FRICTION REDUCING ADDITIVE COMPRISING METAL SOAP SOLUBILIZED IN OIL BY AN N-CONTAINING DISPERSANT


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U.S. Cl. 252—34.7 8 Claims

ABSTRACT OF THE DISCLOSURE

Metal soaps solubilized into oil by oil-soluble nitrogen containing sludge dispersants, which are reaction products of C₂₉ to C₃₀ carboxylic acids with amines, are friction reducing additives for lubricating oils.

This invention relates to friction reducing additives for lubricating oils, said additives comprising metal soaps of fatty acid solubilized into the oil by certain oil-soluble nitrogen-containing sludge dispersants.

Metallic soaps of fatty acids are excellent boundary lubricants and provide low levels of friction. However, they are substantially insoluble in oil, and their use has been largely limited to forming greases since their insolvability impairs solid grease structures to oil. The present invention is directed towards solubilizing these normally oil-insoluble soaps so that they can be used in fluid lubricating oil compositions to reduce friction. In addition, it has been found that these solubilized soaps also act as copper corrosion inhibitors for the oil. The solubilizing is achieved by using certain nitrogen-containing materials which have recently become known as sludge dispersants for crankcase motor oils.

The friction reducing additives of the invention are particularly suitable for use in automatic transmission oils. In automatic transmissions, the frictional properties of the lubricating oil have a large effect on the actual performance of the automatic transmission. See the article "Fricction Characteristics of Automatic Transmission Fluids as Related to Transmission Operations" ASLE meeting, June 1960, Preprint No. 60 AM 6A—1 by M.L. Haviand and J. J. Rodgers. For example, if the coefficient of friction should increase in the clutches of certain automatic transmissions (especially those manufactured by G.M.) as the sliding speed decreases, stick-slip and possibly squawk, i.e., audible stick-slip, can occur. In this case, also, a harsh shift is produced. To meet the requirements of no stick or a smooth shift, a lubricating oil for use in the transmission is needed whose change in coefficient of friction as the sliding speed of the friction members decreases is minimal; even better is a fluid whose coefficient of friction decreases with a decreasing speed of the friction members, and whose coefficient of friction at static conditions (0 ft./min.) is less than at high (>100 ft./min.) speeds. The additives of the invention have been found to have properties which will enable the lubricant to meet these requirements.

The metal components of the soap are preferably the Group I and Group II metals, including alkalai metals such as barium, magnesium, calcium and strontium; and metals such as zinc, lead, etc.

The fatty acids used for forming the soap include naturally-occurring or synthetic, substituted or unsubstituted, saturated or unsaturated, mixed or uncombined fatty acids having about 12 to 24, e.g. 16 to 24, carbon atoms per molecule. Example of such acids include myristic, palmitic, stearic, 12-hydroxy stearic, arachidic, oleic, linoleic, ricinoleic, hydrogenated fish oil, tallow acids, etc.

The nitrogen-containing dispersant additives used to solubilize the soap are those known in the art as sludge dispersants for crankcase motor oils. These dispersants include mineral oil-soluble salts, amides, imides, and esters of mono- and dicarboxylic acids and where they exist the corresponding acid anhydrides and various amines of nitrogen-containing materials having amino nitrogen or heterocyclic nitrogen and at least one amido or hydroxy group capable of salt, amide or ester formation. These dispersants are characterized by a long chain hydrocarbon group, or groups, attached to the acid, so the acid contains a total of about 50 to 250 carbon atoms, said acid being attached to the amine either through salt, amide, amine, or ester groups. Usually, these dispersants are made by condensing a monocarboxylic acid or a dicarboxylic acid, preferably a succinic acid producing material such as alkenyl succinic anhydride, with an amine or polyamine.

Monocarboxylic acid dispersants have been described in U.S. patent specification 983,040, Here, the high molecular weight monobutyrinobutyric acid can be derived from a polyolefin, such as polyisobutylene, by oxidation with nitric acid or oxygen; or by addition of halogen to the polyolefin followed by hydrolyzing and oxidation. The monocarboxylic acid may also be obtained by oxidizing a monohydric alcohol with potassium permanganate, or by reacting a halogenated polyolefin with a ketone. Another method is taught in Belgian Patent 658,236 where polyolefin, such as polymers of C₃ to C₄ monoolefin, e.g. polypropylene or polyisobutylen, is halogenated, e.g. chlorinated, and then condensed with an alpha, beta-unsaturated, monocarboxylic acid of from 3 to 8, preferably 3 to 4, carbon atoms, e.g. acrylic acid, alpha-methyl-acrylic acid i.e., 2-methyl propionic acid), crotonic, or isocrotonic acid, fumaric acid (alpha, methylacrylontic acid), angelic acid (alpha-methylcrotonic acid), sorbic acid, cinnamic acid, etc. Esters of such acids, e.g. ethyl methacrylate, may be employed if desired in place of the free acid.

The most commonly used dicarboxylic acid is alkenyl succinic anhydride wherein the alkenyl group contains about 60 to 250 carbon atoms. Primarily because of its ready availability and low cost, the hydrocarbon portion of the mono- or dicarboxylic acid is preferably derived from a polymer of a C₉ to C₉ monomolefin, said polymer generally having a molecular weight of about 700 to 4,000, e.g. about 700 to 1,300. Particularly preferred is polyisobutylene.

Polyalkyleneamines are usually the amines used to make the dispersant. These polyalkyleneamines include those represented by the general formula:

H₂N(CH₂)ₙ—(NH(CH₂)ₙ)ₙ—NH(CH₂)ₙNH₃

wherein n is 2 or 3, and m is 0 to 10. Examples of such polyalkyleneamines include diethylete triamine, tetraethylylene pentamidine, octaethylenetetramine, tetrapropylene pentamine, as well as various cyclic polyalkyleneamines. Dispersants formed by reacting about equal molar amounts of polyisobutyl en succinic anhydride and a tetraethylenepentamine are described in U.S. Patent 3,202,678. Similar dispersants, but made by reacting a molar amount of alkenyl succinic anhydride with about two molar amounts of polyalkyleneamines, are described in U.S. Patent 3,154,560. Other dispersants, using still other molar ratios of alkenyl succinic anhydride and polyalkyleneamines are described in U.S. Patent No. 3,172,892. Still other dispersants of alkenyl succinic anhydride with other amines are described in U.S. Patents 3,024,195 and 3,024,237 (piperazine amines); and 3,219,666. An ester
3 derivative is taught in Belgian Patent 662,875 where N-alkyl morpholinone esters, e.g. N-(2-hydroxyethyl)-2-morpholinone, are formed by reaction with polyisobutylene succinic anhydride. The prior art also teaches that the alkenyl succinic polyamine type dispersants can be further modified by reacting a fatty acid, having up to 22 carbon atoms, e.g. acetic acid, with the reaction product of the alkenyl succinic anhydride and polyamine (see U.S. Patent 3,216,936).

For the purposes of the present invention any of the nitrogen-containing dispersants described in any of the aforementioned patents can be used in carrying out the present invention.

The friction reducing additives of the invention are best made by neutralizing the fatty acid with metal base to form the soap in an inert fluid menstruum, e.g., water and/or mineral lubricating oil, in the presence of the nitrogen-containing sludge dispersant. Preferably, a small amount of water is used to promote the neutralization. Usually about .5 to 1.0, preferably 1 to 8 parts by weight of the dispersant will be used per part by weight of soap that is formed. The resulting composition can then be heated to about 200° F. to 350° F., preferably 225° to 400° F. to hydrolyze the composition. Oil concentrations containing 10 to 80 wt. percent of the resulting friction reducing additive, i.e., the soap plus dispersant, can be made in this way, which concentrates can later be added to oil in small amounts to give finished lubricants. Generally, the amount of additive in the finished lubricant will be such as to incorporate about 0.05 to about 1.0 wt. percent, preferably .05 to .5 wt. percent soap in the finished lubricant.

The lubricating oil used in forming the concentrates and the finished lubricants 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. C13 Oxalic 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-ethoxynaphthalic acid), halocarbon oils, alkyl silicates, sulfite esters, mercaptans, formals, polycycloalkylene type synthetic oils, etc., or mixture of any of the above in any proportions. If the soaps 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 soap formation. However, the soaps once formed, can be used in lubricants containing the synthetic soaps noted above.

The additives of the invention can be used together with various other conventional lubricating oil additives including detergents such as calcium petroleum sulfonate; antirust additives such as zinc dialkyl dithiophosphate; oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors, such as sorbitan monooleate; pour point depressants and V.I. improvers such as copolymers of vinyl acetate and alkyl fumarates; dyes; and the like. Additive packages consisting of about 10 to 30 wt. percent of these various conventional additives and about 1 to 20 wt. percent of the additive of the invention, i.e., soap plus its suspending dispersant, can be made by simple mixing in mineral lubricating oil. These packages can then be further diluted with additional lubricating oil to form finished lubricants.

The invention will be further understood by reference to the following examples which include a preferred embodiment of the invention:

**EXAMPLE I**

17 parts of oleic acid, 2.4 parts of zinc oxide (ZnO), 2.9 parts of water, and 77.7 parts of an oil concentrate consisting of 65 wt. percent of a nitrogen-containing sludge dispersant in 35 wt. percent mineral lubricating oil, were stirred together with heating to a temperature of 250° F., which temperature was held until all the water had been evaporated. The resulting product was then filtered through filter paper and cooled to form a clear transparent solution.

The sludge dispersant used above, it represented by the structure:

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\[
\begin{align*}
\text{R} & \quad \text{(polyisobutylene group of about 800 molecular weight)} \\
N-(2\text{-hydroxyethyl})-2\text{-morpholinone esters} & \quad \text{(e.g. N-(2-hydroxyethyl)-2-morpholinone, formed by reaction with polyisobutylene succinic anhydride and tetraethylene pentamine)}
\end{align*}
\]
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**EXAMPLE II**

5.5 parts of linoleic acid, 5.9 parts of Ba(OH)₂·8H₂O, and 8.6 parts of a concentrate consisting of 65 wt. percent sludge dispersant in 35 wt. percent mineral lubricating oil, were heated together with stirring to a temperature of about 250° F. and maintained at this temperature until no more water evaporated. The resulting product was then filtered while hot, i.e., about 250° F., through filter paper and then cooled to room temperature to form a transparent solution.

The dispersant used above was made by first condensing two moles of polyisobutylene succinic anhydride having a polyisobutylene group of about 800 mol wt. with 1 mole of tetraethylene pentamine, followed by further condensing with 1 mole of acetic acid.

**EXAMPLE III**

An automatic transmission base oil was prepared consisting of a mineral lubricating oil of the type used in automatic transmission fluids, a pour point depressant, a viscosity index improver, a sludge dispersant, antioxidants and antioxidant aids. Varying amounts of the products of Examples I and II were added to the base oil and then tested for friction in a Kinetic Oiliness Test Machine (KOTM) and also for copper strip corrosion according to ASTM D-130 Test.

The Kinetic Oiliness Test Machine is described in U.S. Patent 3,020,565. Briefly, the machine normally involves 3 steel buttons carried by a revolving spindle which buttons rotate on a track immersed in the test oil being evaluated. Heating means are provided to heat the test oil so as to simulate the temperature of actual use. Also means are provided for loading the spindle so as to increase the pressure between the steel buttons as they are tracked across the metal track.

However, for testing the coefficient of friction of automatic transmission lubricating oil compositions, the KOTM was slightly modified. The usual three steel buttons attached to the revolving spindle were replaced by a machine ground flat steel disc. A full-sized Powersludge transmission clutch plate, manufactured by Delco-Moraine, was rotated against said flat steel disc, while both these rubbing friction members, i.e. the disc and clutch plate, were immersed in the test oil, and the spindle was loaded so as to increase the pressure on the clutch plate surface against said flat steel disc. The machine is adjustable for varying speeds which are measured in terms of feet per minute as the clutch plate makes rubbing contact with the flat steel surface. Coefficients of friction are measured by the amount of deflection of the arms attached to the steel disc from their normal position perpendicular to the center spindle.

The above-mentioned copper strip corrosion test is carried out by immersing a copper strip for 3 hours in a sample of the test composition maintained at 300° F. and then visually rating the copper strip for corrosion. The strips are evaluated on a scale ranging from 0 to 10, wherein 0 indicates no corrosion and 10 indicates bad corrosion.
For comparison, similar tests were carried out on the base oil per se, and on the base oil containing oleic acid which is a known friction-reducing additive. The results obtained and the compositions tested are summarized in Tables I and II which follow:

### Table I—Coefficient of Friction in KOVTM

<table>
<thead>
<tr>
<th>Sliding speed (ft./min.)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>115</th>
<th>200°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. percent friction reducing additive:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None (base oil per se)</td>
<td>0.160</td>
<td>0.127</td>
<td>0.117</td>
<td>0.102</td>
<td>0.068</td>
</tr>
<tr>
<td>0.1 wt. percent barium linolate (2.0 wt. percent of Ex. I)</td>
<td>0.095</td>
<td>0.095</td>
<td>0.095</td>
<td>0.095</td>
<td>0.095</td>
</tr>
<tr>
<td>0.2 wt. percent barium linolate (2.0 wt. percent of Ex. I)</td>
<td>0.068</td>
<td>0.068</td>
<td>0.068</td>
<td>0.068</td>
<td>0.068</td>
</tr>
</tbody>
</table>

As seen by Table I, the additives of the invention (i.e., the products of Examples I and II) gave an overall lower coefficient of friction than the base oil without these additives. Moreover, the inventive additives reduced the coefficient of friction at static conditions (0 ft./min.) to a value below that at the high speed (115 ft./min.) at both temperatures. Particular improvement in the anti-squawk behavior is seen in the use of 0.2 wt. percent barium linolate at 290°F where the coefficient of friction decreases with decreasing speed over the whole range of speeds. The base oil per se illustrates a formulation with a strong tendency to cause squawk and harshness of shift because of the particularly large increase in coefficient of friction with decreasing sliding speed. The inventive additives overall gave better performance in this regard, with a lesser amount of change in coefficient of friction with speed, particularly at the 0.2 wt. percent concentration level. Moreover, an improvement over oleic acid, which is sometimes used as a friction modifier, is also noted. In general, the table shows that the inventive additives alter the properties of the base oil in such a way that the coefficient of friction is reduced as the sliding speed approaches zero. This makes them particularly valuable in automatic transmission fluids since, generally speaking, operation of the transmissions is thereby made smoother and squawk is avoided.

While Table I shows that the soap plus the dispersant gave good results and were soluble in the base oil composition, similar soaps without the dispersant were insoluble. Thus, nickel oleate, lead oleate and zinc oleate were all insoluble in the same base oil composition.

### Table II—Copper Strip Corrosion (ASTM D-130)

<table>
<thead>
<tr>
<th>Friction reducing additives:</th>
<th>Corrosion rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil—0.2% oleic acid</td>
<td>J-9</td>
</tr>
<tr>
<td>Base oil—0.2% Ba linolate (2.0 wt. percent)</td>
<td>J-3</td>
</tr>
<tr>
<td>Base oil—0.5% zinc oleate (2.5 wt. percent)</td>
<td>J-3</td>
</tr>
<tr>
<td>Base oil—0.4% zinc oleate (2.0 wt. percent)</td>
<td>J-3</td>
</tr>
</tbody>
</table>

As seen by Table II, oleic acid gives a J-9 rating which represents a corrosive fluid (the copper specimen is discolored black), while the J-3 rating of the inventive additive represents an essentially non-corrosive fluid. While the preceding examples illustrated the use of the friction reducing additives of the invention in a fully compounded automatic transmission fluid, the invention additives can be used in oil per se without the presence of other additives. For example, 1 wt. percent of the product amount of mineral lubricating oil, and about .005 to 1 wt. percent of metal soap of C12 to C24 fatty acid solubilized in said oil by a nitrogen-containing amide or imide lubricating oil sludge dispersant comprising the condensation product of a carboxylic acid or anhydride containing 50 to 250 carbon atoms and one to two carboxylic groups with a polyamine having the general formula:

\[ H_2N(CH_2)_n\_\text{NH(CH}_2)_m\_\text{NH}_2\]

wherein \( n \) is 2 to 3, and \( m \) is 0 to 10, said metal being selected from the group consisting of Group I and Group II metals, and wherein there are about 0.5 to 10 parts by weight of said dispersant per part by weight of said soap.

2. A method according to claim 1, wherein said soap is zinc oleate.

3. A method according to claim 1, wherein said metal soap is barium linolate.

4. A method according to claim 1, wherein said dispersant comprises the condensation product of polyisobutyl succinic anhydride and tetraethylene pentamine.

5. A method according to claim 4, wherein said dispersant is the condensation product of substantially 2 moles of polyisobutyl succinic anhydride with 1 mole of tetraethylene pentamine followed by further condensing with one mole of acetic acid.

6. A method of lubricating an automatic transmission by using as the automatic transmission fluid, a composition consisting essentially of a major amount of mineral lubricating oil containing a poor point depressant, a viscosity index improver, a sludge dispersant, an antioxidant, an antiwear agent, and characterized by a friction modifying additive which consists essentially of about .005 to 1 wt. percent of metal soap of C12 to C24 fatty acid solubilized in said oil by 0.5 to 10 parts by weight of a nitrogen-containing amide or imide lubricating oil sludge dispersant comprising the condensation product of a carboxylic acid or anhydride containing 50 to 250 carbon atoms and one to two carboxylic groups with a polyamine having the general formula:

\[ H_2N(CH_2)_n\_\text{NH(CH}_2)_m\_\text{NH}_2\]

wherein \( n \) is 2 to 3, and \( m \) is 0 to 10, and wherein said metal is selected from the group consisting of Group I and Group II metals.

7. In a method according to claim 6, said dispersant being the condensation product of polyisobutyl succinic anhydride containing 60 to 250 carbon atoms and tetraethylene pentamine.

8. In a method according to claim 7, said dispersant being the condensation product of about 2 moles of polyisobutyl succinic anhydride with about 1 mole of tetraethylene pentamine followed by further condensing with about one mole of acetic acid.
<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,247,577</td>
<td>7/1941</td>
<td>Flaxman</td>
<td>252—34.7</td>
</tr>
<tr>
<td>2,854,410</td>
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</tr>
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</tr>
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</tr>
<tr>
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<td>3/1965</td>
<td>Le Suer</td>
<td>252—51.5 XR</td>
</tr>
<tr>
<td>3,203,896</td>
<td>8/1965</td>
<td>Latos et al.</td>
<td>252—34.7 XR</td>
</tr>
<tr>
<td>3,202,606</td>
<td>8/1965</td>
<td>Morway et al.</td>
<td>252—17</td>
</tr>
</tbody>
</table>

DANIEL E. WYMAN, Primary Examiner.
W. CANNON, Assistant Examiner.
U.S. Cl. X.R. 252—37.2, 40.7, 42.1, 75, 76
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,073,648 Dated May 27, 1963
Jerome Panzer, Roselle Park, Edward J. Longosz, North Plainfield, and Gerald D. Staffin, Westfield, N.J.
Inventor(s) and Robert M. Goodman, Midlothian, Va.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Add -- Rosemary O'Halloran, Union, New Jersey and Donald Borden, Princeton, New Jersey -- as additional co-inventors of this application.

SIGNED AND SEALED
MAR 24 1970

(Seal)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents