

1

3,385,792

## LUBRICANTS CONTAINING MIXED METAL SALT OF FATTY ACID AND DIPHENOLS

Arnold J. Morway, Clark, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware  
No Drawing. Filed Nov. 5, 1965, Ser. No. 506,604  
8 Claims. (Cl. 252-33.6)

### ABSTRACT OF THE DISCLOSURE

A shear-hardening lubricating grease for bearing lubrication comprising lubricating oil thickened with a mixture of alkali metal salt of C<sub>2</sub> to C<sub>4</sub> fatty acid, a diphenol containing 13 to 25 carbon atoms and a C<sub>12</sub> to C<sub>24</sub> fatty acid.

This invention relates to lubricants containing mixed metal salt of fatty acid and diphenol. In its preferred form, the invention relates to lubricating grease suitable for lubrication of anti-friction bearings, comprising lubricating oil thickened with a mixture of alkali metal salt of: low molecular weight fatty acid, diphenol, and a high molecular weight fatty acid, in certain proportions.

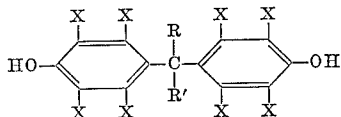
The greases of the invention can be formulated to shear-harden when a shearing stress is exerted. This ability to shear-harden is of particular importance in the lubrication of anti-friction ball and roller bearings. In such bearing lubrication, a non-hardening type grease tends to churn in the rotating bearing, thereby imparting resistance to the rotation of the bearing, which in turn increases friction and generates unwanted heat. On the other hand, when using the shear-hardening greases of this invention, the rotating balls, or rollers, will after a time harden the grease so as to form a channel through the grease. Once the channel is formed, the grease is still available for lubrication, but does not impede the rotating balls or bearing movement, thereby giving lower torque requirements, less friction, a lower power requirement and cooling bearings.

The mixed-salt thickener systems of the invention are best made to contain metal salt of 1 to 10, preferably 1 to 4 molar hydrogen equivalents of low molecular weight fatty acid per molar hydrogen equivalent of diphenol. These systems can also contain salt of .1 to 4, preferably .5 to 3 molar hydrogen equivalents of C<sub>12</sub> to C<sub>24</sub> high molecular weight fatty acid per molar hydrogen equivalent of said diphenol. Greases can be thus prepared comprising a major amount of lubricating oil and having a total content of said mixed salts of 5.0 to 49.0 weight percent, preferably 20 to 45 weight percent, based on the weight of the grease. These greases 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.

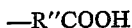
The metal component of the mixed thickeners in an alkali metal, including sodium and lithium.

Suitable low molecular weight fatty acids for forming the aforesaid mixed salt compositions include C<sub>2</sub> to C<sub>4</sub> fatty acids such as acetic, propionic and butyric acids. Acetic acid or its anhydride is preferred.

The diphenols of the invention can be represented by the general formula:

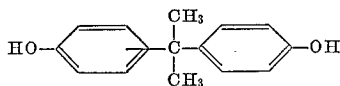


wherein each X is hydrogen or chlorine, and R and R' can be hydrogen, C<sub>1</sub> to C<sub>10</sub> saturated, branched or straight chain hydrocarbon groups, or acyl groups, i.e.,

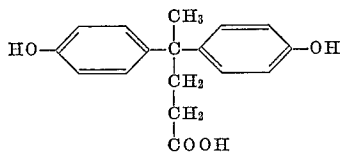


2

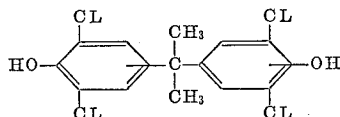
where R'' is a divalent C<sub>1</sub> to C<sub>9</sub> branched or straight chain saturated hydrocarbon group. The total of carbon atoms in the molecule will usually be about 13 to 25, preferably 14 to 18. Monophenols do not give the same desirable results as the diphenols in the compositions of the invention. Representative materials of the above types which were used in the examples of the invention are as follows:



4,4'-isopropylidenediphenol



4,4-bis(4-hydroxyphenyl)pentanoic acid



Chlorinated 4,4'-isopropylidenediphenol

The high molecular weight fatty acids useful for forming the mixed salt of the invention include the usual soap-making acids conventionally used in grease making, including naturally-occurring or synthetic, substituted or unsubstituted, saturated or unsaturated, mixed or unmixed fatty acids having about 12 to 24, e.g., 16 to 24 carbon atoms per molecule. Examples of such acids include myristic, palmitic, stearic, 12-hydroxy stearic, arachidic, oleic, ricinoleic, hydrogenated fish oil, tallow acids, etc.

The lubricating oil used in the compositions of the invention can 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<sub>13</sub> 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.

The lubricants of the invention can be formed in a number of different ways. The most convenient is to neutralize a mixture of the fatty acid and diphenol in at least a portion of the oil, with metal base, e.g. metal hydroxides. Usually, the resulting composition will then be heated to about 225° to 550° F. to dehydrate the composition. Heating at high temperatures of about 420° to 550° F. will usually result in the formation of a mixed salt material having greater thickening effect and better load and E.P. properties than the same salt material formed at lower dehydration temperature. Other methods of manufacture can be used. For example, preformed metal salt of the fatty acid and preformed metal salt of the diphenolic acid can be simply mixed together in the oil and then heated, preferably to 420° to 550° F. etc.

Various other additives may also be added to the lubricating composition in amounts of 0.1 to 10.0 weight

percent each. Examples of such additives include oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors, such as sorbitan monooleate, trisodium phosphate; dyes; other grease thickeners, and the like.

The invention will be further understood by reference to the following examples wherein all parts are by weight and which include a preferred embodiment of the invention, and wherein all of the greases were substantially neutral.

#### EXAMPLE I

72.6 parts of a naphthenic mineral lubricating oil of 60 SUS. viscosity at 210° F., 15 parts of Hydrofol Acid 51, and 4 parts of said 4,4-isopropylidenediphenol (known commercially as Bisphenol A) were charged to a fire-heated grease kettle and intimately mixed while warming to 130° F. 5.2 parts of lithium monohydride (LiOH·H<sub>2</sub>O) in the form of an aqueous solution consisting of 20 wt. percent of said LiOH·H<sub>2</sub>O and 80 wt. percent water, was then added. After mixing for 15 minutes, 3.0 parts of glacial acetic acid was added. The temperature of the reaction mass was raised to 220° F., and after boiling for 5 minutes, the wet grease was passed through a Charlotte mill and returned to the cooling kettle in order to remove any lumps. The temperature was then raised to 420° F. in order to completely dehydrate the grease. The grease was then cooled, while mixing, to 250° F. where 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor. After this, the grease was further cooled to 150° F. where it was again homogenized in the Charlotte set at a 0.020 inch opening, thereby forming a uniform smooth structure.

Hydrofol Acid 51 is a commercial fatty acid prepared by hydrogenating fish oil acid and has an average chain length of about 18 carbon atoms and a maximum Wijs iodine number of 3.

#### EXAMPLE II

A grease was prepared in the same general manner as that of Example I except that slightly different proportions of ingredients was used, and in addition 3 parts of a 50/50 wt. blend of finely pulverized sodium nitrite (ranging in particle size from about 1 to 35 microns) in oil was added as an antirust agent when the grease was cooled to the 150° F. temperature before the Charlotte milling.

#### EXAMPLE III

62.05 parts of naphthenic mineral lubricating oil of 60 SUS. viscosity at 210° F., 12.75 parts of tallow fatty acid and 3.4 parts of 4,4-isopropylidenediphenol were charged to a fire-heated grease kettle and intimately mixed. 9.8 parts of 100% sodium hydroxide was added in the form of an aqueous solution consisting of 40 wt. percent of sodium hydroxide and 60 wt. percent water.

Heating was then initiated and the temperature of the reaction mass was raised to 220° F. After 15 minutes at 220° F., the kettle contents was then circulated from the kettle, through the Charlotte mill having an opening of 0.020 inch, and returned to the kettle, to remove any lumps. The grease was then heated to 330° F. where 2.50 parts of trisodium phosphate (Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O) in the form of an aqueous solution consisting of 50 wt. percent Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O in 50 wt. percent water was added as an anti-rust and oxidation inhibitor. The grease was then heated to 425° F. to dehydrate the grease. The grease was then quickly cooled to 250° F. by passing cooling water through the kettle jacket while mixing, then 1 part of phenyl-alpha-naphthylamine was added as additional oxidation inhibitor. After this, the grease was further cooled to 150° F. where it again homogenized by passage through said Charlotte homogenizer thereby forming a uniform smooth structure.

The tallow fatty acids were commercial acid from beef tallow and having a Sap. No. of 195 mg. KOH/gram and an iodine number of 55.

#### EXAMPLE IV

This grease was prepared in a manner similar to that of preparing the grease of Example I, except that 4,4-bis(4-hydroxyphenyl)pentanoic acid, known commercially as Bisphenol B, was used in place of Bisphenol A.

#### EXAMPLE V

This grease was prepared in the manner of the grease of Example IV, except that a neutralizing amount of sodium hydroxide in the form of an aqueous solution containing 40 wt. percent NaOH was used in place of the lithium hydroxide solution.

#### EXAMPLE VI

This grease was prepared in a manner similar to that of Example I except that the aforesaid chlorinated 4,4-isopropylidenediphenol was used in place of the 4,4-isopropylidenediphenol.

#### EXAMPLE VII

This grease was made by adding additional oil to a portion of the grease of Example VI just before the last homogenization in the Charlotte mill.

#### EXAMPLE VIII

This grease was prepared in a manner similar to the grease of Example V, but using the chlorinated 4,4-isopropylidenediphenol in place of the 4,4-isopropylidenediphenol.

The formulations and properties of the greases of the preceding examples are summarized in the following table:

TABLE

	Examples							
	I	II	III	IV	V	VI	VII	VIII
Composition (wt. percent):								
Glacial Acetic Acid	3.0	2.31	-----	2.8	2.8	3.0	2.3	10.0
Hydrofol Acid 51	15.0	11.55	8.50	12.0	12.0	15.0	11.5	15.0
Tallow Fatty Acids			12.75					
4,4-isopropylidenediphenol	3.0	2.31	3.40					
4,4-bis(4-hydroxyphenyl)pentanoic acid				2.4	2.8			
Chlorinated 4,4-isopropylidene diphenol						3.0	2.3	4.0
Lithium Hydroxide Monohydrate (LiOH·H <sub>2</sub> O)	5.4	4.38	-----	4.2	-----	5.4	4.2	-----
NaOH			9.80		4.8			11.5
Sodium phosphate (Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O)			2.50					4.0
Phenyl α-naphthylamine	1.0	1.00	1.00	1.0	1.0	1.0	1.0	1.0
50/50 NaNO <sub>2</sub> in Mineral Lubricating Oil		3.00						
Mineral Lubricating Oil, 60 SUS at 210° F.	72.6	75.45	62.05	77.6	77.6	72.6	78.7	54.5
Mol. eq. ratio:								
Acetic/Diphenol	1.9	1.9	-----	1.9	1.7	3.0	3.0	7.5
High M.W. Fatty Acid/Diphenol	2.3	2.3	0.3	1.6	1.0	2.1	2.1	2.4
Properties:								
Appearance			Excellent, smooth, uniform grease					
Dropping Point, ° F.	395	420	499+	400	400+	425	420	450
ASTM Penetrations, 77° F., mm./10:								
Unworked	200	270	279	240	200	200	275	200
Worked 60 strokes	200	274	254	250	210	205	280	180
Worked 10,000 strokes	185	252	233	265	225	185	260	210
Rust Test, CRC L-41			Pass		Pass			

TABLE

	Examples							
	I	II	III	IV	V	VI	VII	VIII
Lubrication Life, <sup>1</sup> Hours:								
250° F.—10,000 r.p.m. ....	2,000+	2,000+	2,500+	2,000+	-----	2,000+	2,000+	-----
300° F.—10,000 r.p.m. ....				1,800+	-----	1,895	2,100	2,000+
Bearing Temp. Rise Test:								
Initial Max., ° F. ....	125	130	120	125	130	120	140	120
Time at Max., Minutes .....	10	15	2	12	10	2	5	3
Steady State, ° F. ....	85	90	90	85	85	85	90	80
Ambient, ° F. ....	80	80	80	85	80	80	80	75
Wheel Bearing Test (220° F.) .....				Pass	-----	Pass	Pass	Pass
Slump .....				None	-----	None	None	None
Leakage .....				None	-----	None	None	None
Norma Hoffman Oxidation (p.s.i. drop):								
100 hours .....				2.5	-----			
200 hours .....				6.5	-----			
Timken Test, Pounds Carried .....								30
Boiling Water Solubility .....	Insol.	Insol.	-----	Insol.	-----	Insol.	Insol.	-----

<sup>1</sup> NLGI=ABEC procedure and equipment.

The CRC L-41 test was carried out by coating chemically clean Timken bearings (cup and bearings) 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.

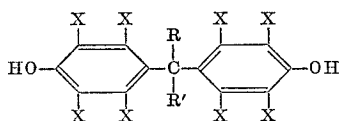
The Bearing Temperature Rise Test was carried out as follows: A 204 mm. steel ball bearing was packed with 3.0 grams of the grease to be tested and the bearing was then operated at 10,000 r.p.m. while the temperature of the grease in the bearing was continually measured by thermocouples placed on the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

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

As seen by the data of the table, the greases of the invention all resulted in excellent, smooth, uniform greases having dropping points ranging from 395° F. up to above 499° F. The grease of Examples I to VIII all had relatively long lubrication lives at elevated temperatures as indicated by the NLGI-ABEC tests. The greases made from lithium were water-insoluble, even in boiling water. All greases of the table were channeling type as illustrated by the fact that they initially rose in temperature due to friction while the channel was being formed, but after 2 to 15 minutes the temperature of the grease began to drop to the steady state temperature ranging from 80° to 90° F., which are only slightly above the ambient temperature. The greases also showed up well in the Wheel Bearing Test which is a conventional test to determine their utility in automobile wheel bearings. The greases of Example VIII prepared from the chlorinated diphenol acids had good E.P. properties as measured by the Timken Test, in addition to still being a good channeling grease. Example III, illustrates the need for the low molecular acid, e.g., the acetic acid, in order to impart sufficient hardness to the grease. Note, that the grease of Example III was softer (as indicated by the higher penetrations) than all the other greases of the table, even though it contained more total salt than the greases of the other examples.

What is claimed is:

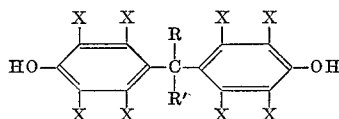
1. A shear hardening, channeling type lubricating grease suitable for ball or roller bearing lubrication comprising a major amount of lubricating oil and 20 to 45 wt. percent of mixed alkali metal salt of: (a) C<sub>2</sub> to C<sub>4</sub> fatty acid, (b) diphenol of 13 to 25 carbon atoms having the formula:



wherein R and R' are selected from the group consisting of hydrogen, C<sub>1</sub> to C<sub>10</sub> saturated hydrocarbon radicals and radicals having the structure —R''COOH where R'' is a saturated divalent C<sub>1</sub> to C<sub>9</sub> hydrocarbon; and X is selected from the group consisting of hydrogen and chlorine, and (c) C<sub>12</sub> to C<sub>24</sub> fatty acid; in a ratio of 1 to 10 molar hydrogen equivalents of said C<sub>2</sub> to C<sub>4</sub> fatty acid per molar hydrogen equivalent of diphenol, and about 0.1 to 4 molar hydrogen equivalent proportions of said C<sub>12</sub> to C<sub>24</sub> fatty acid per molar hydrogen equivalent of said diphenol.

2. A lubricating grease according to claim 1 wherein: said oil is mineral lubricating oil, said C<sub>2</sub> to C<sub>4</sub> fatty acid is acetic acid and said diphenol contains 14 to 18 carbon atoms.

3. A shear-hardening, channeling type lubricating grease suitable for ball or roller bearing lubrication comprising a major amount of mineral lubricating oil, about 20 to 45 wt. percent of an alkali metal mixed salt thickener system of: acetic acid, diphenol of 14 to 18 carbon atoms having the formula:



wherein R and R' are selected from the group consisting of hydrogen, saturated hydrocarbon groups and groups having the structure —R''COOH where R'' is a saturated divalent hydrocarbon radical; and X is selected from the group consisting of hydrogen and chlorine; and C<sub>16</sub> to C<sub>24</sub> fatty acid which is predominantly saturated, in a mole hydrogen equivalent ratio of about 1.0 to 4.0 mole equivalent proportions of said acetic acid per mole equivalent of said diphenol and about 0.5 to 3.0 mole equivalent proportions of said C<sub>16</sub> to C<sub>24</sub> fatty acid per molar equivalent of said diphenol.

4. A grease according to claim 3, wherein said metal is sodium.

5. A grease according to claim 3, wherein said metal is lithium.

6. A grease according to claim 3, wherein said diphenol is 4,4-isopropylidenediphenol.

7. A grease according to claim 3, wherein said diphenol is 4,4-bis(4-hydroxyphenyl) pentanoic acid.

8. A grease according to claim 3, wherein said diphenol is chlorinated 4,4-isopropylidenediphenol.

#### References Cited

##### UNITED STATES PATENTS

2,776,260	1/1957	Klicker et al.	252—39
2,976,242	3/1961	Morway	252—39
3,065,179	11/1962	Morway et al.	252—33.6
3,130,160	4/1964	Morway et al.	252—33.6

DANIEL E. WYMAN, *Primary Examiner*.

I. VAUGHN, *Assistant Examiner*.