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LUBRICATING COMPOSITIONS

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This invention relates to novel organo-metallic complexes and to compositions containing the same. More particularly, the present invention pertains to soap-salt complexes comprising a metal salt of a low molecular weight carboxylic acid, a metal salt of an aryl sulfonic acid and a metal soap of a high molecular weight carboxylic acid and to lubricant compositions containing the same.

In brief compass, the invention relates to compositions containing soap-salt complexes consisting of a metal salt of a low molecular weight, aliphatic, monocarboxylic acid having about 1 to 3 carbon atoms per molecule, a metal salt of an aromatic sulfonic acid having from about 6 to 9 carbon atoms per molecule, and a metal soap of a high molecular weight monocarboxylic acid having from about 12 to 30 carbon atoms per molecule in which the mol ratio of the low molecular weight aliphatic monocarboxylic acid, e. g., acetic acid, to the other acids employed exceeds about 7:1. The compositions of the invention include novel and improved gear oils, filter oils, lubricating greases, etc. In particular, the fluid or semi-fluid lubricant compositions have been found to have excellent extreme pressure and structural stability characteristics.

The use of soap-salt complexes in lubricant compositions has been previously suggested. When these compositions are formed at or subjected to temperatures above 300° F. they tend to form solid compositions which do not liquefy on cooling. It has, therefore, been difficult to prepare lubricant compositions containing soap-salt complexes which will retain their fluid or semi-fluid structure as well as their load carrying properties after being subjected to temperatures exceeding 300° F. The advantages of having a lubricant composition capable of retaining a fluid or semi-fluid structure and characterized by outstanding extreme pressure properties are obvious.

In accordance with the present invention, it has now been found that fluid lubricant compositions having structural stability at elevated temperature can be prepared by employing an aryl sulfonic acid in conjunction with the low and high molecular weight carboxylic acids. Thus, the soap-salt complexes of the invention comprise a metal salt of an aryl sulfonic acid, at least one metal salt of a low molecular weight carboxylic acid having from about 1 to 3 carbon atoms per molecule and at least one metal soap of a high molecular weight carboxylic acid having from about 12 to 30 carbon atoms per molecule. As previously noted, the lubricant compositions of the invention have outstanding extreme pressure and structural stability properties as well as other desirable lubricant characteristics.

The aryl sulfonic acids employed in accordance with the invention are those aromatic sulfonic acids which have from about 6 to 9 carbon atoms per molecule and a molecular weight below about 250, preferably within the range of about 140 to 200. Such aryl sulfonic acids are exemplified by the following: benzene mono- or di-sulfonic acids; ortho, meta or para toluene sulfonic acids and ortho, meta or para xylene sulfonic acids. Operable sulfonic acids are exemplified by the following structural formula:

$$R_mX(SO_3H)_n$$

wherein R is a methyl group, X is an aryl or aromatic group, m is an integer from 0 to 3, and n is an integer from 1 to 2. For the purposes of the present invention, the xylene monosulfonic acids are preferred. In general, about 10 to 25 wt. percent, preferably about 15 to 20 wt. percent, based on the soap-salt complex, and about 2 to 5 wt. percent, preferably about 2.5 to 3.5 wt. percent, based on the total lubricant composition, of the aryl sulfonic acid will be employed.

The low molecular weight, aliphatic, monocarboxylic acids capable of being utilized in preparing the novel soap-salt complexes of the invention include formic, acetic, propionic, arcylic, lactic, thio-glycolic, glycolic, chloro-acetic, oxalic acids, etc. Acetic acid is especially preferred. Mixed low molecular weight carboxylic acids, wherein the acids contain from about 1 to 3 carbon atoms per molecule and have an average saponification value of above about 540, may also be employed. In general, the low molecular weight carboxylic acid will be employed in amounts ranging from about 50 to 75 wt. percent, preferably about 60 to 70 wt. percent, based on the soap-salt complex, and about 10 to 20 wt. percent, preferably about 12 to 15 wt. percent, based on the total lubricant composition.

The high molecular weight fatty acids useful in this invention are those aliphatic, monocarboxylic acids having from about 12 to 30, preferably about 18 to 22, carbon atoms per molecule. These acids may be derived from saturated or unsaturated naturally occurring or synthetic fatty material. The fatty acids normally used in the manufacture of conventional greases, particularly the more saturated acids, are preferred. Examples of such acids include lauric, myristic, palmitic, stearic, mono- or poly-hydroxy stearic, arachidic, lignoceric, cerotic, behenic and the hydrogenated fish oil or tallow acids, which contain chiefly stearic acid. However, unsaturated fatty acids such as oleic, ricinoleic, and similar acids may also be employed. In general, about the amount of high molecular weight carboxylic acid utilized will range from about 10 to 25 wt. percent, preferably about 15 to 20 wt. percent, based on the soap-salt complex, and about 2 to 5 wt. percent, preferably about 2.5 to 3.5 wt. percent, based on the total lubricant composition.

The novel soap-salt complexes of the invention will have a mol ratio of the low molecular weight monocarboxylic acid to the sulfonic acid plus the high molecular weight carboxylic acid of about 8:1 to about 20:1, and a mol ratio of the sulfonic acid to the high molecular weight carboxylic acid of about 1:1 to 3:1.

The metal component of the complexes of the invention is used in a form which can combine chemically with the carboxylic acids and the aryl sulfonic acids to form salts or soaps. Ordinarily, the metal hydroxide is used. The choice of metal component depends to a certain extent on the use to which the soap-salt complex of the invention is to be put. The alkaline earth metal hydroxides or carbonates such as those of calcium, barium and strontium are useful for many purposes of the present invention. Calcium hydroxide is the preferred metal base for preparing the soap-salt complex containing lubricants of the invention. In general, about 6 to 10 wt. percent, based on the total composition, of the alkaline earth metal base will be utilized.

In accordance with one feature of the invention, the novel soap-salt complexes of the invention may be in-

corporated in a wide variety of liquid and semi-liquid materials of natural or synthetic origin to improve the utility of these materials. More specifically, these soap-salt complexes may be incorporated in mineral and/or synthetic lubricating oils in an extreme pressure imparting proportion of about 10 to 40 wt. percent, preferably about 20 to 30 wt. percent, based on the total composition. In general, the mineral or synthetic lubricating oil should have a viscosity within the range of about 50 to 2000 SUS at 100° F. and 30 to 150 SUS at 210° F., a pour point of about +20 to −75° F., a flash point of about 350° to 650° F., and a viscosity index of about 0 to 60 or higher. As mentioned above, synthetic as well as mineral lubricating oils can be employed as part or all of the liquid phase of the lubricant composition, and they include synthetic lubricating oils of the hydrocarbon, hydrocarbon polymer, ester, complex ester, formal, mercaptal, polyalkylene oxide, silicone or similar types. Synthetic oils such as di-2-ethyhexyl sebacate, di-C_8 Oxo azelate and other branched chain simple esters of dicarboxylic acids can be used, as well as complex esters prepared from glycols, dicarboxylic acids and alcohols or monocarboxylic acids.

The metal soap-salt complexes of the invention may be prepared by coneutralization of a mixture of the carboxylic and sulfonic acids with suitable bases. The coneutralization may be carried out in situ in the liquid menstruum in which the complex is to be incorporated. For example, the mixed acids may be coneutralized in a portion or all of a lubricating oil which then forms the dispersant of the complex. The coneutralized material is heated to a temperature above about 400° F., preferably about 450° to 550° F., in order to effect complex formation. When this heating step is carried out in a liquid dispersant, the latter should have a boiling point above 400° F. or heating should be carried out under pressure.

The coneutralization method of preparation is not necessary as long as the metal salts and soap are present when heating to the complex-forming temperature. Thus, the complex of the invention may be prepared by separately preforming at least a portion of the aryl sulfonic acid salt, the low molecular weight carboxylic acid salt and/or the high molecular weight carboxylic acid soap, intimately mixing the preformed materials, and subjecting the mixture to the complex-forming temperatures.

In general, the lubricant compositions of the invention are prepared by dispersing a metal aryl sulfonate, a high molecular weight carboxylic acid and the alkaline earth metal base in the lubricating oil with mixing, heating the mixture to a temperature within the range of about 130° to 180° F., then adding acetic acid to the heated mixture, and continuing the heating to a temperature within the range of about 450° to 550° F. and maintaining this temperature for about 10 to 15 minutes or until complex formation has taken place. The resulting product is then cooled to a temperature of about 180 to 200° F. and conventional lubricating additives added, if desired. The product is further cooled to about 120 to 150° F. and homogenized at high rates of shear. If shearing mechanisms are employed which incorporate large amounts of air into the lubricant, a means for deaeration should be employed.

The conventional additives which may be utilized include oxidation inhibitors, metal deactivators, corrosion preventatives, etc. as will be understood by those skilled in the art.

As noted above, the lubricant compositions of the invention may be finished by being subjected to homogenization. The homogenization equipment may be any known in the art such as, for example, the Gaulin homogenizer (3000 to 6000 p. s. i. g.), Morehouse mill or Charlotte mill.

The invention will be more fully understood by reference to the following specific examples illustrating various modifications of the invention.

EXAMPLE I

A lubricant composition was prepared as follows:

Formulation:	Percent weight
Glacial acetic acid	12.0
Stearic acid	3.0
Calcium xylene sulfonate	3.4
Hydrated lime	8.7
Phenyl alpha-naphthylamine	0.5
Mineral lubricating oil 55 SUS @ 210° F	72.4

Preparation

The mineral lubricating oil, lime, stearic and calcium xylene sulfonate (prepared from 3,4-xylene sulfonic acid) were charged to a fire heated kettle and mixed while heating to 150° F. The acetic acid was then added, and the heating continued to 500° F. At this temperature, heating was discontinued, the lubricant product cooled to 250° F., and the phenyl alpha-naphthylamine added. The lubricant was then cooled to 180° F. and finished by being passed through a Gaulin homogenizer at 6500 p. s. i.

Properties

Appearance	Smooth, uniform fluid product.
E. P. Properties:	
Almen tests—	
Gradual loading:	
Wgts. carried	15.
Pin condition	Excellent.
Shock loading:	
Wgts. carried	15.
Pin condition	Faint scratches.
SAE test 1000 R. P. M.—	
Scale reading	290.
Timken test—	
Load carried, lbs	60.
Scar condition	Narrow.
Phase changes	Remains fluid up to 500° F.
Stability	No tendency of constituents to settle out or separate after 2 weeks storage.

The above data shows that by employing an aryl sulfonic acid in combination with low and high molecular weight carboxylic acids, stable fluid lubricants having excellent extreme pressure properties can be prepared. It should be particularly noted that the data show that by employing the aryl sulfonic acid the thickening effect of the soap is materially prevented even at elevated temperatures without decreasing the extreme pressure characteristics associated with soap-salt complex containing lubricants.

In accordance with another feature of the invention, the fluid lubricant composition, as shown in Example I, may be effectively blended with other lubricants, such as greases, to produce solid or semi-solid compositions having outstanding load carrying properties as well as other desirable grease characteristics. It will be understood that these blended lubricant compositions may be prepared in any conventional manner. In general, however, they may be prepared by blending about 25 to 75 wt. percent, preferably about 40 to 60 wt. percent, of the fluid lubricant composition of the invention with about 75 to 25 wt. percent, preferably about 60 to 40 wt. percent, of the other lubricant at temperatures within the range of about 100° to 150° F. If desired, the blended lubricant composition may be finished by being homogenized in the equipment referred to above.

The lubricants blended with the fluid lubricant compositions of the invention may be any of the solid grease compositions known to the art. These greases may, for example, be any of the simple soap thickened greases such as the sodium, calcium, lithium soap thickened

greases; the soaps being prepared from the high molecular weight carboxylic acids having from about 12 to 30 carbon atoms per molecule, as described above. The greases may also constitute any of the recently proposed soap-salt or mixed salt complex thickened greases. For example, the grease component of the blended lubricant composition of the invention may comprise the grease prepared by thickening a mineral lubricating oil with a soap-salt complex consisting of the calcium salt of a low molecular weight monocarboxylic acid having from about 1 to 3 carbon atoms per molecule and a high molecular weight carboxylic acid having from about 12 to 30 carbon atoms per molecule. These complexes contain about 7:1 to 40:1, preferably about 7.5:1 to 25:1, mols of the low molecular weight carboxylic acid per mol of the high molecular weight carboxylic acid. The preparation of these greases is not an inventive feature of the present invention and is, therefore, not described here in detail.

This aspect of the invention is shown in the following example.

EXAMPLE II

A lubricating grease composition was prepared by blending 50 wt. percent of component A, the fluid lubricant of Example I, with 50 wt. percent of component B, a grease having the following formulation:

Grease B:	Wt. percent
Acetic acid	8.00
Hydrofol acids 51[1]	2.00
Hydrogenated castor oil	2.00
Hydrated lime	6.00
Phenyl alpha-naphthylamine	0.50
Diol 55	81.50

[1] Hydrogenated fish oil acids.

After intimately mixing the two components at 150° F., the grease was finished by being passed through a Gaulin homogenizer at 5000 p. s. i. g.

The resulting grease composition had the following properties:

Properties

Appearance	Excellent, smooth uniform.
Dropping point, ° F	500+.
Penetrations, 77° F. mm./10:	
Unworked	310.
Worked 60 strokes	325.
Timken test (40 lbs. load)	Pass.
Lubrication life (10,000 R. P. M.–250° F.) hours	1500+[1].
Norma Hoffmann oxidation test	225 hours.

[1] Not a failure—test discontinued for need of apparatus.

As shown in the foregoing data, the fluid lubricants of the invention may either be employed alone or blended with other grease compositions to impart outstanding extreme pressure properties to the final grease composition.

The invention is not limited to the specific conditions and materials of the foregoing examples. As will be understood by those skilled in the art, the conditions and materials may be varied within the limits indicated in the general portions of the specification.

What is claimed is:

1. The method of preparing lubricating compositions which comprises dispersing an alkaline earth metal base, low molecular weight carboxylic acids having about 1 to 3 carbon atoms per molecule, high molecular weight monocarboxylic acids having from about 12 to 30 carbon atoms per molecule and an aryl sulfonic acid having 6 to 9 carbon atoms in a lubricating oil, heating the dispersion to a temperature within the range of about 450° to 550° F., and then cooling to obtain said lubricating composition, wherein the mol ratio of low molecular weight carboxylic acid to the high molecular weight monocarboxylic acid plus the sulfonic acid is about 8:1 to 20:1, the molar ratio of said sulfonic acid to said high molecular weight acid is about 1:1 to 3:1, and said metal base is present in an amount sufficient to neutralize said acids.

2. The method of claim 1 wherein said alkaline earth metal base is a calcium base.

3. The method of claim 1 wherein said lubricating oil is a mineral lubricating oil.

4. The method of claim 1 wherein said aryl sulfonic acid is selected from the group consisting of benzene sulfonic acid, toluene sulfonic acid and xylene sulfonic acid.

5. The method of preparing lubricant compositions which comprises dispersing 2 to 5 wt. % of high molecular weight monocarboxylic acid having from about 12 to 30 carbon atoms per molecule, 6 to 10 wt. % of alkaline earth metal base, and 2 to 5 wt. % of an alkaline earth metal salt of an aryl sulfonic acid having 6 to 9 carbon atoms in a major proportion of a mineral lubricating oil, heating the dispersion to a temperature of about 130° to 150° F., adding 10 to 20 wt. % of low molecular weight carboxylic acid having from about 1 to 3 carbon atoms per molecule to said mildly heated dispersion, heating the resulting mixture to a temperature in the range of 400° to 550° F., and then cooling to obtain said lubricating composition, said weight percentages being based on the final lubricant composition.

6. The method of claim 5 wherein said high molecular weight carboxylic acid is stearic acid and said low molecular weight carboxylic acid is acetic acid.

7. The method of claim 5 wherein said alkaline earth metal aryl sulfonate is calcium xylene sulfonate.

8. The method of claim 5 wherein said lubricant composition is homogenized.

9. A lubricant composition comprising a major proportion of a lubricating oil base stock and a minor proportion of an alkaline earth metal soap-salt complex formed at a temperature in the range of 400° to 550° F., said complex consisting essentially of a high molecular weight monocarboxylic acid having from about 12 to 30 carbon atoms per molecule, a low molecular weight carboxylic acid having from about 1 to 3 carbon atoms per molecule and an aryl sulfonic acid having from about 6 to 9 carbon atoms per molecule, wherein the mol ratio of low molecular weight carboxylic acid to the high molecular weight monocarboxylic acid plus the sulfonic acid is about 8:1 to 20:1 and the mol ratio of said sulfonic acid to said high molecular weight acid is about 1:1 to 3:1.

10. The lubricant composition of claim 9 wherein said alkaline earth metal is calcium.

11. The lubricant composition of claim 9 wherein said high molecular weight carboxylic acid has from about 18 to 22 carbon atoms per molecule, said low molecular weight carboxylic acid is acetic acid and said aryl sulfonic acid is selected from the group consisting of benzene, toluene and xylene sulfonic acids.

12. A blended lubricating grease composition comprising (1) about 40 to 60 wt. percent of the lubricating grease composition of claim 9, and (2) about 60 to 40 wt. percent of a lubricating grease composition comprising a major proportion of a mineral lubricating oil and a minor but grease-thickening proportion of soap-salt complex of a high molecular weight carboxylic acid having about 12 to 30 carbon atoms per molecule and a low molecular weight carboxylic acid having about 1 to 3 carbon atoms per molecule, the mol ratio of the low to high molecular weight carboxylic acids being about 7:1 to 40:1.

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