REACTION PRODUCTS OF A POLYALKYLENE AMINE SULFONIC ACID AND AN ALKENYL SUCCINIC ACID OR ANHYDRIDE

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Related U.S. Application Data

Continuation of Ser. No. 649,102, June 27, 1967, abandoned.

Foreign Application Priority Data

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ABSTRACT

Long chain sulfonated amine compounds having amide or imide linkages are prepared by polymerizing a compound containing a polymerizable aziridine ring with sulfuric acid and reacting the resulting sulfur-containing polyalkylene polyamine with a long chain carboxylic acid, such as, a long chain mono-alkenyl succinic acid or anhydride. The products are useful in lubricating compositions.

7 Claims, No Drawings
REACTION PRODUCTS OF A POLYALKYLENE AMINE SULFONIC ACID AND AN ALKENYL SUCCINIC ACID OR ANHYDROME

This application is a streamlined continuation of application Ser. No. 649,102, filed June 27, 1967, now abandoned.

This invention relates to improvements in or modifications to the invention described in and claimed in our copending United States application Ser. No. 519,008, filed Jan. 7, 1966, now U.S. Pat. No. 3,367,884.

The invention relates to additives for lubricating compositions and also to lubricating compositions containing the additives. In particular, the additives with which this invention is concerned are detergents which are effective cold sludge dispersants.

In the lubrication of modern internal combustion engines deposits may be formed in the engines in two ways and there are two distinct problems involved in keeping the engines clean. One problem is the deposition of soot, lacquers and other deposits, mainly in the piston ring zone, under high speed and consequently high temperature operating conditions. These deposits may arise from partial combustion products of the fuel or as the result of the oxidation or thermal degradation of the lubricant or both. This problem is alleviated by the addition to the lubricating oil of what are known in the art as conventional detergents, or high temperature detergents or normal detergents. The other problem is the deposition of another kind of "dirt." This "dirt" has become known as "cold sludge." Cold sludge is formed in engines in cold weather and under driving conditions obtaining in cities and in other conditions when the engines never truly warm up. This latter problem is alleviated by the addition to the lubricant of additives known as cold sludge dispersants. "Cold sludge" is derived almost entirely from the fuel and is normally wet.

In the past the conventional detergents have in general been metal-containing derivatives of organic compounds such as basic alkaline earth metal petroleum or alkyl benzene sulphonates, basic alkaline earthmetal salts or phosphosulfurized polybutenes or alkaline earth metal phenates. The cold sludge dispersants, on the other hand, have in general been copolymers of polar monomers such as N-vinyl pyrrolidone with oil-solubilizing copolymerizable monomers such as long-chain alkyl methacrylates.

According to the present invention there is provided a novel oil-soluble compound, particularly suitable as an additive for lubricating compositions, which compound comprises at least one long saturated or unsaturated alkyl chain linked through an amide or an imide group to a group of the formula:

\[
-R_2-(NH-R_2)_n-(SO_2H)_m
\]

wherein \( n \) is an integer of from 1 to 20, \( m \) is an integer of from 1 to 3, the ratio of \( n:m \) being not less than 1:1 and \( R_2 \) is a group having the general formula:

\[
\begin{align*}
R & R \\
C & C \\
R & R
\end{align*}
\]

in which each \( R \) is a hydrogen atom or an alkyl, aralkyl, alkaryl or alicyclic group. Preferably \( n \) is an integer of from 1 to 12 and \( R \) is hydrogen or a methyl group.

The novel oil-soluble compounds of the present invention may be described as compounds having the general formula:

\[
R_1-X-A-SO_2H_m
\]

wherein \( R_1 \) is a long saturated or unsaturated alkyl chain, \( X \) is an amide or imide group, and \( A \) is a group of the formula:

\[
-R_2-(NH-R_2)_n-
\]

in which \( R_2 \), \( m \) and \( n \) have the same significance as hereinbefore defined.

The amide or imide group may have the formula:

\[
\begin{align*}
R_1 & -CH_2-CR \nonumber \\
\nonumber & \text{or} \\
R_1 & -C \nonumber \end{align*}
\]

The compound may be an internal salt rather than a free sulfonic acid. Preferably the novel compounds of the present invention have the general formula:

\[
\begin{align*}
R_1 & -CH_2-CR \nonumber \\
\nonumber & \text{or} \\
R_1 & -C \nonumber \end{align*}
\]

wherein \( R_1 \) is an alkenyl or alkyl group having at least 12 carbon atoms and preferably at least 50 carbon atoms.

The present invention also provides a process for preparing a novel compound as hereinbefore described which process comprises polymerizing a compound containing a polymerizable aziridine ring with sulphurous acid and reacting the polyalkylene polyamine produced with a long chain carboxylic acid, preferably a long chain mono alkenyl succinic acid or anhydride.

The general formula for the aziridine compounds employed in the process of the present invention is:

\[
R_1-R_2-(NH-R_2)_n-SO_2H
\]

Preferably the aziridine compound has the formula:

\[
R-C\nonumber
\]

wherein \( R \) is a hydrogen atom, an alkyl group or substituted alkyl group.

The preferred aziridines are ethylene imine and propylene imine but in addition C-ethyl ethylene imine, C-hexadecyl ethylene imine, 2,3-di ethyl ethylene imine, and 2,3-di ethyl propylene imine may also be employed in the process of the present invention.
Preferably the aziridine compound is polymerized by dissolving the aziridine compound in water, heating the aqueous solution and adding an aqueous solution of sulphuric acid, the water being optionally removed by a suitable means before reacting the product with the long chain mono-alkenyl succinic acid or anhydride. The aqueous solution of the aziridine compound may contain from 5 to 70 percent by weight of the aziridine compound. In a preferred embodiment 10–50 percent aqueous solution of the aziridine compound is employed. It is particularly preferred to employ an aqueous solution containing from 20 to 40 percent by weight of the aziridine compound.

Polymerization may be carried out in a reaction mixture containing the aziridine compound and the sulphuric acid in a molar ratio of from 2:3 to 20:1. It is preferred that the molar ratio of the aziridine compound and the sulphuric acid is from 2:1 to 12:1. In a particularly preferred embodiment the molar ratio is in the range of from 4:1 to 10:1.

In one embodiment of the process according to the present invention polymerization of the aziridine compound with sulphuric acid is carried out at a temperature of from 50°C to 100°C. A reaction temperature of from 80°C to 90°C is particularly preferred. Polymerization of the aziridine compound with sulphuric acid may be carried out for from 4 to 12 hours and in a preferred embodiment of the process polymerization is carried out for from 6 to 10 hours.

The polyalkylene polyamines prepared by polymerization of an aziridine compound with sulphuric acid are believed to consist essentially of a straight chain polymer terminating in sulphonic acid group. However, a limited amount of chain branching may occur during polymerization. Accordingly some molecules of the polymer may have more than one sulphonie acid group present.

The long chain monoalkenyl succinic acid or anhydride may be obtained from the reaction between a normally liquid oil soluble polyolefin having a molecular weight of from 700 to 3000, preferably from 750 to 1500, and maleic anhydride. Preferably the polyolefin is polyisobutylene.

Long chain derivatives of mono carboxylic acids may also be used in the process of the present invention and may be obtained by controlled oxidation of a normally liquid oil soluble polyolefin having a molecular weight of from 700 to 3,000, preferably from 750 to 1500, or by halogenation of the same polyolefin followed by condensation with an unsaturated acid such as acrylic or methacrylic acid. The preferred polyolefin is polyisobutylene.

Whilst the additives of the present invention are valuable ashless dispersants it may be desirable, in certain circumstances, particularly for use in diesel engines, to include a minor proportion, for example, up to 10 percent by weight of an alkaline earth metal base, e.g. calcium carbonate. This may be incorporated by any of the well-known methods.

This invention also includes a lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient at least to impart detergency or dispersancy to the oil, of the said novel composition.

The preferred additives of the present invention are long chain mono-substituted succinimides having an average of from 4 to 10 nitrogen atoms per molecule and a terminal sulphonate group. Particularly preferred are long chain mono-substituted succinimides having an average of from 5 to 6 nitrogen atoms per molecule.

The lubricating compositions of this invention may exhibit adequate cold sludge dispersancy and high temperature detergency by the incorporation wherein of quite small amounts of the additive, and the compositions may contain, preferably, from 0.5 to 5.0 percent by weight of the additive on the weight of the composition. However, in some cases, particularly in the case when a lubricating oil concentrate is required, it may be desirable to use amounts greater than 10 percent.

It is to be understood that the lubricating compositions of the present invention may contain also copper deactivators, pour-point depressants, antioxidants, viscosity index improvers and other conventional additives as necessary.

Particularly preferred antioxidants which may be used in conjunction with the additives of the present invention are the metal salts of dialkyl or dialkyl dithiophosphates, especially the zinc salts of dialkyl dithiophosphoric acids derived from C4—C10 alcohols. The dithiophosphate may be present in the composition in amounts from 0.2 to 2% and preferably from 0.5 to 1.5 percent by weight based on the weight of the composition.

Following is a description by way of example of a method of preparing a typical additive in accordance with the present invention.

EXAMPLE I

The Preparation of Polyisobutylene Succinic Anhydride.

1. 330 g. (0.3 mole) of a polyisobutylene of average molecular weight 1100, 32.34 g. (0.33 mole) of maleic anhydride and 5.82 g. (0.04 mole) of di-t-butyl peroxide were refluxed with stirring in 210 mls. of toluene, in a 2-liter flask fitted with thermometer pocket, nitrogen inlet, condenser and rotational stirrer, for 30 hours. The toluene was distilled off and 210 mls. of hexane added, whereupon unreacted maleic anhydride was precipitated and this was removed by filtration using a filter aid. The hexane was distilled off and the product vacuum stripped for 1 hour at 200°C. and 10 mm. Hg. pressure. The product was again filtered through a steam-heated filter funnel to yield 296 g. of a clear brown product. The purity of the product was determined by saponification. The saponification value was 73.5 mg. KOH/g. (calculated = 93.5). The product therefore contained about 79 percent of polyisobutyl succinic anhydride together with 21 percent of unreacted hydrocarbon.

2. A similar product was obtained by stirring 475 gm. of polyisobutylene (M.W. 950) with 54 gm. maleic anhydride at 240°C. for 30 hours. The reactants were allowed to cool, 300 mls. of hexane added and the solution filtered through a diatomaceous filter aid. The hexane was distilled off and the product vacuum stripped for 2 hours at 200°C. and 10 mm. Hg. pressure. 361 gms. of clear viscous liquid was obtained.

The saponification value of the product was 83.8. This product therefore also contained 79 percent of polyisobutylene succinic anhydride.

This alternative method of preparation has been described in Belgian Pat. No. 619,375.
Polymerization of Propylene Imine in the Presence of Sulphurous Acid.

Water (66 ml.) was measured into a flask fitted with a stirrer and condenser. 29 g. (0.5 mole) of propylene imine was added and the mixture heated to 80°C. in a water bath. A solution of 3.2 g. (0.05 mole) of sulphur dioxide, dissolved in approximately 50 ml. of water, was added and the temperature kept at 80°C-90°C for a further 8 hours. The mixture was vacuum stripped to remove all water and 32 g. of a viscous yellow liquid were obtained. Vacuum stripping was best carried out at about 170°C. at 10 mm. Hg pressure.

This product contained 5.56 percent sulphur (4.76 percent calculated) and had a total acid number of 95 mg.KOH/g. (81 calculated). It was believed to be a mixture of low molecular weight polypropylene polyamine sulphonic acids or internal salts thereof.

Preparation of a Polysobutylben Succinimide.

76.5 g. (0.05 mole) of a polysobutylben succinic anhydride of 75% purity prepared by a process similar to the second alternative procedure outlined above, from polysobutylene of average molecular weight 1050, was heated with stirring at 200°C. for 4 hours with 16.35 g. of the intermediate polypropylene polyamine sulphonic acid material. The reaction mixture was cooled to about 100°C. and diluted to 50 percent concentration with mineral oil. The mixture was filtered through filter aid in a steam heated filter funnel.

The product obtained contained 1.32 percent sulphur of which about 0.8 percent was due to the mineral oil.

Similar compounds were prepared using substantially the same method and the details of these preparations are given in Tables I, II and III. Tables I and II give the quantities of the reactants and analyses of the products of the preparation of the intermediate polyalkylene imine sulphonic acids, which were prepared in a similar manner to that described in Example I.

In these tables the product number refers to the imine from which the intermediate was prepared and the theoretical ratio of the average number of nitrogen atoms to one sulphur atom in the product. Thus PN4 was prepared from 0.76 moles of propylene imine and 0.2 moles of sulphur dioxide and the theoretical ratio of nitrogen to sulphur atoms in the product was approximately 4:1.

Table III shows the preparation of typical lubricating oil additives according to the present invention, these being prepared from the intermediate polyalkylene sulphonic acid and the polysobutylene succinic anhydride in a similar manner to that described in Example I.

### TABLE I

#### (Preparation of polypropylene imine sulphonic acids)

<table>
<thead>
<tr>
<th>Product number</th>
<th>Wt. (g.)</th>
<th>Sulphur dioxide</th>
<th>Percent</th>
<th>Wt. (g.)</th>
<th>In Water (ml.)</th>
<th>N (theory)</th>
<th>S (theory)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN 1</td>
<td>21.9</td>
<td>0.28</td>
<td>59.3</td>
<td>12.4</td>
<td>15.0</td>
<td>18.8</td>
<td>39</td>
</tr>
<tr>
<td>PN 2</td>
<td>21.8</td>
<td>0.78</td>
<td>59.1</td>
<td>12.4</td>
<td>15.1</td>
<td>14.1</td>
<td>15.1</td>
</tr>
<tr>
<td>PN 4</td>
<td>45.7</td>
<td>1.78</td>
<td>100.1</td>
<td>14.9</td>
<td>18.1</td>
<td>8.6</td>
<td>16.3</td>
</tr>
<tr>
<td>PN 5</td>
<td>37.7</td>
<td>1.0</td>
<td>100.9</td>
<td>17.6</td>
<td>19.1</td>
<td>8.4</td>
<td>9.7</td>
</tr>
<tr>
<td>PN 15</td>
<td>21.5</td>
<td>0.38</td>
<td>59.1</td>
<td>21.8</td>
<td>22.5</td>
<td>3.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

### TABLE II

#### (Preparation of polyethylene imine sulphonic acids)

<table>
<thead>
<tr>
<th>Product number</th>
<th>Ethylene Imine</th>
<th>Sulphur dioxide</th>
<th>Percent</th>
<th>Wt. (g.)</th>
<th>In Water (ml.)</th>
<th>N (theory)</th>
<th>S (theory)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN 5</td>
<td>21.5</td>
<td>0.5</td>
<td>59.4</td>
<td>6.4</td>
<td>100</td>
<td>21.2</td>
<td>19.6</td>
</tr>
<tr>
<td>EN 7</td>
<td>21.5</td>
<td>0.5</td>
<td>59.4</td>
<td>6.4</td>
<td>100</td>
<td>21.2</td>
<td>19.6</td>
</tr>
<tr>
<td>EN 10</td>
<td>21.5</td>
<td>0.5</td>
<td>59.4</td>
<td>6.4</td>
<td>100</td>
<td>21.2</td>
<td>19.6</td>
</tr>
<tr>
<td>EN 20, B.1</td>
<td>43.1</td>
<td>1.0</td>
<td>100</td>
<td>8.2</td>
<td>20.6</td>
<td>25.8</td>
<td>25.5</td>
</tr>
<tr>
<td>EN 20, B.2</td>
<td>43.1</td>
<td>1.0</td>
<td>100</td>
<td>8.2</td>
<td>20.6</td>
<td>25.8</td>
<td>25.5</td>
</tr>
</tbody>
</table>

### TABLE III

#### (Typical products according to the present invention)

<table>
<thead>
<tr>
<th>Example number</th>
<th>Polyisobutylene succinimide anhydride</th>
<th>Wt. (g.)</th>
<th>Mole</th>
<th>Product number</th>
<th>Wt. (g.)</th>
<th>Mole</th>
<th>Percent N of filtered 50% oil concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>66.5</td>
<td>0.05</td>
<td>PN1</td>
<td>6.25</td>
<td>0.05</td>
<td>11</td>
</tr>
<tr>
<td>IV</td>
<td>B</td>
<td>20.8</td>
<td>0.05</td>
<td>PN1</td>
<td>10.05</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>V</td>
<td>C</td>
<td>21.5</td>
<td>0.05</td>
<td>PN4</td>
<td>2.45</td>
<td>0.05</td>
<td>0.65</td>
</tr>
<tr>
<td>VI</td>
<td>D</td>
<td>38.2</td>
<td>0.05</td>
<td>EN7</td>
<td>9.6</td>
<td>0.05</td>
<td>2.0</td>
</tr>
<tr>
<td>VII</td>
<td>E</td>
<td>17.05</td>
<td>0.0125</td>
<td>PN13</td>
<td>16.13</td>
<td>0.0125</td>
<td>1.0</td>
</tr>
<tr>
<td>VIII</td>
<td>F</td>
<td>38.2</td>
<td>0.028</td>
<td>EN20</td>
<td>22.4</td>
<td>0.028</td>
<td>3.6</td>
</tr>
<tr>
<td>IX</td>
<td>G</td>
<td>123</td>
<td>0.1</td>
<td>PN3</td>
<td>15.4</td>
<td>0.1</td>
<td>1.62</td>
</tr>
<tr>
<td>X</td>
<td>H</td>
<td>24.6</td>
<td>0.025</td>
<td>EN3</td>
<td>6.75</td>
<td>0.025</td>
<td>1.51</td>
</tr>
</tbody>
</table>

1. Approximate.
2. 50% oil concentrate.
3. Polyisobutylene succinimide anhydride A was similar to that used in Example I except that the purity was 75%.
4. Polyisobutylene succinimide anhydride B was prepared in a similar manner to that described in Example I with a polyisobutylene having n.m.w. of 1,500. The purity of the product was 7%.
EXAMPLE XI

Preparation of a Polyisobutylene Substituted Propionic Acid

3150 g. (3.0 moles) of a polyisobutylene having a molecular weight of about 1050, 2000 mls. of carbon tetrachloride and a crystal of iodine were placed in a flask fitted with a stirrer, an air condenser and a sintered glass bubbler.

The mixture was stirred vigorously at room temperature while chlorine was bubbled in for 17 hours. After this period the solvent was removed by vacuum stripping at 130°C. The product was found to contain 6.78 percent chlorine (calculated 6.8%).

1050 g. (1.0 mole) of this product and 77g. (1.1 mole) of acrylic acid were placed in a flask fitted with a condenser, stirrer and nitrogen bleed and stirred at 230°C. for 18 hours, after which time nitrogen was bubbled through for 30 minutes and the product filtered through a steam heated funnel. It was found to contain 0.13 percent residual chlorine and had a saponification value of 48.8 (calculated 50), thus showing the product to be 97.6 percent pure. Infra-red analysis also showed that the expected product had been obtained.

Preparation of a Typical Additive of the Present Invention

30 g. (0.025 mole) of the product obtained above and 7.45 g. (0.025 mole) of product No. PN4 from Table I were reacted in the same manner as in the final stage of Example I. The product was found to contain 0.92 percent nitrogen.

In order to obtain some information on the dispersancy of the additives of the present invention at relatively high temperatures, such as those encountered in the piston ring-belt area of diesel engines, lubricating compositions containing them were subject to "Panel Coker Tests."

In this test the oil sample (250 ml. approx.) was contained in a sump which was fed by a chicken feed to maintain a constant level of oil. The oil was splashed continuously for 24 hours by means of wires on a rotating spindle on to a heated sloping aluminum panel maintained at 275°C.

The weight change and appearance of the panels were observed after test, the appearance of the panels being assigned merit ratings which were determined by comparing with a set of 28 panels divided into four groups. Where the panels were merely stained these panels were given numbers 1 – 7 in increasing order of staining, i.e. number 1 was practically clean and number 7 was black. In the second group the same numbers were assigned 1 – 7 but the suffix "L" was placed after the number to indicate that it had the same staining but was lacquered. Similarly in group 3 the suffix "B" showed the appearance of bubbles on the same background. In Group 4, the suffix "S" showed that the panel was sooted, the number referring to the panel color. A rating of 4 or less was considered to be reasonable.

The results of these tests are given in Table IV, from which it will be seen that the additives of the present invention were effective dispersants under high temperature conditions.

It has been found by experience that this test gives results which correlate well with tests in the Petter AV.1 engine when operated under the standard AT-4 conditions.

Table IV gives the results of tests carried out on simple and fully formulated blends. The simple blends consisted of a mineral base oil (Mineral Oil A) having a viscosity of about 160 seconds Redwood at 140°F. containing 0.9 percent of a mineral oil concentrate of a zinc dialkyl diithiophosphate (ZDPP) derived from isopropyl alcohol and capryl (1-methyl heptyl) alcohol containing about 8 percent phosphorus and 2 percent of the compound according to this invention. The fully formulated blends were SAE 10W/30 oils made up as follows:

- Mineral Oil B
- Mineral Oil C
- Methacrylate V.I. Improver (15% in mineral oil B)
- Additive A
- ZDPP
- Additive according to the present invention

Mineral Oil B was a pale spindle oil having a viscosity of about 52 seconds Redwood No. 1 at 140°F.

Mineral Oil C was a solvent refined mineral oil having a viscosity of about 100 seconds Redwood No. 1 at 140°F.

Additive A was the barium salt of a phosphosulphurized polyisobutylene of molecular weight about 1000, the neutralization having been effected in the presence of an alkyl phenol, followed by treatment with carbon dioxide.

To test the cold sludge dispersancy properties of lubricating compositions comprising the compounds of the present invention, the following tests were performed.

One test which was used to compare the dispersancy of the additives of the present invention was the Spot Test. In this test samples of the blend containing the dispersant were thoroughly shaken with a standard engine sludge obtained from the Motor Industry Research Association to which 20 percent by weight of water had been added. The proportions were such that 5 and 30 percent by weight dispersions of the wet sludge in the oil were obtained. The mixture was then placed in a test tube at 90°C. and one drop was removed from the top of the mixture immediately by means of a glass rod. A further drop was removed after three days and subsequently at daily intervals. The drops were placed on chromatographic paper placed horizontally and allowed to develop. The intensity of the spots and the manner in which they spread was taken as a measure of dispersancy. The darker the spot the better the dispersancy and the more evenly spread the better the dispersancy.

Another test which was used to test dispersancy was
the "asphaltene test." In this test a solution of about 3.5 percent by weight of asphaltum powder in chloroform was prepared. Approximately 0.1 mls. of this solution was added to 5 mls. of a solution of 0.5 percent of the dispersant in a thin white oil in a 100 ml beaker and stirred rapidly. This solution, which was optically bright, was placed in an oven at 120°C, and the time taken for the first appearance of turbidity in the solution was measured by placing the beaker on a mirror and shining a powerful light from one side. The longer the time for turbidity to appear the better the dispersant.

In general the additives of the present invention when subjected to these tests were found to have dispersant properties of the same order as those possessed by prior art dispersants and were, in some cases, better. However, the additives of the present invention were found to have particularly good high temperature dispersant properties and this was demonstrated by the very stringent Petter AV-1 engine test using the HD 1A procedure. The operating conditions were as follows:

| Test duration | 120 hours |
| Spindle speed | 1500 r.p.m. |
| B.H.P. | 5.0 |
| Engine cooled with kerosine | |
| Sump temperature | 131°F ± 4°F |
| Coolant outlet temperature | 185°F |
| Coolant inlet temperature | 173°F ± 3°F |
| Fuel | 1.0% Sulphur |

In this test the maximum rating for each of the components A, B and C was 10.0, the general cleanliness of the piston giving a measure of the high temperature dispersancy of the oil.

The results of the Petter AV-1 tests in Table V, in which the composite merit rating A+B+C was the most important criterion, showed clearly that the high temperature dispersancy of a typical additive of the present invention, when employed in a fully formulated motor oil composition, was outstandingly good, being definitely superior to the prior art ashless dispersant.

In this Table blend Q was a fully formulated 10W/30 blend having the composition given above but containing 1.9 percent of a commercially available polyamino substituted polyisobutenyl succinimide dispersant, whilst Example XVI was a similar blend containing 1.9 percent of the product of Example IV instead.

**TABLE V**

<table>
<thead>
<tr>
<th>Petter AV-1 Engine Test Results — HD 1A Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Q</td>
</tr>
</tbody>
</table>

We claim:

1. An oil-soluble additive for lubricating compositions, said additive being produced by polymerizing an aziridine compound selected from the group consisting of ethylene imine, propylene imine, C-ethyl ethylene imine, 2,3-diethyl ethylene imine and 2,3-diethyl propylene imine with sulphurous acid in aqueous solution in a molar ratio of about 2:3 to 20:1 at a temperature of about 50°C to 100°C to provide a polyalkylene polyamine reaction product having from one to three sulphonic acid groups on the molecule and reacting the sulphonated polyalkylene polyamine reaction product so produced with an alkenyl succinic acid or anhydride wherein the alkenyl group has a molecular weight of from 700 to 3000.

2. A process for the preparation of an oil-soluble additive for lubricating compositions comprising polymerizing an aziridine compound selected from the group consisting of ethylene imine, propylene imine, C-ethyl ethylene imine, 2,3-diethyl ethylene imine and 2,3-diethyl propylene imine with sulphurous acid in aqueous solution in a molar ratio of about 2:3 to 20:1 at a temperature of about 50°C to 100°C to provide a polyalkylene polyamine reaction product having from one to three sulphonic acid groups on the molecule and reacting the sulphonated polyalkylene polyamine reaction product so produced with an alkenyl succinic acid or anhydride wherein the alkenyl group has a molecular weight of from 700 to 3000.

3. The oil soluble additive of claim 1 wherein the aziridine compound from which said additive is produced is ethylene imine.

4. The oil soluble additive of claim 1 wherein the aziridine compound from which said additive is produced is propylene imine.

5. The oil soluble additive of claim 1 wherein the aziridine compound is polymerized with sulphurous acid in a molar ratio of about 5:1.

6. The oil soluble additive of claim 1 wherein the sulphonated polyalkylene polyamine reaction product is reacted with a polyisobutenyl succinic anhydride having a molecular weight of about 750 to 1500.

7. The oil soluble additive of claim 1 wherein the aziridine compound is ethylene imine or propylene imine, the molar ratio of aziridine compound to sulphurous acid is from about 2:1 to 12:1, the polymerization is carried out at a temperature of from about 80°C to 90°C and the resultant sulphonated polyalkylene polyamine reaction product is reacted with a polyisobutenyl succinic anhydride having a molecular weight of about 750 to 1500.

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