United States Patent Office 3,223,633 Patented Dec. 14, 1965

3,223,633

LUBRICANT

Arnold J. Morway, Clark, and Hugh E. Ramsden, Scotch Plains, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed July 1, 1963, Ser. No. 292,079
9 Claims. (Cl. 252—40)

This application is a continuation-in-part of application Serial No. 243,058 filed December 7, 1962, under the title "Lubricating Grease."

This invention relates to lubricants and particularly to greases. More particularly, the invention relates to water-insoluble, channelling, lubricating grease suitable for lubrication of anti-friction bearings and comprising a lubricating oil containing lithium salt of: dicarboxylic acid, C_2 to C_4 fatty acid, and a higher fatty acid, in certain proportions. Optionally, calcium salts of said acids can also be present in addition to said lithium salt.

When used in ball-bearings, the greases of the invention will form a channel. Once the channel is formed, the grease is still available for lubrication, but does not impede the rotating balls or bearing movement, thereby giving low torque requirements, low friction, low power requirements and cool-running bearings. For these reasons, channelling-type greases are preferred for lubrication of anti-friction bearings for lubricated-for-life electric motors and other mobile apparatus.

The lithium greases of the present invention represents a further improvement over the alkali metal greases of our prior invention described in our Serial No. 243,058. Thus, we have further found that by using lithium and predominantly saturated high molecular weight acid the resultant grease is water-insoluble in both cold and boiling water. In view of this water insolubility, the grease can be employed in marine service and other services where these bearings, or the grease itself, may be subjected to high humidity, water vapor or other sources of moisture. This water insolubility, however, will require the use of a ferrous metal rust inhibitor for most applications. We have also found that certain mole ratios of the various acid components are particularly preferred for making lithium greases, that by using these mole ratios, azelaic acid as the dicarboxylic acid component can be used, and that some calcium salt can be also used to advantage in the grease. The use of azelaic acid permits the formation of a more economical grease due to its relative low cost as compared to other suitable dicarboxylic acids. Using calcium in place of part of the lithium permits further economy in manufacture due to the lower cost of the calcium base. Also by using calcium, a larger amount of unsaturated fatty acid can be used, without destroying the water-insolubility of the grease. Thus, an all-lithium grease with all-unsaturated fatty acid will become water-soluble, particularly in hot water. An all-calcium grease using the acids and relative ratio of acids of the present invention would have poor structural stability without the presence of water or other stabilizing agents. However, the presence of water is undesirable since it prevents the effective use of the grease at high temperatures due to loss of the water at high temperatures, while stabilizing agents would increase the cost of the lubricant, and in some cases undesirably change its properties.

The mixed-salt thickener systems of the invention are best made to contain metal salt of 0.5 to 3.0, preferably 1 to 2 molar hydrogen equivalents of low molecular weight C_2 to C_4 fatty acid per molar hydrogen equivalent of dicarboxylic acid. These systems will also preferably contain metal salt of 0.5 to 3.0, preferably 1 to 2 molar hydrogen equivalents of C_{12} to C_{24} high molecular weight

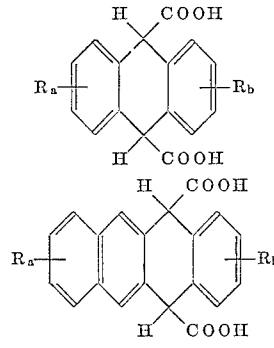
fatty acid per molar hydrogen equivalent of said dicarboxylic acid. Greases can be thus prepared having a total content of said metal salts of 5.0 to 49.0 weight percent, preferably 15 to 35 weight percent, based on the total weight of the grease. The grease, in turn, can be diluted with additional oil to form fluid or semi-fluid compositions containing about 0.1 to 5.0% of the mixed salt.

The metal can be all lithium, or a mixture of lithium and calcium in a ratio of 1 to 4 parts by weight of lithium per part by weight of calcium.

Suitable low molecular weight acids for forming the mixed salt compositions of the invention include fatty acids such as acetic and propionic acids. Acetic acid or its anhydride is preferred.

The high molecular weight fatty acids or aliphatic carboxylic acids useful for forming the mixed salt of the invention include naturally occurring or synthetic, substituted or unsubstituted, mixed or unmixed fatty acids having about 12 to 24, e.g., 16 to 24 carbon atoms per molecule. Substantially, saturated acids are preferred, although fatty acids or fatty acid mixtures, containing some unsaturation, but predominantly saturated can be used. Examples of such acids include myristic, palmitic, stearic, 12-hydroxy stearic, arachidic, ricinoleic, hydrogenated fish oil acids, etc. Saturated acid as used herein will be considered as acid or acid mixture having a Wijs iodine number of about 5 or less. Unsaturated acid will include those mono-ethylenically unsaturated acids.

The dicarboxylic acid of the invention includes aliphatic acid of 9 to 16, preferably 9 to 12 carbon atoms, which can be either straight or branched chain. Examples of such acids include azelaic, sebacic and dodecanedioic acids. Azelaic acid is preferred due to its readily availability and lower cost. Higher aliphatic dicarboxylic acids, e.g., a C_{19} Koch acid, appear to result in greases of shorter lubrication life at elevated temperatures and therefore are not preferred for this invention. In addition to said C_9 to C_{16} aliphatic dicarboxylic acid, certain polynuclear aromatic dicarboxylic acids can be used. These polynuclear acids can be typified by the formulas:



where R represents alkyl groups containing 1 to about 8 carbon atoms, *a* and *b* can be 0 to 4, but the sum of *a* and *b* will usually be no greater than about 6. A particularly preferred aromatic polynuclear dicarboxylic acid is available from petroleum refining and can be formed by treatment of the highly aromatic extract derived by extraction of catalytic cracking cycle stock, with CO_2 and sodium, to form a salt of the aromatic acid, said salt being subsequently hydrolyzed with strong acid to separate the free dicarboxylic acid. The exact nature of the resulting dicarboxylic acid is not known with certainty. However, analysis shows it to be mainly 3 and 4 ring alkyl polynuclear dicarboxylic acids of the two types shown by the formulas above.

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), ester 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, sulfite esters, mercaptals, formals, polyglycol type synthetic oils, etc., or mixtures of any of the above in any proportions. If the salts are formed in situ in the oil, then this in situ reaction is best carried out in a mineral oil, since many synthetic oils will tend to decompose or hydrolyze during the salt formation. However, the salts once formed, can be used in lubricants containing the synthetic oils noted above.

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

The lubricants of the invention can be formed in a number of different ways. The most convenient is to coneutralize all the carboxylic acids in at least a portion of the oil, with the metal base. Usually, the resulting composition will then be heated to about 300° to 550° F., preferably 400 to 500° F. to dehydrate the composition. The higher temperature of 400 to 500° F. will usually result in the formation of a salt material having greater thickening effect and better load and e.p. properties than the lower dehydration temperatures.

The invention will be further understood by reference to the following examples wherein all parts are by weight.

Example I

68.3 parts of mineral lubricating oil of 60 SUS at 210° F., 15 parts of Hydrofol Acids 51 as the higher fatty acid, and 3 parts of azelaic acid were added to a fire heated grease kettle and mixed while stirring to 125° F. 3 parts of glacial acetic acid was rapidly added to the

kettle contents, followed by the addition of 5.7 parts of lithium hydroxide monohydrate added in the form of an aqueous solution containing 10 wt. percent of the lithium monohydrate. The kettle contents were mixed and heated to 425° F. to dehydrate the composition. The 425° F. temperature was held for about 15 minutes. The heat was turned off and the kettle cooled by passing water through the kettle jacket. In about 60 minutes, the kettle contents was cooled to about 250° F., while continuously stirring. Then 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor, after which the grease was cooled to 120° F. At this point, 2 parts of finely divided sodium nitrite (about 1.0 to 35 microns) was added in a 50/50 mixture of sodium nitrite and mineral lubricating oil of 50 SUS viscosity at 210° F. After the addition of the sodium nitrite, the product was homogenized by passage through a Morehouse mill to form the finished grease.

Hydrofol Acid 51 is a commercial acid having an average chain of about 18 carbon atoms and similar to stearic acid in degree of unsaturation, having a Wijs iodine number of about 3 maximum. Hydrofol Acid 51 is prepared by hydrogenating fish oil acid (menhaden).

Example II

A grease was prepared following the same general procedure of Example I, except that the higher fatty acid consisted of a mixture of (a) Hydrofol Acid 51 and (b) tallow fatty acid having a saponification number of 203 and a Wijs iodine number of 55. Also, slightly different amounts of mineral oil and lithium hydroxide were used.

Example III

A grease was prepared in the general manner of Example I, except that a portion of the lithium hydroxide monohydrate was replaced by hydrated lime, slightly different proportions of reactants were used.

The compositions of Examples I to III and their main properties are compared with a prior art premium ball bearing grease made from lithium hydroxy stearate in the following table:

TABLE

Composition (Wt. Percent)	Examples			Lithium Hydroxy Stearate Grease
	I	II	III	
Glacial Acetic Acid	3.0	3.0	3.0	
Hydrofol Acid 51	15.0	10.0	15.0	
Tallow Fatty Acids		5.0		
Azelaic Acid	3.0	3.0	3.0	
Lithium Hydroxide Monohydrate	5.7	1.0	4.1	
Hydrated Lime			2.0	
Phenyl α-Naphthylamine	1.0	1.0	1.0	
$NaNO_2$	2.0	2.0	2.0	
Mineral lube oil 60 SUS at 210° F.	68.3	67.9	67.9	
Mineral lube oil 50 SUS at 210° F.	2.0	2.0	2.0	
Mole H. eq. ratio, acetic/azelaic	1.57	1.57	1.57	
Mole H. eq. ratio, higher fatty acid/azelaic	1.66	1.66	1.66	
Properties:				
Appearance	Excellent	Excellent	Excellent	Excellent.
Dropping Point, ° F.	450+	450+	450+	355.
ASTM Penetration, 77° F., mm./10—				
Unworked	205	220	240	260.
Worked 60 Strokes	210	225	245	265.
Worked 10,000 Strokes	225	230	285	280.
400° F. Beaker Test	Other than slight softening, no phase change.			Phase change at 325° F. Melts at 350° F.
Solubility in Boiling Water	Insoluble	Insoluble	Insoluble	Insoluble.
Norma Hoffman Oxidation Test, Hrs. to 5 p.s.i. Drop	6	6	5	25.
Accelerated Wheel Bearing Test, 220° F., 1 Hour, 45° Angle	Pass	Pass	Pass	Pass.
Slump	None	None	None	None.
Leakage, Grams	0.6	0.2	1.0	5.0.
Lubrication Life,[1] Hours, 10,000 r.p.m.—				
250° F.[2]	2,000+	2,000+	2,000+	1,120.
300° F.	400	625	740	120.
Ball Bearing Temperature Rise Test at 10,000 r.p.m., ° F.—				
Initial Rise	10	15	15	65.
Steady State Condition, ° F.	80	80	80	175.
Rust Test CRC L-41	Pass	Pass	Pass	Pass.

[1] ABEC-NLGI Spindle Test.
[2] Test discontinued after 2,000 hours.

The lithium hydroxy stearate in the table was made from a formulation consisting of 11.8 wt. percent of 12-hydroxy stearate acid, 1.8 wt. percent lithium hydroxide monohydrate, 1.0 wt. percent phenyl-alpha-naphthylamine, 2.0 wt. percent of powdered $NaNO_2$ dispersed in 2 wt. percent mineral lubricating oil of 50 SUS at 210° F., and 82.2 wt. percent of mineral lubricating oil of 60 SUS viscosity at 210° F.

The 400° F. Beaker Test was carried out by slowly heating the grease in a beaker while stirring to determine if there was any change in structure:

The Wheel Bearing Test was carried out as described in ASTM Designation D–1263–53T with the exception that the test was run at 45° angle to accelerate any leakage.

The Ball Bearing Temperature Rise Test was carried out as follows: A 204 mm. steel ball bearing was packed with 3.0 grams of the grease to be tested and the bearing was then operated at 10,000 r.p.m. while the temperature of the grease in the bearing was continually measured by thermocouples placed on the outer bearing race.

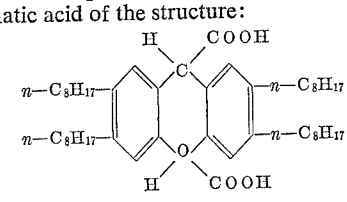
The CRC L–41 test was carried out by coating chemically clean Timken bearings (cup and bearing) with a thin coating of the grease and subjecting the bearing to turning at 1600 r.p.m. under a load to spread the grease in a thin layer. The cup and bearing assembly were then dipped in water and stored for 14 days in a closed glass jar containing a small amount of water so as to maintain a humid atmosphere. After 14 days the bearing was then examined for rust.

As seen by the data of Table I, the greases of the invention, represented by Examples I to III, had dropping points in excess of 450° F. These are extremely high dropping points for lithium grease since the lithium hydroxystearate grease, which is a premium ball bearing lithium grease, has a dropping point of 355° F. In the 400° Beaker Test, there was no change in the inventive greases of Examples I to III, other than a slight softening, whereas the comparison grease melted at 350° F. The inventive lithium greases were all insoluble in boiling water and had improved wheel bearing test characteristics as noted by their lack of slump and their low leakage. In addition, the greases of the invention had lubrication lives at 250° F. in excess of 2,000 hours as compared to only 1,120 hours for the lithium hydroxystearate grease. At the 300° F. test level, the lithium hydroxystearate grease lasted only 120 hours, while the greases of the examples ranged from 400 to as much as 740 hours of operation before failing. The improvement represented by the inventive greases is even more strikingly demonstrated by their operation in a ball bearing. Here it is seen that upon operating the bearing, the greases of Examples I to III gave an initial temperature rise of only 10 to 15° F. above the ambient temperature of 75° F., after which the temperature fell to 80° F. after which the bearing then operated continuously at 80° F. On the other hand, the prior art lithium hydroxystearate grease, which was non-channelling, gave an initial bearing rise of 65° F. and then began to further increase in temperature until it settled at a temperature of 175° F., although the ambient temperature was 75° F.

Example I thus illustrates an all-lithium grease of the invention prepared from a saturated commercial fatty acid. Example II illustrates that good greases can be prepared using predominantly (i.e., more than 50%) saturated high molecular weight fatty acid. While Example III illustrates the replacement of part of the lithium with calcium.

Example IV

Example I is repeated except that 3 parts of dibasic alkyl aromatic acid of the structure:



is used in place of the azelaic acid of Example I, and the amount of lithium hydroxide monohydrate used is such as to give a neutral product.

What is claimed is:

1. A water-insoluble channelling lubricating grease composition suitable for bearing lubrication comprising a major amount of lubricating oil and 5 to 49 wt. percent of lithium salt of: (A) C_2 to C_4 fatty acid, (B) dicarboxylic acid selected from the group consisting of C_9 to C_{16} aliphatic saturated dicarboxylic acid and alkyl polynuclear aryl dicarboxylic acids having a total of 0 to 6 alkyl groups of 1 to 8 carbon atoms each and wherein the number of rings is about 3 to 4 and (C) C_{12} to C_{24} fatty acid which is predominantly saturated, in a molar hydrogen equivalent ratio of about 0.5 to 3.0 molar hydrogen equivalent proportions of said C_2 to C_4 fatty acid per molar hydrogen equivalent of said dicarboxylic acid, and about 0.5 to 3.0 molar hydrogen equivalent proportions of said higher C_{12} to C_{24} fatty acid per molar hydrogen equivalent of said dicarboxylic acid.

2. A lubricating grease composition according to claim 1, wherein said C_2 to C_4 fatty acid is acetic acid.

3. A lubricating grease composition according to claim 2, wherein said dicarboxylic acid is said C_9 to C_{16} aliphatic dicarboxylic acid.

4. A lubricating grease composition according to claim 1, wherein said C_2 to C_4 fatty acid is acetic acid, said dicarboxylic acid is azelaic acid and said C_{12} to C_{24} fatty acid has a Wijs iodine number of less than 5.

5. A water-insoluble, high-temperature lubricating grease composition suitable for ball-bearing lubrication comprising a major amount of mineral lubricating oil, and about 15 to 35 wt. percent of a metal mixed salt thickener system of: acetic acid, C_9 to C_{16} aliaphatic saturated dicarboxylic acid, and C_{12} to C_{24} fatty acid which is predominantly saturated, in a mole hydrogen equivalent ratio of about 1 to 2 mole equivalent proportions of said acetic acid per mole equivalent of said dicarboxylic acid, and about 1 to 2 mole equivalent proportions of said C_{12} to C_{24} fatty acid per molar equivalent of said dicarboxylic acid, and wherein said metal is selected from the group consisting of (A) lithium and (B) lithium-calcium mixtures in a weight ratio of about 1 to 4 parts of lithium per part of calcium.

6. A grease composition according to claim 5, wherein said dicarboxylic acid is azelaic acid.

7. A grease composition according to claim 6, wherein said metal is lithium.

8. A grease composition according to claim 6, wherein said metal is lithium-calcium.

9. A method of lubricating a ball-bearing which comprises lubricating said bearing with the grease composition of claim 5.

References Cited by the Examiner

UNITED STATES PATENTS

2,417,428	3/1947	McLennan	252—39
2,417,429	3/1947	McLennan	252—39
2,641,577	6/1953	O'Halloran	252—40
2,699,428	1/1955	Lux et al.	252—35
2,710,838	6/1955	Morway et al.	252—41
2,846,392	8/1958	Morway et al.	252—39
2,880,174	3/1959	Morway et al.	252—39
2,908,645	10/1959	Morway	252—40
2,940,930	6/1960	Pattenden et al.	252—39

DANIEL E. WYMAN, *Primary Examiner.*