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LUBRICATING GREASE COMPOSITIONS CONTAINING SOAPS OF OXIDIZED PETROLEUM HYDROCARBONS

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The present invention relates to improved lubricating grease compositions and the process of making the same. It relates particularly to improvements in lubricating greases suitable for use in ball and roller bearings, containing the soaps of materials produced by the oxidation of highly refined petroleum oils of naphthenic nature.

In many instances such anti-friction bearings run at fairly high temperatures and due either to these high temperatures or the churning action of the bearings, or both, many types of greases become too soft or fluid to remain in situ and properly perform their functions. A lubricant to be used under such conditions should have certain definite characteristics that would produce satisfactory results. It should have a stable structure, that is, it should not have a tendency to melt or separate oil from the thickener at the maximum operating temperature. In spite of its high melting point, the grease should be capable of giving adequate lubrication at substantially lower temperatures as well. It must not be too hard or stiff in order to provide protection at ordinary temperatures, even though its principal use be for high temperature operation.

In the past, various methods have been employed to give greases a higher melting point as well as other properties desirable for use in anti-friction bearings. One of these methods consists of increasing the soap content of the grease, which frequently results in producing lubricants that are too stiff for satisfactory lubrication at normal temperatures or for application in commercial grease dispensing equipment. Another method comprises the preparation of the so-called complex greases in which the lubricating oil base is thickened with a combination of the usual alkali-metal soap of tallow fatty acids, stearic acid, hydrogenated fatty acids and the like, and certain low molecular weight compounds. Lubricating grease compositions of this type are found to have superior stability at high temperatures, higher melting points, a firmer consistency for a given soap content as well as other advantages over greases of the conventional type. Along with the usual metal soaps of the higher fatty acids, it has been suggested that the corresponding metal salts of acetic acid, propionic acid, furoic acid, formic acid, acrylic acid, crotonic acid, low molecular weight ethoxy acids, such as ethoxypropionic acid, and other homologous and analogous compounds may be so combined. While such combinations constitute an improvement over greases containing soap alone, insofar as their performance in anti-friction bearings is concerned, they may be further improved. Under certain exacting circumstances, the complex-type greases tend to harden, particularly at relatively high soap contents, while, on the other hand, at very low soap contents they tend to break down and separate oil. It is thus an object of this invention further to improve greases of this type in this respect with-

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out adversely affecting their well established desirable properties.

According to the present invention, these disadvantages may be eliminated and still further improvements may be made in greases of the combined soap-salt complex type by substituting synthetic acids for a substantial portion of the high molecular weight fatty acids of the conventional type. These synthetic acids are obtained by the oxidation of mixtures of aliphatic and alicyclic hydrocarbons, preferably of naphthenic nature, and more specifically, highly refined petroleum oils of the type of white oils. The preferred method of producing the synthetic acids is by blowing the highly refined petroleum oils with oxygen or air at 210° F. to 390° F., preferably at about 300° F., until the desired degree of oxidation has taken place. As a rule, about 50 to 60 percent conversion makes for easy operation of the process. At this point the oxidized material may be topped to remove the unchanged hydrocarbon or if preferred, the whole material may be extracted with aqueous alkali or with concentrated ammonia. For easy operation, isopropyl alcohol may be added in an amount equal to the amount of water used in making the alkali or ammonia solution. The unchanged hydrocarbon and non-acidic oxidation materials are removed by extraction with naphtha. On acidification of this aqueous solution, the acids are precipitated in the form of oil. These may be used as such or they may be purified by distillation before incorporation into the greases.

The employment of soaps of these oxidation products in combination with certain vegetable or animal fats or fatty acids, together with the salt of a low molecular weight acid, results in greases with high dropping points, increased structure stability at high temperatures and no tendency to separate oil when the soap content is low. Accordingly, it is an object of the present invention to compound a grease of the combined soap-salt complex type from an alkali-metal soap of high molecular weight acids, a substantial portion of which consists of synthetic acids obtained by oxidation of a highly refined petroleum oil of the type specified above, and a metal salt of a low molecular weight carboxylic acid.

Greases in accordance with the invention may be prepared by admixing the desired amount of a mineral oil base stock with the desired amounts of the oxidized petroleum acids and high molecular weight fatty acids and heating the mixture in a grease kettle to a moderate temperature. The low molecular weight aliphatic acid is then added, followed immediately by the desired amount of the alkali metal hydroxide. Heating is continued and when the heavy concentrate in the kettle becomes relatively dry, the balance of the mineral oil is added. When the temperature reaches approximately 500° F., heating is discontinued and the grease composition is allowed to cool with or without agitation. The grease thus obtained may be blended further with a lubricating oil and the mixture homogenized. The resulting product constitutes a grease of excellent quality suitable for the purposes described above.

In the preferred embodiment of the invention, the high molecular weight fatty acids are hydrogenated fish oil acids. It is understood, however, that other high molecular weight fatty materials commonly used in grease manufacture, may be employed. The preferred alkali metal hydroxide is either sodium hydroxide or lithium hydroxide monohydrate. If the former is used, the preferred low molecular weight carboxylic acid is acetic acid, while calcium acetate is preferably employed in the presence of lithium hydroxide. The lubricating

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oils used in the first step of the grease formulation are preferably naphthenic crude distillates with a viscosity of approximately 40–80 S. S. U. at 210° F., while the oils used in the subsequent blending are preferably solvent extracted paraffinic Mid-Continent neutral oils with a viscosity of about 38–60 S. S. U. at 210° F. Other mineral oils of a wide range may of course be used, as will be understood by those skilled in the art.

The synthetic acids employed are preferably derived from the oxidation of highly refined petroleum oils of the type of white oils, whose molecules contain naphthenic or cycloparaffinic rings with paraffinic side chains. In the examples described below, use was made of synthetic acids which were prepared in the following fashion:

1200 g. of a highly acid-treated petroleum distillate, essentially free of aromatics and naphthenic in nature, containing on the average about 16 carbon atoms per molecule, was charged into a glass reactor equipped with a porcelain thimble for the introduction of oxygen and a trap and return condenser for condensing and separating the water formed during the reaction. Then while stirring, a rapid stream of oxygen was passed through the reaction mixture at 300° to 320° F. Once this reaction started, the external heating was discontinued and the temperature was regulated merely by regulating the flow of oxygen. The heat of reaction was sufficient to maintain the temperature at the desired level.

The blowing with oxygen was continued until 150 ml. of water were caught in the water trap. The oxidized material was topped then under 1 mm. pressure to 275° F. metal bath temperature. The distillate consisted of 616 g. of amber colored oil which in turn consisted partly of unchanged hydrocarbon and partly of acids, esters, and other oxygenated products. The undistilled residue consisted of 514 g. of a viscous light red oil. Henceforth this product shall be referred to as the topped oxidation product.

In the normal course of operation the distillate described above can be recycled until the whole material is oxidized.

The topped material referred to above was transferred into a separatory funnel and was treated with a mixture of 600 cc. of isopropyl alcohol and 600 cc. of concentrated ammonia. The mixture was thoroughly shaken, whereupon it was extracted several times with petroleum ether in order to remove unchanged white oil, and non-acidic oxidized products. Ether extracts were discarded, though these, too, can be recycled if desired.

The alcoholic-ammonia solution was treated on the steam bath for a short time in order to remove most of the excess of ammonia. The solution was then treated with an excess of hydrochloric acid. The liberated acids separated in the form of an oil.

The latter was extracted with ethyl ether. The extract was washed free of HCl with water and was then dried over sodium sulfate. On removal of the ether, the acids were obtained as viscous red oil weighing 228 g. These were then distilled under 1 mm. pressure. 122 g. of the product distilled between 300°–390° F. of which about 80% distilled at 300°–335° F. The undistilled residue was discarded.

In the examples below, these synthetic acids are referred to as "oxidized white oil acids."

The quantities of the ingredients disclosed above may vary widely, depending on the particular characteristics of the desired lubricating composition. For instance, the high molecular weight fatty acid material may vary from about 5% to 10% by weight, the synthetic acids between about 5% and 10% by weight, the alkali metal hydroxide from about 1.65% to 6% by weight, the low molecular weight aliphatic acid from about 2% to 4% by weight and the metal salt of the latter acid, when used, between about 2.5% to 5% by weight.

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The invention may be further explained by reference to the following specific examples, though it is obviously not limited thereby.

EXAMPLE 1

Formulation

Ingredients:	Percent weight
Hydrogenated fish oil acids.....	10.00
Oxidized white oil acids ¹	10.00
Glacial acetic acid	4.00
Sodium hydroxide	6.50
Phenyl alpha-naphthylamine	1.00
Mineral oil (80 S. S. U. at 210° F.)	34.25
Mineral oil (40 S. S. U. at 210° F.).....	34.25

¹ Acid No. —145 mg. KOH/gram.

Preparation

The hydrogenated fish oil acids, oxidized white oil acids and a portion of the mineral oil (80 S. S. U. at 210° F., naphthenic distillate) were charged to a fire heated grease kettle and warmed to 150° F. At this temperature the acetic acid was charged, followed immediately by a 40% aqueous solution of the sodium hydroxide. Heating was continued and when the heavy concentrate in the kettle was relatively dry the balance of the mineral oil (40 S. S. U. at 210° F.) was added. The temperature was then raised to 500° F. At this temperature, heating was discontinued and the grease allowed to cool. At 275° F., while cooling and still agitating, the inhibitor, phenyl alpha-naphthylamine was charged and the grease further cooled to 200° F. A sample of the grease was drawn from the kettle at 500° F. and cooled without agitation (pan cooling). The product was Gaulin homogenized at 5000 p. s. i. after cooling. It had an excellent, smooth structure, indicating grease of excellent quality could be prepared by either method.

Properties:

Percent free alkalinity as NaOH—	0.36	
	Before homogenization	After homogenization
ASTM penetration 77° F., mm./10:		
Unworked.....	250	163
Worked, 60 strokes.....	287	179
Worked, 67,000 strokes.....	345	330
Dropping point, ° F.....		500+
Water washing, percent loss.....		None
Norma-Hoffmann oxidation: Hours to 5 p. s. i. drop in O ₂ pressure.....		132

EXAMPLE 2

Formulation

50% above grease (Example 1)
50% mineral oil (paraffinic, 44 S. S. U. at 210° F.)
or
5.00% oxidized white oil acids
5.00% hydrogenated fish oil acids
2.00% glacial acetic acid
3.25% sodium hydroxide
0.50% phenyl alpha-naphthylamine
34.25% mineral oil (naphthenic, 50 S. S. U. at 210° F.)
50.00% mineral oil (paraffinic, 44 S. S. U. at 210° F.)

Preparation

To the grease in Example 1 was added a very stable, less polar type mineral oil and the grease and oil were blended together by mixing cold. (This non-polar oil is of an unsatisfactory nature for dispersing soap by heating, since the formed soap will not crystallize satisfactorily

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to form a grease structure.) This soft oily nonhomogeneous mass was then Gaulin homogenized at 5000 p. s. i., resulting in an excellent, homogeneous product. Properties (after Gaulin homogenization):

ASTM penetrations 77° F. mm./10:	
Unworked	283
Worked 60 strokes	303
Worked 67,000 strokes	355
Dropping point, °F.	410
Water washing test, percent loss	10.0
Norma-Hoffmann oxidation, hours to 5 p. s. i. drop in O ₂ pressure	117

EXAMPLE 3

Formulation

Ingredients:	Percent weight
Oxidized white oil acids	10.00
Hydrogenated fish oil acids	10.00
Lithium hydroxide monohydrate	3.30
Calcium acetate	5.00
Phenyl alpha-naphthylamine	1.00
Mineral oil (naphthenic, 40 S. S. U. at 210° F.)	35.35
Mineral oil (naphthenic, 80 S. S. U. at 210° F.)	35.35

Preparation

The acids extracted from the oxidized white oil, hydrogenated fish oil acids and a portion of the mineral oil (80 S. S. U. at 210° F.) were charged to a fire heated grease kettle and warmed to 150° F. A 10% aqueous solution of LiOH·H₂O was then added to the kettle and the mass heated to 300° F. to dehydrate. When appreciably dry, the balance of the mineral oil (40 S. S. U. at 210° F.) and calcium acetate were added and the grease heated to 500° F. Heating was discontinued, the grease was cooled to 250° F., the phenyl alpha-naphthylamine was added and the grease was then further cooled to 200° F. The hard dry grease was then Gaulin homogenized at 5000 p. s. i.

Properties:

Percent free alkalinity as NaOH	0.17
ASTM penetration 77° F. mm./10:	
Unworked	113
Worked 60 strokes	168
Worked 67,000 strokes	178
Dropping point ° F	328
Water washing test, percent loss	None
Norma-Hoffmann oxidation, hours to 5 p. s. i. drop in O ₂ pressure	232

EXAMPLE 4

Formulation

50.00% base grease Example 3	
50.00% mineral oil (paraffinic, 44 S. S. U. at 210° F.)	
or	
5.00% hydrogenated fish oil acids	
5.00% oxidized white oil acids	
1.65% LiOH·H ₂ O	
2.50% calcium acetate	
0.50% phenyl alpha-naphthylamine	
35.35% mineral oil (naphthenic, 50 S. S. U. at 210° F.)	
50.00% mineral oil (paraffinic, 44 S. S. U. at 210° F.)	

Preparation

The base grease of Example 3 and the mineral oil were blended together at 200° F. as drawn from the kettle after cooling by mixing in a Hobart mixer. The blended, soft, somewhat lumpy product was then Gaulin homogenized at 5000 p. s. i.

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Properties:

ASTM penetrations 77° F. mm./10:

Unworked	323
Worked 60 strokes	325
Worked 67,000 strokes	350
Dropping point, ° F	275
Water washing test, percent loss	None
Norma-Hoffmann oxidation, hours to 5 p. s. i. drop in O ₂ pressure	176
Solubility in boiling water	Insoluble

As is evident from the data listed above, the grease compositions made in accordance with this invention have excellent high temperature characteristics, their dropping points ranging up to 500° F+. They also have good structural stability even where the soap content is low, as shown by the penetration tests. Their insolubility in water indicates that they are especially suited for use at high temperatures in the presence of moisture.

Conventional additives, such as anti-oxidants, e. g. N-acyl p-amino phenols, oiliness agents, e. g. fatty acid esters and amines, corrosion inhibitors, e. g. partial esters of polyhydric alcohols, extreme pressure agents, e. g. phospho-sulfurized hydrocarbons, and the like, may be incorporated into the grease compositions to impart to them certain desirable characteristics, as will be understood by those skilled in the art.

To summarize briefly, this invention is concerned with the formulation of a superior complex soap-salt type of grease suitable for use in anti-friction bearings. A substantial portion of the conventional high molecular weight fatty acids used in the formation of the soap thickener is replaced by synthetic acids resulting from the oxidation of highly refined petroleum oils, such as white oils, and being predominantly naphthenic in character. These acids can be produced at a low cost, even when the conventional acids are in short supply. The resulting greases are of superior quality for the desired purposes, have a relatively low thickener concentration and can be produced economically. In general, the lubricating grease composition of the invention will comprise a major proportion of mineral base lubricating oil thickened to a grease consistency with a thickener consisting essentially of 5% to 15% by weight, based on the total composition, of a metal soap of high molecular weight carboxylic acids derived from fatty materials, 5% to 15% by weight of a metal soap of saponifiable materials produced by the oxidation of highly refined petroleum oils of naphthenic nature, and 2% to 6% by weight of a metal salt of a carboxylic monobasic acid containing 1 to 5 carbon atoms per molecule.

What is claimed is:

1. A lubricating grease composition comprising a major proportion of mineral base lubricating oil thickened to a grease consistency with a thickener consisting essentially of 5% to 15% by weight, based on the total composition, of an alkali metal soap of high molecular weight carboxylic acids derived from fatty materials, 5% to 15% by weight of an alkali metal soap of saponifiable materials produced by the oxidation of white oils which are highly refined petroleum oils of naphthenic nature, and 2% to 6% by weight of a salt of a carboxylic monobasic acid containing 1 to 5 carbon atoms per molecule and a metal selected from the group consisting of alkali metals and alkaline earth metals.

2. Composition as in claim 1 wherein the saponifiable materials produced by the oxidation of highly refined petroleum oils contain an average of about 14 to 18 carbon atoms per molecule.

3. Composition as in claim 1 wherein the metal is an alkali metal.

4. Composition as in claim 1 wherein the metal is sodium.

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5. Composition as in claim 1 wherein the metal in the soaps is lithium and the metal in the salt is calcium.

6. Composition as in claim 1 wherein the aliphatic monobasic acid is acetic acid.

7. A lubricating grease composition comprising a major proportion of mineral base lubricating oil, an alkali metal soap of 5 to 10 wt. percent of high molecular weight carboxylic acids derived from fatty materials, an alkali metal soap of 5 to 10 wt. percent of water-soluble saponifiable materials produced by the oxidation of white oils which are highly refined petroleum oils of naphthenic nature, and metal salt of about 2 to 4 wt. percent of carboxylic monobasic acids containing 1 to 5 carbon atoms per molecule and wherein the metal component of said metal salt is selected from the group consisting of alkali and alkaline earth metals.

8. A method of preparing a stable high temperature lubricating grease which comprises simultaneously forming a soap and a low molecular weight salt by reacting a mixture of 5 to 10 wt. percent of high molecular weight carboxylic acids derived from fatty materials, 5 to 10 wt. percent of water-insoluble saponifiable materials produced by the oxidation of white oils which are highly refined petroleum oils of naphthenic nature and 2 to 4 wt. percent of a low molecular weight carboxylic acid with a saponifying compound of an alkali metal base in the presence of lubricating oil to convert the said high molecular weight acids and the said oxidation products of highly refined petroleum oils to soaps, and convert the low molecular weight carboxylic acid to salt, and admixing further quantities of lubricating oil sufficient to produce a grease of the desired consistency.

9. A method as in claim 8 wherein the oxidation products of highly refined petroleum oils of naphthenic nature are obtained by blowing oxygen through said oil, recovering the oxidized material by distillation, extracting the saponifiable material from the said oxidized matter

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with the aid of an alcohol and ammonia and acidifying the same by treatment with hydrochloric acid.

10. A method of preparing a stable high temperature lubricating grease which comprises forming a soap by reacting a mixture of 5 to 10 wt. percent of high molecular weight carboxylic acids derived from fatty materials and 5 to 10 wt. percent of water insoluble saponifiable materials produced by the oxidation of white oils which are highly refined petroleum oils of naphthenic nature in the presence of lubricating oil with an alkali metal base saponifying compound, and adding 2.5 to 5.0 wt. percent of a salt of a low molecular weight carboxylic acid and of a metal selected from the group consisting of alkali metals and alkaline earth metals and further quantities of lubricating oil sufficient to produce a grease of the desired consistency.

11. A method as in claim 10 wherein the oxidation products of highly refined petroleum oils of naphthenic nature are obtained by blowing oxygen through said oil, recovering the oxidized material by distillation, extracting the saponifiable material from the said oxidized matter with the aid of an alcohol and ammonia and acidifying the same by treatment with hydrochloric acid.

12. A method as in claim 10 wherein the saponifying compound is lithium hydroxide monohydrate and the metal salt is calcium acetate.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 23,082	Zimmer et al. _____	Jan. 25, 1946
2,188,864	Jolly _____	Jan. 30, 1940
2,258,300	Morway et al. _____	Oct. 7, 1941
2,270,620	Bray _____	Jan. 20, 1942
2,455,892	Fraser _____	Dec. 7, 1948
2,495,651	Butcosk _____	Jan. 24, 1950
2,637,695	McKinley _____	May 5, 1953
2,682,553	Kirk et al. _____	June 29, 1954