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LUBRICATING GREASE CONTAINING ODD AND EVEN-NUMBERED FATTY ACIDS

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ABSTRACT OF THE DISCLOSURE

Lubricating greases thickened with alkali or alkaline earth metal salts of low molecular weight fatty acid and a mixture of odd and even numbered fatty acids averaging at least 14 carbon atoms wherein 25 to 75 wt. percent of said mixture is acid containing an odd number of carbon atoms.

This invention relates to lubricating greases thickened with alkali or alkaline earth metal salts of low molecular weight fatty acid and soap of high molecular weight fatty acids, wherein the soap of the high molecular fatty acid component is formed from a mixture of C_{10} to C_{23} monocarboxylic fatty acids having even and odd numbers of carbon atoms.

Greases formed by thickening lubricating oil with alkali metal or alkaline earth metal soap-salt combinations are in wide spread commercial use. An example of one such grease comprises mineral oil thickened with lithium or sodium salt of acetic acid and the corresponding metal soap of various higher fatty acids such as stearic acid. Another example comprises mineral oil thickened with calcium salt of acetic acid with calcium soap of stearic acid. In the past, it has been conventional to use naturally occurring fatty acids as the soap-forming component. However, nature, for some unknown reason, provides only even-numbered fatty acids and all of the aforesaid commercial greases known to the instant inventors are made from higher fatty acids of even-numbered carbon chains. It has now been found, that the aforesaid soap-salt greases can be improved in various ways by the use of a mixture of odd and even-numbered saturated fatty acids as the high molecular weight soap-forming acid. In the case of alkali metal, e.g. sodium, soap-salt greases, soaps of this mixture of odd and even-numbered saturated acids materially increases the lubricating life of the grease in ball-bearings at elevated temperatures, show no tendency to form crusts or to harden excessively on long storage, and show greater stability with less tendency to separate oil in storage. In the case of the alkaline earth metal soap-salt greases, particularly those made from calcium, the mixture of odd and even-numbered saturated soap-forming fatty acids inhibits crust formation, i.e. surface hardening of the grease, which is common to alkaline earth metal mixed salt greases made from saturated high molecular weight fatty acids of an even number of carbon atoms. The reason for the increased effectiveness of this mixture of odd and even-numbered fatty acids in forming the soap component of soap-salt greases is not known.

In general, soap-salt greases are usually made by neutralizing with metal base about 0.1 to 4, preferably 0.1 to 2.0 parts by weight of low molecular weight fatty acid per part by weight of high molecular weight fatty acid. These systems can also contain salt of 0.1 to .5 part by weight of intermediate molecular weight, aliphatic saturated, dicarboxylic acid per part of weight of the high molecular weight fatty acid. Usually, all the acids are simultaneously coneutralized with metal base, e.g. lime or NaOH, in situ in at least a portion of the oil, and then

the mixture is usually heated to 225° to 500° F. to effect dehydration. Lubricating greases generally contain 15 to 45 weight percent of the soap-salt. These greases, in turn, can be diluted with additional oil to form fluid or semi-fluid cmpositions containing 5 weight percent or more of the soap-salt. The preceding weight percents are based on the total weight of the composition.

Suitable low molecular weight acids for forming soap-salt compositions include fatty acids having 1 to 6 carbon atoms such as formic, acetic, propionic, and similar acids including their hydroxy derivatives such as lactic acid, etc. Acetic acid or its anhydride is preferred.

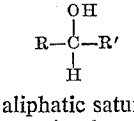
Intermediate molecular weight dicarboxylic acids which may be used include those acids containing 7 to 12 carbon atoms per molecule, e.g. pimelic, suberic, sebacic, pelargonic, etc.

The high molecular weight fatty acids useful in the present invention for forming the grease is a mixture of saturated fatty acids having at least one odd-numbered acid and at least one even-numbered acid in the mixture, said acids having a carbon atom content within the range of 10 to 23, e.g. 10 to 17 carbon atoms per molecule, in which mixture 25 to 75 wt. percent of said mixture contains an odd number of carbon atoms and in which the average number of carbon atoms in the acids is about 14 or more.

The lubricating oil used in the compositions of the invention may be either a mineral lubricating oil or a synthetic lubricating oil. Synthetic lubricating oils which may be used include esters of dibasic acids (e.g. di-2-ethylhexyl sebacate), esters of glycols (e.g. C_{13} oxo acid diester of tetraethylene glycol), complex esters (e.g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid), halocarbon oils, alkyl silicates, sulfate esters, mercaptals, formals, polyglycol type synthetic oils, etc.

One source of the fatty acid mixture of odd and even acids is from secondary alcohol produced from mixed hydrocarbons which alcohols are fused at high temperatures with caustic alkali, using about 1 to 2 or more moles of alkali per mole of secondary alcohol materials. An alkali salt results from the fusion reaction which can be utilized directly in lubricating oil as part of the thickener, or this alkali salt can be sprung with a strong mineral acid to form the corresponding fatty acid mixture.

The aforementioned secondary alcohols include those represented by the general formula:



where R and R′ are aliphatic saturated hydrocarbon radicals. R will usually contain about 7 to 21 carbon atoms, while R′ will usually contain 1 to 15. The total carbon atom content of the molecule will usually range from 11 to 24, preferably 12 to 22, carbon atoms. Specific examples of such secondary alcohols include mixtures of 2-dodecanol, 3-dodecanol, 4-dodecanol, 5-dodecanol, 6-dodecanol, 2-tetradecanol, 3-tetradecanol, 4-tetradecanol, 5-tetradecanol, 6-tetradecanol, 7-tetradecanol, 2-octadecanol, 3-octadecanol, 4-octadecanol, 5-octadecanol, 6-octadecanol, 7-octadecanol, 8-octadecanol, 9-octadecanol 2-eicosanol, 3-eicosanol, 4-eicosanol, 5-eicosanol, 6-eicosanol, 7-eicosanol, 8-eicosanol, 9-eicosanol, 10-eicosanol, 2-tricosanol, 3-tricosanol, 4-tricosanol, 5-tricosanol, 6-tricosanol, 7-tricosanol, 8-tricosanol, 9-tricosanol, 10-tricosanol, 11-tricosanol, 12-tricosanol, etc.

As mentioned above, one source of these secondary alcohols is by reaction of an aliphatic hydrocarbon stream with air using boric acid as a catalyst. The resulting alcohol is a mixture of secondary alcohols wherein the hy-

droxy group is more or less randomly distributed along the hydrocarbon chain with only a trace of primary alcohols. This boric acid process is described in the article by J. Germain and J. Cognion, Chemie et Industrie 91 #5, 519 (1964).

In brief, this process is carried out by passing air through n-paraffin mixtures at temperatures above 150° C. in the presence of boric acid. The product of the reaction is hydrolyzed before or after any unreacted paraffin is removed. The oxygenated products may be purified by distillation.

During the fusion process, the alkali appears to primarily react with the secondary alcohol to break the molecule at the oxygen atom to form an acid of the longer chain hydrocarbon group and a saturated hydrocarbon from the smaller chain group, as typified by the following reaction:

where R and R' have the same meanings as previously given. If an alcohol mixture is used, such as that produced by the aforesaid boric acid process from a mixture of linear hydrocarbons, then a mixture results where R will be divided between odd and even numbers of carbon atoms.

The aforesaid alkali fusion can be carried out at as follows: alkali metal oxide, or alkali metal hydroxide such as sodium hydroxide or potassium hydroxide, preferably in flake or pellet form, is dispersed in an inert mineral oil menstruum. The mixture can then be heated to about 450° to 700° F., e.g., 525° to 625° F., and the secondary alcohodl slowly added, either in increments or continuously, over a period of about ½ to 15 hours, e.g. 1 to 5 hours, while vigorously stirring and maintaining a reaction temperature of about 450° to 700° F., e.g. 525° to 625° F. Or, all of the components can be charged to the reactor at the same time and then heat is applied, etc. In any event, the resulting reaction product includes oil containing alkali metal salt of mixed odd and even-numbered fatty acids.

The acid mixture per se can be prepared from this reaction product as follows: the reaction product is cooled and water is added. The resulting mixture can then be extracted with a light hydrocarbon solvent, such as heptane or the like, in order to remove the oil and unreacted secondary alcohol material to thereby leave an aqueous phase. The remaining aqueous phase is acidified with a mineral acid, e.g. hydrochloric acid, to form monocarboxylic acid. The carboxylic acid can then be removed from the aqueous phase by extraction with a light solvent, e.g. heptane or diethyl ether, and finally crude carboxylic acid is obtained by evaporation of the solvent. While the crude acid may be directly utilized without further purification, it can be purified by vacuum distillation or other known procedures. This acid can then be used for various purposes as previously indicated.

Greases can be prepared directly by carrying out the fusion in lubricating oil in the presence of other acids to form the alkali metal soap-salt system. This in situ grease-making process is preferably carried out by dispersing the other acid and the secondary alcohol material in the lubricating oil, adding the alkali, preferably in the form of an aqueous solution containing 40 to 50 wt. percent alkali, heating to about 250° to 300° F., until the other acid is converted to its salt, and all the water of reaction is volatilized. The alkali fusion is then carried out by further heating to about 450° to 700° F., e.g. 500° to 600° F., until hydrogen and light hydrocarbon evolution substantially ceases, e.g. about ¼ to 5 hours. The grease may then be cooled and finished by conventional means.

Various other additives may also be added to the lubricating composition (e.g. 0.1 to 10.0 weight percent), e.g. detergents such as calcium petroleum sulfonate; oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors, such as sorbitan monooleate; dyes; other grease thickeners, and the like.

The invention will be further understood by the following examples, wherein all parts are by weight and which include preferred embodiments of the invention.

Example I

A one gallon nickel reactor equipped with a stirrer, condenser, thermometer and feed line was charged with 370 gms. NaOH pellets, 330 gms. of KOH pellets and 500 gms. of a mineral white oil. This mixture was then heated to 320° C. and maintained at 320° to 340° C. for 95 minutes while 779 grams of a mixture of C_{18} secondary alcohols, prepared by the aforesaid boric acid catalysis method, were slowly added over said 95 minute period. The temperature was then allowed to drop to 280° C. during the next 30 minutes. During this total time of 2 hours and 5 minutes, 5.6 standard cubic feet of gas were evolved. At the end of this period, the mixture was further cooled by a slow addition of water. It was then removed from the reactor and given 2 extractions with petroleum ether. The aqueous layer was acidified but no acids separated. Evaporation of the petroleum ether left a residue of 1113 g. This was then dispersed in 60% isopropyl alcohol (60 vol. percent alcohol and 40 vol. percent water) and extracted with petroleum ether to remove the white oil and other hydrocarbon soluble material. The aqueous alcohol phase was acidified with HCl to spring the fatty acids which amounted to 338 g. 302 g. of the resulting crude fusion acid was then distilled in a short path still under reduced pressure to remove any remaining petroleum ether and isopropyl alcohol. Then the distillation was continued under reduced pressure to obtain the cuts shown in the following table:

DISTILLATION OF CRUDE FUSION ACID

Cut	Vapor Temp., ° C.	Pressure, mm. Hg	Amount, g.
1	82	1.0	39
2	180	0.5	170
3	220	0.4	22
Bottoms			10

Cut 1 was mainly petroleum ether and isopropyl alcohol. The main fraction (Cut 2) of 170 g. had a neutralization number of 214.7 mg. KOH/g. which is equivalent to a molecular weight of 261. Analysis of this fraction by gas chromatography gave the following result:

No. of C-atoms in acid:	Wt. percent
<10	6.6
10	5.0
11	5.4
12	6.5
13	6.8
14	6.5
15	11.1
16	10.2
17	35.3
17+	6.6

The average carbon atom content is about 16.

The weight percent of acid of even number of carbon atoms=28.2.

The weight percent of acid of odd number of carbon atoms=58.6

The weight percent of acid less than C_{10} and greater than C_{17}=13.2.

The acid of preceding Cut 2, which contains at least 58.6 weight percent of odd-numbered acid, was used to prepare the greases described in the following examples, wherein all parts are by weight.

Example I-A

13.8 parts of hydrated lime and 57.2 parts of mineral lubricating oil having a viscosity of 80 SUS at 210° F. were intimately mixed. 10 parts of the acid mixture (Cut 2) prepared above was added. 18.0 parts of glacial acetic

acid was then added. The free alkalinity was adjusted to 0.7 weight percent as NaOH. The mass was heated at 325° F. until dehydrated. Heating was then discontinued and the reaction mass cooled rapidly to 250° F. where 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor. The composition was then further cooled to 110° F. where it was homogenized by passing through a Morehouse mill having 0.003" clearance.

Example I–B

Example I–A was repeated exactly except that 10 parts of Hydrofol Acid 51 (a hydrogenated fish oil acid having a Wijs iodine number of 3.0 and having about a C_{18} average chain length was used in place of the Cut 2 acid mixture.

Example II

10 parts of Hydrofol Acid 51, 10 parts of the Cut 2 acid mixture and 67 parts of mineral lubricating oil having a viscosity of 55 SUS at 210° F. were added to a fire-heated kettle. The kettle contents were then stirred while heating to 120° F. Then 8.0 parts of sodium hydroxide (100% was added in the form of an aqueous solution consisting of 40 weight percent of sodium hydroxide and 60 weight percent water. The mixture was then heated to a maximum of 640° F. and maintained at this temperature for about 3 hours. 1 part of phenyl α-naphthylamine as an antioxidant was added at a temperature of about 250° F. during the cooling cycle. The product was then finished by homogenizing by passing it through a Morehouse mill having about 0.003" clearance.

Example III

15 parts of the Cut 2 acid mixture were mixed with 71.9 parts of a mineral lubricating oil of 60 SUS viscosity at 210° F. in a kettle. 3 parts of azelaic acid were added and the kettle contents then were warmed to 130° F. 6.1 parts of lithium hydroxide monohydrate in the form of an aqueous solution containing 20 weight percent lithium hydroxide monohydrate was next added, followed by the addition of 3.0 parts of glacial acetic acid. The temperature of the mixture was raised to 440° F. to dehydrate the grease, after which the grease was allowed to cool. 1 part of phenyl α-naphthylamine was added after the grease had cooled to 250° F. The grease was further cooled to 120° F. and homogenized in a Morehouse mill. The grease was stirred continuously during the aforesaid cooling.

The grease compositions of Example I, II and III prepared above and their physical properties are summarized in Table I which follows:

TABLE I

Grease Composition (Wt. Percent)	I–A	I–B	II	III
Cut 2 [1]	10.0		10.0	15.0
Hydrofol Acid 51		10.0	10.0	
Glacial Acetic Acid	18.0	18.0	4.0	3.0
Azelaic Acid				3.0
Hydrated lime	13.8	13.8		
Sodium Hydroxide			8.0	
Lithium Hydroxide Monohydrate				6.1
Phenyl α-naphthylamine	1.0	1.0	1.0	1.0
Mineral lubricating oil, 80 SUS. at 210° F	57.2	57.2		
Mineral lubricating oil, 55 SUS. at 210° F			67.0	
Mineral lubricating oil, 60 SUS. at 210° F				71.9
Properties:				
Appearance	Excellent	Excellent	Excellent	Excellent
Dropping Point, ° F	None	None	500+	450+
ASTM Penetration, 77° F., mm./10:				
Unworked	260	185	181	210
Worked 60 strokes	280	200	210	215
Worked 10,000 strokes	275	210	220	230
Lubrication Life [1] (hrs.):				
10,000 r.p.m.:				
300° F			2,000+	750
250° F	1,890			2,000+
Timken e.p. test, lbs	60			
Storage Stability	(2)	(3)		
Water Solubility	Insoluble			Insoluble

[1] Mixture of odd and even number acids.
[2] Soft after 6 mos.
[3] Forms crust after 24 hrs.

As seen in Table I, the grease of Example I–A, containing Cut 2, i.e. the odd and even carbon atom fatty acid mixture, resulted in a softer grease (as indicated by the ASTM penetrations with better storage stability than the grease of Example I–B, made from saturated even-numbered carbon atom fatty acid.

The grease of Example II illustrates a sodium grease of a type suitable for ball-bearing lubrication made from a mixture of even-numbered fatty acid, i.e. Hydrofol Acid 51, and the mixed odd and even carbon atom fatty acid. At least about 29.3 weight percent of the total high molecular weight fatty acid

$$\left(58.6\% \times \frac{10}{20}\right)$$

therefore, has an odd-number of carbon atoms. The resulting grease gave a lubrication life in excess of 2000+ hours at 300° F. This was exceptionally good since a premium grade commercial sodium grease made by alkali fusion of rapeseed oil has a lubrication life at this temperature of only about 300 to 400 hours. In addition, the grease of Example II is a channeling type grease. Thus, in a 204 mm. ball-bearing rotating at 10,000 r.p.m. and packed with the grease of Example II, the temperature of the bearing rose to 130° F. due to initial churning and then after 15 minutes of operation fell to a steady temperature of 100° F. as the channel formed.

The grease of Example III represents another ball-bearing type grease made from lithium utilizing the mixed odd and even acids of the invention. This grease was also tested in a 204 mm. ball-bearing operating at 10,000 r.p.m. and showed an initial temperature rise from the ambient temperature of 80° to 140° F. after 5 minutes of operation. At the end of 10 minutes of operation, the temperature had fallen to 85° F. which temperature was then maintained as a steady state condition. This grease was also a channeling grease and is particularly suitable for ball-bearing lubrication. These channeling greases are frequently desired since they provide adequate bearing lubrication with a minimum power loss and heat rises due to reduction of friction engendered by churning of the grease.

As a further example of the greases of the invention, a grease can be prepared by coneutralizing with a neutralizing amount of lime a mixture consisting of 10 parts of a C_{13} aliphatic straight chain monocarboxylic acid, 10 parts of C_{18} aliphatic straight chain monocarboxylic acid, and 4 parts of acetic acid in 70 parts of mineral lubricating oil of 60 SUS viscosity at 210° F. and heating to 440° F. to dehydrate the resulting grease.

What is claimed is:

1. A soap-salt lubricating grease comprising a major amount of mineral lubricating oil and about 15 to 45 weight percent of a metal soap-salt thickener of C_1 to C_6 fatty acid and a mixture of high molecular weight monocarboxylic fatty acid having carbon atoms contents in the range of about 10 to 23 carbon atoms, wherein said metal is selected from the group consisting of alkali metal and alkaline earth metals, wherein the weight amount of said low molecular weight acid is about .1 to 4 times the amount of said mixture of high molecular weight fatty acid, and wherein said mixture has at least one odd-numbered fatty acid and at least one even-numbered fatty acid, said mixture averaging at least 14 carbon atoms and wherein 25 to 75 weight percent of said mixture is acid containing an odd number of carbon atoms.

2. A lubricating grease according to claim 1, wherein said metal is calcium and said low molecular weight fatty acid is acetic acid.

3. A lubricating grease according to claim 1, wherein said metal is an alkali metal and said low molecular weight fatty acid is acetic acid.

4. A lubricating grease according to claim 1, wherein said thickener also includes metal salt of 0.1 to 0.5 part of C_7 to C_{12} dicarboxylic acid per part of said mixture of high molecular weight fatty acid.

5. A lubricating grease according to claim 1, wherein said high molecular weight fatty acid is the acid reaction product obtained by caustic fusion of a mixture of C_{17} secondary aliphatic saturated alcohols wherein the hydroxy group is randomly distributed along the hydrocarbon chain.

6. A lubricating grease comprising a major amount of mineral lubricating oil and about 15 to 45 weight percent of metal soap-salt of about 0.1 to 4.0 parts of acetic acid per one part of higher monocarboxylic fatty acid which consists of about 25 to 75 weight percent of saturated fatty acid having an odd number of carbon atoms in its molecules and 75 to 25 weight percent of higher fatty acid having an even number of carbon atoms in its molecules, said higher fatty acid having carbon atom contents within the range of 10 to 23 carbon atoms and averaging at least 14 carbon atoms, and wherein said metal is selected from the group consisting of alkali metal and alkaline earth metal.

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