooling.

Greases I, J, K, L and M

These greases were prepared by blending Greases G and H, separately prepared as described above, in accordance with the formulations listed in the table below at a temperature of 180° F.

TABLE

Grease No.	Components		Pen. mm./10 (1,000 strokes in ASTM Worker in the presence of 10% H_2O)	Lube Life (hrs.)
	1	2		
	Grease A (Percent)	Grease B (Percent)		
A	100	----------	Fluidized	1,150
B	----------	100	298	310
C	40	60	300	--------
D	50	50	300	635
E	75	25	335	840
F	80	20	350	--------
	Grease G (Percent)	Grease H (Percent)		
G	100	----------	Fluidized	651
H	----------	100	275	636
I	40	60	290	--------
J	50	50	242	[1] 2,500
K	75	25	310	--------
L	75 (+20% H_2O)	25	325	--------
M	80	20	350	--------

[1] Stopped—didn't fail.

It will be noted that the water resistance ability of calcium complex thickened greases and the lubricating life of lithium soap thickened greases can be improved by blending the separately prepared greases in certain definite proportions. Blends containing from about 20 to 60% of a lithium soap thickened grease impart good water emulsion stability to the calcium complex thickened grease. See Greases C, D, E, I, J, K, L and M. By employing a grease thickened with a lithium soap the methyl ester of 12-hydroxy stearic acid in conjunction with a calcium caprylate-acetate complex thickened grease, the lubricating life of the final grease composition was markedly increased while satisfactory water resistance was maintained. See Grease J.

In summation, this invention relates to new and improved lubricating grease compositions comprising blends of (1) soap-salt complex or mixed salt complex thickened greases having a high combined metal content and (2) lithium soap thickened greases. The blended grease compositions prepared in accordance with the invention have lubricating lives superior to the individual lithium soap thickened greases and a water resistance superior to the individual complex thickened greases.

The invention is not necessarily limited to the specific conditions and materials of the foregoing example. These conditions and materials may be varied within the limits indicated in the general portions of the specification. Moreover, the conventional grease additives such as oxidation inhibitors, pour point depressors, corrosion inhibitors and the like can be effectively incorporated in the grease blends of this invention.

What is claimed is:

1. A blended grease composition comprising a blend of two component greases, one component being a grease thickened with a calcium mixed salt complex of low and intermediate molecular weight mono-carboxylic acids, wherein the mol ratio of low to intermediate weight acid is about 2:1 to 40:1, the other component being a lithium base grease thickened with the lithium soap of a high molecular weight fatty acid, said blend consisting essentially of from 40 to 80% by weight of the first component and 20 to 60% by weight of the second component.

2. The blended grease composition of claim 1, wherein said blend consists essentially of from about 40 to 60% by weight of the first component and from about 40 to 60% by weight of the second component.

3. The blended grease composition of claim 1, wherein said calcium mixed salt complex is a mixed salt complex of a low molecular weight carboxylic acid having from 1 to 3 carbon atoms per molecule and an intermediate molecular weight carboxylic acid having from 7 to 10 carbon atoms per molecule.

4. The blended grease composition of claim 1, wherein said lithium base grease is thickened with lithium 12-hydroxystearate.

5. The blended grease composition of claim 1, wherein the first component is a grease thickened with the mixed salt complex of calcium acetate and calcium caprylate, and the second component is a lithium base grease thickened with lithium 12-hydroxystearate said blend consisting essentially of from about 40 to 60% by weight of the first component and 40 to 60% by weight of the second component.

References Cited in the file of this patent

UNITED STATES PATENTS

2,397,956	Fraser	Apr. 9, 1946
2,417,428	McLennan	Mar. 18, 1947
2,641,577	O'Halloran	June 9, 1953
2,844,536	Morway	July 22, 1958