LUBRICATING OIL COMPOSITIONS CONTAINING ACYLATED POLYAMINE SALTS


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This invention relates to improved lubricating oil compositions, and more particularly to highly detergent lubricating oils which possess improved spreading pressure properties.

Until recently, lubricating oil detergents or dispersants were generally polyvalent metal salts or soaps of organic carboxylic or sulfonic acids such as organic naphthenic or organic sulfonic acids. Detergents of this type are relatively ineffective at extremely low or extremely high temperatures and do not improve the spreading pressure of lubricating oils on various surfaces.

lt has now been discovered that the detergent properties of lubricating oils over a wide temperature range as well as the spreading pressure on various solid surfaces e.g., metals, can be greatly improved by incorporation in the oil of a small amount of certain oil-soluble partially acylated aliphatic polyamine salts of aromatic acid compounds, particularly of one which is a sulfonic acid, carboxylic acid or phenolic compound, such as a petroleum or a synthetic alkylation sulfonic acid, an alkylation sulfonic acid, a simple alkylphenol or a poly(alkylphenol).

These acylated polyamine salts are, thus, amidolylene amine salts of the aromatic acid. The N-acyl radical forming the amido group(s) is an acyl radical of a carboxylic acid, preferably an aliphatic (cyclic or acyclic) monocarboxylic acid.

The polyamines from which the amido amine bases are derived are aliphatic polyamines which may be simple polyaminoalkanes, such as the diaminoalkanes, 1,2- or 1,3-diaminopropanes, 1,2-, 1,3- or 1,4-diaminobutanes, 2,3-diaminohexanes, poly(alkylenediamines), such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, dipropylene triamine, tripropylene tetramine and the monomonoalkanes such as N-buty1 ethylene diamine, dialkylalkyl ethers, including thioethers, such as di-(2-aminoethyl)sulphide, and the like.

The N-acyl group(s) of the amido group(s) corresponds to acyl radicals of any carboxylic acid, such as benzoic acid, salicylic acid, acetyl salicylic acid, naphthoic acid, naphthenic acids, caproic acid, lauric acid, stearic acid or palmitic acid. Particularly suitable are the naphthenic acids obtained by by-products in the refining of petroleum fractions, such as kerosene, gas oil and lubricating oil.

The following are typical specific partially acylated aliphatic di- or poly-amines which, in the form of their oil-soluble salts with aromatic acids, particularly with the specific aromatic acids mentioned above, may be used as lubricating oil additives in accordance with this invention: the monophenathenic amide of 1,2-diaminoethanes, of 1,2-diaminopropanes, of diethylene triamine or of triethylene tetramine, the monolauric amide of tetraethylene pentamine, and the monoammonium amide of hexamethylene diamine or of 2,3-diaminohexane.

The partially acylated aliphatic di- or poly-amine may be prepared by the action of a carboxylic acid or a halide, nitrile or ester thereof on the di- or poly-amine by methods which are well-known in the art. The preferred method involves mixing equimolecular parts of acid and amine and heating in an autoclave at a temperature of from about 170° C. to about 200° C. for about 5 to 8 hours. The crude reaction mixture so obtained may be used as such to form the salts which are used in accordance with the present invention. These salts may be prepared by any of the methods known for preparing salts of amines. For instance a solution of the partially acylated di- or poly-amine with the alkali metal salt of the acid in a solvent which facilitates the removal of the inorganic salt produced.

The aromatic acid compounds from which the oil-soluble acylated polyamine salts are derived include aromatic sulfonic acids such as the nonyl or dodecyl benzene sulfonic acids, di-isopropylsalicylic acid, sulfonic acid, butyl phenol sulfonic acid and sulphonated acids derived from aromatic fractions from petroleum oils or the alkylation products of such fractions; alkyl salicylic acids such as octadecyl and diisopropyl salicylic acids and mixtures of alkylated salicylic acids in which the alky groups contain 8 to 18 carbon atoms; or phenols such as octyl and dodecyl phenols, the butyl and amyl naphthols or polyphenols obtained by condensing simple phenols at open positions ortho and/or para to the phenolic hydroxy group through alkylidene (methylene) radicals such as are obtained by condensing alkylated phenols e.g. p-octylphenol with formaldehyde or acetaldehyde. Particularly useful products of this type range in molecular weight from 500 to about 1100.

The preparation of the acylated polyamines (amidoamines) and their salts is illustrated in the following examples. In these examples, parts by weight (d. c. v.) and petroleum spirit (1 p. b. v.) were added. The reaction mixture separated to give a yellow petroleum spirit

Example 1

N - (2 - aminophenyl)naphthenamide was prepared by heating naphthenic acids (1.5 p. b. w.) with ethylene diamine (1.09 p. b. w.), in a mol ratio of 1 to 4, respectively, at reflux for 160 hours, at the end of which time the reaction was about 85 percent complete. Most of the excess ethylene diamine was then removed under reduced pressure. The crude material (about 2 p. b. w.) was dissolved in 50 percent aqueous isopropyl alcohol (3 p. b. v.) and neutralized to p.H. 7 with concentrated hydrochloric acid (ca. 1.5 p. b. v.). Petroleum spirit (1 p. b. v.) and water (1 p. b. v.) were added, whereupon two layers formed and the aqueous lower ethylene diammonium chloride layer was removed. One further wash with water (1 p. b. v.) was given, after which isopropyl alcohol (6 p. b. v.) and petroleum spirit (1 p. b. v.) were added. The reaction mixture separated to give a yellow petroleum spirit
3. The top layer, and a bottom layer containing N-(2-aminoethyl)naphthenamide hydrochloride (2 p. b. w.) dissolved in isopropyl alcohol (13 p. b. v.). The bottom layer was washed six times with petroleum spirit (1 p. b. v. portions) and the combined petroleum spirit extracts were back extracted with 35 percent aqueous isopropyl alcohol (1 p. b. v.). The combined aqueous alcoholic layers were made alkaline to phenolphthalein with 40 percent sodium hydroxide solution and petroleum spirit (5 p. b. v.) was added. A brown petroleum spirit layer separated, the aqueous layer was run off and washed once with petroleum spirit (0.5 p. b. v.). The combined petroleum spirit solutions were washed three times with water (0.1 p. b. v. portions) and the solvent removed.

Approximately 1.1 p. b. w. (62 percent based on acid) of product was obtained. It has a neutralization value of 148 mg. KOH/g. (theory 151 mg. KOH/g. for the monoamidoamine).

Example II

N-(2-aminomethyl)naphthenamide was prepared by heating naphthenic acid (331 p. b. w.) and commercial grade ethylene diamine (279 p. b. w.) containing 14 percent by weight of water, at 180° C. under a pressure of about 7 atmospheres for 6 hours. The reaction mixture was stripped of excess ethylene diamine under reduced pressure and worked up as described under Example I. The yield of N-(2-aminomethyl)naphthenamide was 252 p. b. w. (67.5 percent of theory). The product had a neutralization value equivalent to 152 milligrams of potassium hydroxide per gram (theory 151 mg. KOH/g.).

The amount of imidazoline derivative formed during the reaction by cyclization of the N-aminomethyl naphthenamide was about 1.5 percent by weight. The neutralization value agreed with that required theoretically and the color of the product was good. Longer reaction times and higher reaction temperatures tended to increase the proportion of imidazoline derivative formed.

The presence of water in the initial reaction mixture had no adverse effect on the reaction as similar yields of the naphthenamide were obtained using anhydrous ethylene diamine.

Example III

N-(3-aminopropyl)naphthenamide was prepared by heating 1,3-diaminopropane (29.6 p. b. w.) and naphthenic acid (331 p. b. w.) at 150° C. for 160 hours at atmospheric pressure. The reaction mixture was worked up as described in Example I to give 22 p. b. w. of naphthenamide having a neutralization value equivalent to 141 milligrams of potassium hydroxide per gram (theory 141 mg. KOH/g.) and nitrogen content 7.9 percent (theory 7.2 percent).

N-(8-aminoctyl)naphthenamide was prepared in a similar manner.

Example IV

1,2-diaminopropane (29.6 p. b. w.) and naphthenic acid (33.1 p. b. w.) were heated together at 150° C. for 160 hours, and the reaction mixture worked up in the manner described in Example I to give 17.7 p. b. w. of naphthenamide having a neutralization value equivalent to 121 milligrams of potassium hydroxide per gram (theory 145 mg. KOH/g.) and nitrogen content 7.2 percent (theory 7.2 percent).

Example V

Naphthenic acid (13.8 p. b. w.) and diethylene triamine (9.1 p. b. w.) were heated together at 180° C. for 6 hours at atmospheric pressure and the reaction mixture was worked up as described in Example I to give a 69 percent yield of N-(5-amino-3-azapentyl)naphthenamide.

The preparation of some of the naphthenamide salts of the invention is described in the following examples.

Example VI

In this example is described the preparation of the Kerex sulphonates of the above amino alkyl naphthenamides. "Kerex," for "kerose" extract, is an aromatic extract of kerose obtained by treating kerose with liquid sulphur dioxide in the Edeleanu process. It has an A. S. T. M. boiling range of 165 to 270° C. and contains approximately 70 percent by weight of aromatic hydrocarbons.

To prepare Kerex sulphonatic, 20 percent tuming sulphonatic (150 p. b. v.) was added to the full Kerex fraction (368 p. b. w.) cooled in ice water, the reaction temperature being maintained at 25 to 30° C. The reaction mixture was poured into water (600 p. b. v.) and unreacted Kerex (49 percent by weight) was separated. The aqueous lower layer was neutralized with aqueous sodium hydroxide solution containing 25 percent by weight of the alkali and the volume adjusted to 2,000 p. b. v. at 25° C. Under these conditions, no crystallization of sodium salt occurred and the solution contained 13.45 percent by weight of sodium Kerex sulphonate.

This solution was used as such as a Kerex sulphonate was extracted from it by means of normal butanol. The butanol extract was dried azetropically, filtered to remove inorganic salts and evaporated under reduced pressure, the residual salt being washed with ether and dried. The solid sodium Kerex sulphonate contained 10 percent by weight of sodium and was obtained in 70 percent yield based on the Kerex consumed or 39 percent yield on total Kerex used.

(a) N-(2-aminomethyl)naphthenamide Kerex sulphonate.—N-(2-aminomethyl)naphthenamide (100 p. b. w.) in aqueous alcoholic solution was neutralized with concentrated hydrochloric acid using methyl red as indicator and then shaken with 4306 p. b. w. of the above 13.45 percent by weight aqueous sodium Kerex sulphonate solution. The mixture was extracted with petroleum spirit and the extract dried by azetropic distillation, filtered to remove precipitated sodium chloride and evaporated to dryness.

The residual salt (146 p. b. w.; 96 percent yield) had a nitrogen content of 5.2 percent (theory 4.9 percent).

(b) N-(aminopropyl)naphthenamide Kerex sulphonate.—This salt was prepared in 95 percent yield by a method similar to that described under (a) above from N-(aminopropyl)naphthenamide hydrochloride (derived from 1,3-diaminopropane) and sodium Kerex sulphonate in aqueous alcohol, and extracting the amine Kerex sulphonate with benzene. The product had a nitrogen content of 4.6 percent (theory 4.5 percent).

(c) N-(3-aminopropyl)naphthenamide Kerex sulphonate containing 4.8 percent nitrogen (theory 4.5 percent) and N-(8-aminoctyl)naphthenamide Kerex sulphonate containing 4.8 percent nitrogen (theory 4.0 percent) were prepared by the procedure similar to that described under (a). The latter product contained some 1,8-diaminocar- taine as impurity.

(d) Kerex sulphonates of N-(5-amino-3-azapentyl)naphthenamide.—By the procedure described in (a) there were prepared the mono Kerex sulphonate (found, N, 6.4, S, 5.2 percent; theory, N, 6.5, S, 5.0 percent) and the diKerex sulphonate (found, N, 5.1, S, 7.4 percent; theory N, 4.8, S, 7.3 percent) of N-(5-amino-3-azapentyl)naphthenamide by reacting one equivalent of the amine hydrochloride with one and two equivalents, respectively, of sodium Kerex sulphonate.

Example VII

In this example is described the preparation of the alkyl Kerex sulphonate of N-(2-aminomethyl)naphthenamide. The sodium alkyl Kerex sulphonate used for this purpose was prepared as follows:

A Kerex fraction boiling at approximately 114° C. at 20 millimeters pressure was used. It had a molecular
weight of 157 and contained 70 percent by weight of aromatics. The alkylation was effected by adding powdered anhydrous aluminum chloride (3.3 p. b. w.) to the Kerex fraction (278.5 p. b. w.) at 25°C and adding gradually to the stirred mixture 44.8 p. b. w. of a cracked petroleum fraction consisting mainly of straight chain olefins containing 8 carbon atoms in the molecule and which had a bromine number of 119 (theory for C2H4Br, 143). These olefins had been obtained by extracting product X with heptane to remove branched olefins. When addition of the olefin was complete, a further 13 p. b. w. of aluminum chloride were added. The stirrer was stopped after 6 hours and the mixture left for a further 10 hours after which the liquid fraction was decanted from the sludge formed and stirred with 10 percent by weight of an aqueous alkali solution containing 20 percent by weight of sodium hydroxide.

The hydrocarbon layer was distilled giving 124 p. b. w. of a fraction boiling at 96 to 122°C at 18 millimeters pressure, molecular weight 166, which was mainly un-reacted Kerex, and 758 p. b. w. of a second fraction boiling at 118 to 144°C and 0.5 millimeter pressure, molecular weight 232 which was the desired alkyl Kerex. There was a small residue.

The C6-alkyl Kerex (70 p. b. w.) was reacted with 100 percent sulphuric acid (70 p. b. w.) at 30 to 35°C for 1 hour. The reaction mixture was poured into ice water and then warmed to 70 to 80°C to break the emulsion which formed. The lower aqueous layer containing very little sulphonate was discarded. 95 percent ethanol (90 p. b. w.) was then added and the upper layer of un-reacted hydrocarbon which separated on standing was removed.

The aqueous alcoholic layer was neutralized at 60°C with solid sodium hydroxide (10 p. b. w.), using phenolphthalein as indicator, and 95 percent ethanol (4 p. b. w.) added. The cooled solution was filtered from inorganic salts and the solvent removed by distillation under reduced pressure. An 84 percent yield of sodium C6-alkyl Kerex sulphonate (51 p. b. w.) was obtained containing 96 percent by weight of the salt.

N-(2-aminoethyl)naphthenamide alkyl Kerex sulphonate was prepared from the above sodium C6-alkyl Kerex sulphonate (34 p. b. w.) and the hydrochloride from N-(2-aminoethyl)naphthenamide (31.1 p. b. w.) in aqueous alcoholic solution. The product was extracted with water and desalted in benzene and yielded N-(2-aminoethyl)naphthenamide C6-alkyl Kerex sulphonate (58 p. b. w.; 96 percent yield) having a nitrogen content of 4.1 (theory 4.1 percent).

**Example VIII**

N-(2-aminoethyl)naphthenamide dodecylbenzene sulphonate was prepared by a method similar to that described under Example VI(a) by reacting sodium dodecylbenzene sulphonate (35 p. b. w.) and the hydrochloride from N-(2-aminoethyl)naphthenamide (34.2 p. b. w.) in aqueous alcohol, the desired salt being extracted with and desalted in benzene and finally obtained by evaporation of the benzene solution (59.6 p. b. w., 90 percent theory). It had a nitrogen content of 4.0 percent (theory 4.2 percent). The dodecyl benzene sulphonic acid was obtained by sulphating benzene which had been alkylated with propylene-tetramer.

The N-(2-aminoethyl)naphthenamide benzene sulphonate was prepared in a similar manner from the naphthenamide and sodium benzene sulphonate.

**Example IX**

N-(2-aminoethyl)naphthenamide naphthasulphonate was prepared by reacting the hydrochloride from N-(2-aminoethyl)naphthenamide with sodium naphthalenesulphonates in aqueous isopropanol alcohol. The sodium naphthasulphonates used are obtained by by-products in the refining of technical white oils and medicinal oils in the petroleum industry. They are oil-soluble salts and are available in a range of molecular weights. Normally they contain a minor proportion of oil which can be removed by washing an aqueous alcoholic solution of the sodium naphthasulphonates with light petroleum. Both oil and de-oiled sodium naphthasulphonates were used to prepare the naphthenamide sulphonates. The preparations are summarized in the following table.

<table>
<thead>
<tr>
<th>Approximate molecular weight</th>
<th>Treatment</th>
<th>Percent N</th>
<th>Percent N</th>
<th>Percent N</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>Not de-oiled</td>
<td>1.5</td>
<td>1.8</td>
<td>87.5</td>
</tr>
<tr>
<td>400</td>
<td>Not de-oiled</td>
<td>2.8</td>
<td>3.1</td>
<td>90.5</td>
</tr>
<tr>
<td>200</td>
<td>Not de-oiled</td>
<td>2.5</td>
<td>2.8</td>
<td>91.5</td>
</tr>
<tr>
<td>100</td>
<td>De-oiled</td>
<td>3.4</td>
<td>2.5</td>
<td>78</td>
</tr>
</tbody>
</table>

**Example X**

N-(2-aminoethyl)naphthenamide di-isopropyl salicylate was prepared by mixing a solution of di-isopropyl salicylic acid (33.6 p. b. w.) in light petroleum (B. P. 40 to 60°C) with a solution of N-(2-aminoethyl)naphthenamide (56 p. b. w.) also in light petroleum. A curdy precipitate formed. The solvent was removed by distillation leaving 95 p. b. w. of the salicylate which had a nitrogen content of 4.7 percent (theory 4.7 percent). The di-isopropyl salicylic acid used was obtained by carboxylating di-isopropyl phenol which had been obtained by alkylating phenol with 2 molecular proportions of propylene in presence of anhydrous aluminum chloride.

**Example XI**

N-(2-aminoethyl)naphthenamide C6-C18-alkyl salicylate was obtained in 99 percent yield by reacting equivalent proportions of sodium C6-C18-alkyl salicylate and N-(2-aminoethyl)naphthenamide hydrochloride in ethyl alcoholic solution. The sodium chloride precipitated was filtered off and the filtrate treated with decolorizing charcoal, filtered and evaporated to dryness under reduced pressure. The product contained 3.7 percent nitrogen (theory 3.8 percent). The alkyl salicylic acids used in this preparation were obtained by carboxylating phenol which had been alkylated with a mixture of C4 to C18 alkenes-1 in the presence of anhydrous aluminum chloride.

The proportion of the oil-soluble salts derived from a partially acylated aliphatic di- or poly-amine and an aromatic acid used in accordance with this invention will vary greatly depending upon the effectiveness of the particular salt employed and the degree of improvement of the properties of the base lubricating oil required. Usually, the salt will be used in a proportion of from 0.1 to 5% by weight of the base oil. More usually, the proportion used will be between 0.2 and 2% by weight.

The lubricating oil used in the compositions of this invention may be any natural (hydrocarbon and polar containing oils) or synthetic oil (olefin polymers, esters, others, etc.) having lubricating properties. Thus, it may be a mineral lubricating oil obtained from a paraffinic, naphthenic, asphalitic or mixed base crude petroleum. The viscosities of these mineral lubricating oils may vary over a wide range such as from 40 SUS at 100°F to 1000 SUS at 210°F. Typical synthetic lubricating oils which may be used are polymerized olefins, organic esters such as di(2-ethylhexyl)succinate, dibutyl sebacate and triocyl phosphate and silicon polymers. The base lubricating oil may be a mineral lubricating oil mixed with a synthetic lubricating oil or with a fatty oil such as castor oil or lard oil.

A typical lubricating composition of the present invention is a solvent-refined mineral lubricating oil having a...
viscosity of 330 seconds Redwood I at 140° F. (hereinafter called "oil A"), to which has been added from 0.2 to 2% by weight of the N-(2-amino-ethyl)napthenamide C_{16}-C_{18} alkyl salicylate described in Example XI. Such a composition containing 2% by weight of the additive was tested for high temperature properties in the following coking test. A hot clean metal plate is maintained at about 200° C. and the oil under test is allowed to run down the surface in a film at the rate of one drop per second. This is continued for 45 minutes, the plate is cooled and washed down with petroleum ether. Applying this test to the base oil, the plate finished up in a black coked condition but, with the oil containing the additive, the plate was unmarked except for a few grey streaks.

To illustrate the effect on the spreading pressure of oil A of adding various quantities of additive of Example XI, the spreading pressures of oil A on steel and on water and of oil A containing varying percentages of additive of Example XI were determined. The results are set out in the following table.

<table>
<thead>
<tr>
<th>Conc. of additive of Example XI, percent w.</th>
<th>Spreading pressure (dynes/square centimeter) on Steel</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.8</td>
<td>9.0</td>
</tr>
<tr>
<td>0.2</td>
<td>16.8</td>
<td>20.4</td>
</tr>
<tr>
<td>0.4</td>
<td>21.0</td>
<td>25.3</td>
</tr>
<tr>
<td>0.5</td>
<td>22.5</td>
<td>26.5</td>
</tr>
<tr>
<td>1.0</td>
<td>&gt;32</td>
<td>32.0</td>
</tr>
</tbody>
</table>

Further, a composition comprising oil A and 0.4% by weight of Example XI was tested as a crankcase lubricant in a test engine and found to result in a far cleaner engine than did oil A alone.

Similar results as noted above can be obtained with the addition of 2% additives of Examples VIII, IX or X to oil A.

Compositions of this invention can be used as engine oils, turbine oils, gear oils, cutting oils and various other fields of lubrication where detergency and stability are essential.

We claim as our invention:

1. A lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor but detergent amount of an oil-soluble mono-acylated aliphatic polyamine salt of an aromatic acidic compound wherein the acidic radical is selected from the group consisting of phenolic hydroxy group, carboxylic acid and sulfonic acid.

2. A lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor, but detergent amount of an oil-soluble mono-acylated aliphatic polyamine salt of an aromatic sulfonic acid.

3. A lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor, but detergent amount of an oil-soluble mono-acylated aliphatic polyamine salt of an alkyl salicylic acid.

4. A lubricating oil composition comprising a major amount of a mineral lubricating oil and a minor, but detergent amount of an oil-soluble mono-acylated aliphatic polyamine salt of a phenol.

5. The composition of claim 2 wherein the salt is N-(2-amino ethyl)napthenamide salt of dodecyl benzene sulfonic acid.

6. The composition of claim 3 wherein the salt is N-(2-amino ethyl)napthenamide salt of C_{16}-C_{18} alkyl salicylate acid.

7. The composition of claim 4 wherein the salt is N-(2-amino ethyl)napthenamide salt of octyl phenol-formaldehyde condensation product.

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