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LUBRICANTS COMPRISING POLYPHENYL ETHERS AND MIXED METAL SALTS OF FATTY ACIDS

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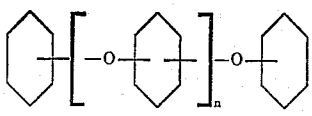
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3 Claims. (Cl. 252—17)

This invention relates to lubricating compositions comprising mixed metal salts of fatty acids in a polyphenyl ether base oil, and methods for preparation of said lubricating compositions. Particularly, the invention relates to lubricating greases and fluids, which are suitable for high temperature use, comprising polyphenyl ether and alkaline earth metal salts of a C_2 to C_4 fatty acid and a C_6 to C_{30} fatty acid.

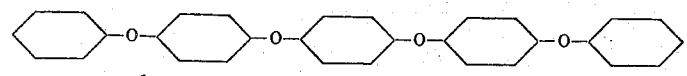
Recently, lubricating compositions containing mixed alkaline earth metal salt of low molecular weight fatty acid and alkaline earth metal salt of higher molecular weight fatty acid, have found wide spread use in commercial applications. These lubricants are generally prepared by coneutralizing with lime, four or more mol equivalents of acetic acid (or its anhydride) per mole of higher fatty acid (such as oleic acid or coconut acids). The resulting mixed salt lubricants have good anti-wear and load-carrying ability, and have gained widespread commercial acceptance. The commercial mixed-salt lubricants have generally been prepared using a mineral oil base. However, during high temperature use for extended periods, e.g. at temperatures of 400° F. and above, such as are encountered in lubrication of aircraft, rocket engines, steel making facilities, etc., the mineral oil compositions do not give good results because of the volatility of mineral oil. A wide variety of base oils have been tested in order to form suitable mixed-salt lubricants for high temperature use. Thus, highly refined mineral oils and synthetic oils such as diesters of dicarboxylic acids, polyoxyalkylene glycols (Ucon oils), silicone oils, etc. have been tested. Even though a number of these oils have been recognized as having good stability at high temperatures, they did not possess the desired characteristics for high temperature bearing lubrication when used as base oils for the mixed salts referred to above. Recently, certain aryl-alkyl silanes such as dilauryl, diphenyl silane were found to form good mixed salt lubricants for high temperature use. It has now been found that a certain range of polyphenyl ethers are superior in several respects to the aforementioned silane oil, which heretofore had been the best oil known to the present inventors for high temperature mixed salt lubricants.

The polyphenyl ether oils of the invention are those normally liquid (at 77° F.) ethers represented by the general formula:

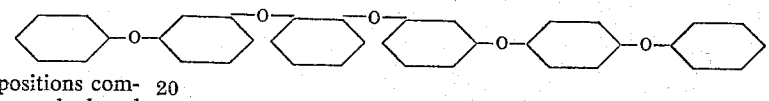


where n is about 3 to 6. The oxygen atoms attached to the hydrocarbon rings intermediate the terminal phenyl groups, can be in an ortho, meta, or para position relative

to each other. Isomeric mixtures of polyphenyl ethers within the above formula are also included in the invention, as well as mixtures of polyphenyl ether molecules having different values for "n." An oil of the above general formula wherein n was 3, obtained from Monsanto Chemical Co. under the designation "High Temperature Functional Fluid and Lubricant OS–124," was used in the working example of the invention. Other specific examples of such polyphenyl ethers include the following:



and



etc.

The lubricating compositions of the invention will comprise a major amount of polyphenyl ether as the base oil and about 5 to 40 wt. percent, preferably 10 to 30 wt. percent, of the mixed salt. The mixed salt in turn, will comprise a mixture of the alkaline earth metal salts of a low molecular weight C_2 to C_4 fatty acid (preferably acetic acid or acetic anhydride) and a C_7 to C_{30} fatty acid. Usually about 4 to 30, preferably 4 to 15, mol equivalents of low molecular weight acid per mol equivalent to C_7 to C_{30} fatty acid will be used.

The mixed salt thickener can be prepared by reacting alkaline earth metal base, such as the hydroxides are carbonates of calcium, barium, strontium or magnesium, with the mixture of fatty acids. Calcium is the preferred metal, being generally used in the form of a lime slurry, while acetic acid, or its anhydride, is preferably used as the low molecular weight acid.

The C_7 to C_{30} fatty acids can be considered as including two groups, the intermediate molecular weight fatty acids and the high molecular weight fatty acids. The intermediate molecular weight fatty acids are generally considered to be the C_7 to C_{12} acids, including straight chain, saturated acids such as capric, caprylic, pelargonic acid, lauric acid, etc. The high molecular weight fatty acids are generally considered to be the C_{14} to C_{30} acids, such as stearic, 12-hydroxy stearic, oleic, tallow acids, hydrogenated fish oil acids, iso-oleic, etc. The fatty acids can also be used in the form of their glycerides.

A high molecular weight fatty acid used in several examples of the invention was a commercial iso-oleic acid. Iso-oleic can be regarded as the cis form of oleic acid. The cis form is also known as elaidic acid. Commercial iso-oleic acid generally constitutes mixtures of a major amount of elaidic acid with minor amounts of oleic acid (i.e. 9-octadeceneoic acid) and other related acids such as 12-octadeceneoic, linoleic, linolic, stearic, palmitic, etc. The commercial iso-oleic acid used in the working examples of the invention is available under the tradename of Emery 635 Fatty Acid.

If desired, various inorganic acids can be used to replace part of the low molecular weight fatty acid component in the preparation of the mixed salt material. Thus, strong mineral acids such as hydrochloric acid, nitric acid, sulfuric acid and orthophosphoric acid can be used. If phosphoric acid is used to replace a portion of the low molecular weight fatty acid, the resulting grease is made more resistant to color and oxidation degradation than if no phosphoric acid was used. Various inorganic salts such as alkaline earth metal or alkali metal (e.g. sodium and lithium) nitrites, phosphates, chromates, and carbonates can also be added to the lubricant. If the metal component of the inorganic salt is an alkaline earth

metal, then the salt can generally be formed from the appropriate acid, in situ, during the neutralization of the fatty acids.

The base oil is preferably 100° polyphenyl ether, but minor amounts of other base oils can be added.

The compositions of the invention can be prepared in several ways. In one method, all the acids are dispersed in the base oil and neutralized with the metal base. The water of reaction may be left in the lubricant by not applying heat, thereby forming a "cold-sett" lubricant. However, generally the product will be heated to about 225° to 600° F. to dehydrate the mixture. Preferably, the mixed salts are formed by co-neutralizing the acids with metal base in the presence of a volatile inert solvent such as Varsol No. 1 (a commercial hydrocarbon solvent marketed by the Enjay Co.), heptane, toluene, etc. The resulting mixture is then mixed with polyphenyl ether and the volatile solvent is evaporated by heating.

A more specific description of the preferred process is as follows: The acids and metal base are added to the inert volatile solvent and intimately mixed. The heat of reaction will usually raise the temperature of the reaction mass, but temperatures above about 200° F. are to be avoided at this phase of the process, so cooling may be necessary. The resulting composition will be relatively fluid due to the solubilizing effect of the volatile solvent upon the resulting mixed fatty acid salts. The composition is then preferably homogenized and filtered. This filtration step will eliminate unreacted metal base as well as various contaminants of commercial metal base. For example, in the case of lime, this filtration will remove calcium carbonate, iron, alumina oxide and silica. Some of these contaminants act as abrasives in close clearance high shear applications, such as anti-friction bearings. After filtration, the volatile solvent concentrate of the mixed salts is added to the polyphenyl ether oil. The resulting mass then is preferably heated to temperatures of about 250° to 450° F., preferably 300° to 350° F., in order to dehydrate the mixture and to drive off the volatile solvent. The mixture can then be cooled to about 200° to 210° F., where conventional additives, if any, can be added. The lubricant is then preferably cooled to below 150° F. where it can be homogenized, as by passing through a Gaulin homogenizer or a Charlotte mill, followed by subsequent cooling to room temperature. If desired, grease concentrates of the mixed salts in the polyphenyl ether can be made by the above techniques and then diluted with additional lubricating oil to form the final grease composition, or even further diluted to form a fluid type lubricant.

The advantages of using the volatile solvent technique described above are: the ability to obtain a more complete reaction of the ingredients due to the lower viscosity of the reaction mass because of the low viscosity solvent and its solubilizing effect, and freedom from possible side reactions with polyphenyl ether.

Conventional additives, which can be added to the compositions of the invention, include oxidation inhibitors such as phenyl-α-naphthylamine; rust preventives such as sodium nitrite; other thickeners such as polyethylene, polypropylene, carbon black, metal soaps; etc.

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

EXAMPLE I

Part A.—13.4 parts of hydrated lime, and 10 parts of iso-oleic acid (Emery 635 Fatty Acid) were mixed into 57.6 parts of Varsol No. 1 to form a smooth slurry. Next, 18 parts of glacial acetic acid was slowly added as the heat of reaction raised the temperature to about 200° F. The composition was then cooled, homogenized by passing through a Morehouse mill having 0.003" clearance and then filtered through a 100 mesh screen.

Part B.—100 parts of the composition of Part A was then blended with 75 parts of polyphenyl ether (Monsanto's OS–124) by slowly pouring the polyphenyl ether into the salt composition while stirring. The temperature of the resulting mixture was then slowly raised to about 350° F., while mixing, thereby volatilizing approximately all of the water of reaction and the Varsol. The residue was then cooled to 200° F., where 1 part of phenyl-alpha-naphthylamine was added. Following this the composition was further cooled to about 90° F. where it was homogenized by passage through a Morehouse mill having 0.003" clearance.

Mineral oil comparison grease

A portion of the mixed salt-Varsol composition of Example I, Part A, was blended with a mineral lubricating oil having a viscosity of 55 SUS at 210° F., by slowly pouring the oil into the salt-Varsol composition, while stirring. The resulting mixture was then heated to 350° F. to volatilize the water of reaction and the Varsol, then cooled to 200° F. where one part of phenyl-alpha-naphthylamine was added. The composition was then homogenized in a Morehouse mill having 0.003" clearance at 90° F. In other words, Example I, Part B, was repeated with the main exception that mineral lubricating oil was used in place of the polyphenyl ether oil. Also, a slightly lesser amount of phenyl-alpha-naphthylamine was used.

Silane oil comparison example

As previously mentioned, the best high temperature mixed salt lubricant previously known to the inventors was one prepared from a dilauryl, diphenyl silane. This lubricant was prepared as follows:

71.5 parts of Dow Corning QF–6–7009 Fluid (dilauryl, diphenyl silane), 9.5 parts of hydrated lime and 2 parts of Hydrofol Acid Code 200 were added to an electrically heated grease kettle and intimately mixed. The Hydrofol Acid Code 200 is a commercial hydroxy stearic acid obtained by hydrogenating castor oil and consists of about 88 wt. percent 12-hydroxy stearic acid and 12 wt. percent of stearic acid. Next, a blend consisting of 12 parts of glacial acetic acid and 4 parts of Wecoline AAC acid was added to the kettle. Wecoline AAC acid is a commercial acid derived from coconut oil and consisting of about 26 wt. percent lauric acid, about 28 wt. percent caprylic acid and about 46 wt. percent capric acid. External heating was then initiated and the temperature of the mixture was raised to about 430° F. and maintained at this temperature for about ½ hour. The heat was then shut off and the material was cooled to 200° F., at which point one part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor. Following this, the mixture was allowed to cool to 100° F. and was then pumped through a Morehouse mill having a 0.003" clearance to form the finished grease.

The properties and final compositions, in terms of ingredients, of the lubricants prepared above are summarized in the following Table I.

TABLE I

Final Composition, Parts By Weight	Example I	Mineral Oil Comparison	Silane Oil Comparison
Glacial Acetic Acid	15.6	15.6	12.0
Iso-oleic Acid	8.7	8.7	----------
Wecoline AAC Acid	----------	----------	4.0
Hydrofol Acid Code 200	----------	----------	2.0
Hydrated Lime	11.6	11.6	9.5
Phenyl-α-naphthylamine	1.2	1.0	1.0
Polyphenyl Ether	62.9	----------	----------
Mineral Lubricating Oil, 55 SUS. at 210° F	----------	63.1	----------
Diphenyl, Dilauryl silane	----------	----------	71.5
Mole Ratio, Acetic/Higher Fatty Acids	10/1	10/1	10/1
Properties:			
Appearance	Excellent	Excellent	Excellent
Dropping Point, ° F	None	None	None
ASTM Penetration, 77° F., mm./10—			
Unworked	250	290	885
Worked 60 strokes	255	300	225
Worked 10,000 strokes	255	300	292
Solubility in Boiling Water	None	None	None

As seen by Table I, all three greases had no dropping points and the same mole ratios of acetic to the higher fatty acid. The advantage of the polyphenyl ether oil grease (Example I) over the two comparison greases is illustrated by the Lubrication Life test. This test is the standard spindle test of the Anti-Friction Bearing Manufacturers Association-National Lubricating Great Institute (AFBNA-NLGI). The test is carried out by determining the lubricating life of the grease in hours in a 204 mm. ball bearing rotating at 10,000 revolutions per minute.

The results obtained in the above test are summarized in Table II, which follows:

TABLE II.—LUBRICATING LIFE IN 204 BALL BEARING TEST OPERATING AT 10,000 R.P.M.

Composition	Temperature, ° F.	Lubrication Life		Grease Condition at End of Test
		Hours	Cumulative	
Example I	300	2,206		
Do	350	522	2,728	Grease still soft and plastic.
Do	400	372	3,100	Bearing failed, grease still plastic.
Mineral Oil Comparison.	300	950	950	Badly coked, bearing frozen.
Silane Oil Comparison	300	1,920	1,920	Bearing failed, grease hardened badly.
Do	350	1,479	1,479	Bearing failed, grease coked.

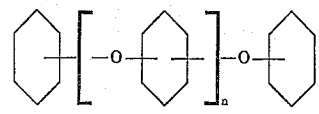
As seen by Table II, a sample of the grease of Example I ran for 2206 hours at 300° F. and was still in good condition. The test temperature was raised to 350° F. where the same sample performed satisfactory for an additional 522 hours or a cumulative total of 2728 hours. At the end of this time, the grease was still soft and plastic. The test temperature of the bearing and grease was then raised to 400° F. where the grease lubricated for another 372 hours before failing. In comparison, the mineral oil comparison grease failed after only 950 hours at 300° F. This grease had badly coked. One sample of the silane oil comparison grease, ran for 1920 hours at 300° F. before failing, while a different sample ran for 1479 hours at 350° F. Although there was a slightly larger amount of phenyl-alpha-naphthylamine in the grease of Example I as compared to the comparison greases, previous experience indicates that this difference had no substantial effect on the test results. Rather, the large difference in test results are attributed to the base oils.

As a further example of the invention, Example I can be exactly repeated but using pure elaidic acid rather than the commercial iso-oleic acid, and using in place of the commercial OS-124 phenyl ether, a polyphenyl ether of the structure:



What is claimed is:

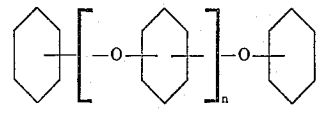
1. A method of preparing a lubricating composition which comprises mixing C_2 to C_4 fatty acid and C_7 to C_{30} fatty acid in a ratio of about 4 to 30 mole equivalents of C_2 to C_4 fatty acid per mole equivalent of C_7 to C_{30} fatty acid, with a neutralizing amount of alkaline earth metal base, in a volatile inert hydrocarbon solvent, adding polyphenyl ether of the general formula:



where n is 3 to 6, and heating to a temperature sufficient to evaporate the water of reaction and said volatile hydrocarbon solvent, wherein the amount of resulting metal salt comprises about 5 to 40 wt. percent of the final lubricating composition.

2. A method according to claim 1, wherein said alkaline earth metal base is lime, said C_2 to C_4 fatty acid is acetic acid, said C_7 to C_{30} fatty acid is a mono-unsaturated C_{18} acid and n is about 3.

3. A method of preparing a lubricating grease which comprises neutralizing 4 to 15 molar proportions of acetic acid and a molar proportion of C_{14} to C_{30} fatty acid with lime, in a volatile inert hydrocarbon solvent while maintaining the temperature below about 200° F., homogenizing the resultant mixture and filtering, then slowly mixing into said mixture polyphenyl ether lubricating oil of the general formula:



where n is 3 to 6 while stirring, heating the resulting mixture to a temperature within the range of about 250° to 450° F. in order to dehydrate the mixture and evaporate the volatile solvent, and then cooling to thereby form said grease, wherein the amount of resulting metal salt comprises about 10 to 30 wt. percent of said grease.

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