ESTER-AMIDES OF ALKENYL SUCCINIC ANHYDRIDE AND DIETHANOLAMINE AS ASHLESS DISPERSANTS

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This application is a continuation-in-part of application Ser. No. 387,216, filed Aug. 3, 1964, for Lubricating Oil Detergent Compositions.

This invention relates to oil-soluble lubricating oil, ashless dispersants and especially to the reaction products of an alkenyl succinic anhydride with diethanolamine.

A large percentage of today's automobiles are used in city stop-and-go driving where the engines do not reach their most efficient operating temperatures. Large amounts of partial oxidation products are formed and reach the crankcase of the engine by blowing past the piston rings. Most of these partial oxidation products are oil insoluble, and tend to form deposits on various operating parts of engines, resulting in sludge and varnish. Other deposits and organic acids result from deterioration of the oil itself. To prevent deposition of these materials on various engine parts, it is necessary to incorporate dispersants in the lubricating oil compositions, thus keeping these polymeric products highly dispersed in a condition unfavorable for deposition on metals.

For the most part, the various dispersants which have been used to effectively disperse the precursors of sludges and varnishes are metallic organic compounds, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. These dispersants also neutralize to some extent the organic acids, and thereby help prevent corrosion of the engine parts. However, such dispersants have the disadvantage of forming ash deposits in the engine which deposits lower engine performance by fouling the spark plugs and valves and by contributing to pre-ignition.

In recent years, various non-ash producing dispersants have been devised to overcome these disadvantages. Among such dispersants are imides, for example, N,N-dialkylaminooalkyl alkenyl succinimide, produced by the reaction of an alkenyl succinic anhydride and an N,N-dialkylaminooalkylamine. Some of these products are very effectively disperse sludge and varnish forming materials. As a result, investigators have synthesized and suggested a multitude of variations, almost indiscriminately. Accordingly, a large number of nitrogen-containing succinic anhydride or acid derivatives have been suggested which are effective in their dispersing action. However, while investigators have concentrated their efforts on improving the dispersing characteristics of their products, they have, to a large degree, disregarded the harmful effects of high dispersancy. One of these harmful effects is an increase in corrosion with dispersancy. In many cases, a product which effectively disperses sludge contributors actually contributes to corrosion of the engine parts, for example, the bearings. The mechanism of such corrosive action is not clear but may be the result of several factors, among which is the dispersancy, away from the metal surface, of metal-coating protective films. Another factor may be the leaching of the metal by an efficient dispersant. Therefore, while some of the ashless dispersants heretofore available are effective in dispersing sludge-forming materials, they are mostly useless as engine oil additives as they often cause corrosion problems.

Accordingly, it is an object of this invention to provide detergent-dispersants which are highly effective dispersants but which do not cause corrosion of the engine parts. Another object is to provide such a detergent-dispersant by the reaction of very carefully defined materials having definite properties. A further object is to provide detergent-dispersants which are complex ester-amide mixtures obtained from the reaction of a carefully defined alkenyl succinic anhydride or acid with diethanolamine in such a manner as to provide a reaction product having a critical ratio of ester to amide groups.

These and other objects are accomplished by providing an ashless dispersant ideally suited for use in lubricating oil, said dispersant being the reaction product of an alkenyl succinic anhydride wherein the alkenyl substituent is a polybutene having a molecular weight of from 700 to 1100 with diethanolamine, further characterized in that from 0.66 to 1.0 moles of diethanolamine are reacted per mole of alkenyl succinic anhydride and the resulting product has an ester/amide ratio, as later defined, of from 0.5 to 1.1.

In a highly preferred embodiment of this invention, the reactant ratio is from 0.8 to 0.95 mole of diethanolamine per mole of alkenyl succinic anhydride.

In a most preferred embodiment of this invention, the reactant ratio is from 0.8 to 0.95 mole of diethanolamine per mole of alkenyl succinic anhydride and the reaction conditions are such that the ester/amide ratio is from 0.85 to 1.0.

Diethanolamine (DEA) reacts with alkenyl succinic anhydride (ASA) or acid to form either ester or amide groups. This is illustrated by the following equations.

**ESTER FORMATION**

```
R-CH-CH=CH-CH-OH + HO(CH₂)₂-N → (CH₃OH)
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**AMIDE FORMATION**

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R-CH-CH=CH-CH-OH + H-N → (CH₃OH)
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Thus, diethanolamine in the reaction described in this invention differs critically from both triethanolamine, which does not have a hydrogen atom bonded to nitrogen and thus cannot form amides, and from monoethanolamine, which has two hydrogen atoms bonded to nitrogen and thus forms not only esters but imides instead of amides. In view of the foregoing, it can be seen that the reaction of alkenyl succinic anhydrides with diethanolamine leads to reaction products differing critically from those formed with either triethanolamine or monoethanolamine or, for that matter, with other amines in general.

In practice, the reaction product of the ASA with DEA leads to polymeric materials having both ester and amide groups. This is because of the poly-functional nature of both the ASA and the DEA. ASA is the anhydride of a dibasic acid and thus is bi-functional. DEA has two reactive hydroxyl groups and one active hydrogen and thus is tri-functional. Thus, in reacting the bi-functional
ASA with the tri-functional DEA, it would be expected that polymeric chains of varying length of the reactant molecules would be formed bonded together by both ester and amide linkages. A further type of reaction product that can be formed are cyclic products which can be formed by the simple reaction of one molecule of an ASA with one molecule of DEA, or may embody more than one molecule of each reactant forming higher molecular weight cyclic products.

In reacting one mole of ASA with one mole of DEA it would statistically be expected that there would be formed two ester groups for every one amide group. This is because a molecule of DEA contains twice as many ester generating hydroxyl groups as amide generating active hydrogen atoms. In practice, this is not the case because of the differing reactivity of the hydroxyl radical and the nitrogen bonded hydrogen atom. Thus, the ratio of ester to amide groups varies depending upon the reactant ratio and reaction conditions. It is this ratio of ester groups to amide groups that is referred to in describing the critical ester/amide ratio of the dispersants of this invention. However, since this ester/amide ratio must be determined using analytical methods, it is best described in conjunction with a description of the method used to determine it. In other words, the "ester/amide" ratio referred to in this invention is obtained using a specifically defined analytical procedure. The ester/amide ratio is determined as follows.

OUTLINE OF METHOD

A weighed sample of dispersant is dissolved in carbon tetrachloride. Its absorption spectrum is recorded between 5.0 µ and 6.5 µ. Using baseline point techniques, C=O as ester and amide are calculated at 5.75 and 6.15 µ, respectively. Results are obtained by using the absorption coefficient based on calibration data for a mixture of ester and amide primary standards.

REAGENTS

(a) Carbon tetrachloride, reagent grade.
(b) Methyl laurate standard, 99.5%.
(c) Monamid 150-LW, amide standard purchased from Mona Industries, Inc.

APPARATUS

(a) Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer (other double beam infrared spectrophotometers may be used).
(b) Cells matched 0.5 mm. sodium chloride cells.
(c) Volumetric flasks, 10 ml. capacity.

SOLUTIONS

Prepare a series of standards containing the mixed ester and amide as follows:

(a) Weigh 53.0 mg. of the ester standard and 70.1 mg. of the amide standard into a 10-ml volumetric flask and dilute to volume with CCl₄. This solution will contain 6.93 mg. of C=O as ester and 6.83 mg. of C=O as amide.
(b) Weigh 53.0 mg. of ester standard and 35.5 mg. of the amide standard into a 10-ml volumetric flask and dilute to volume with CCl₄. This solution will contain 6.93 mg. of C=O as ester and 3.46 mg. of C=O as amide.
(c) Weigh 29.0 mg. of ester standard and 70.1 mg. of amide standard into a 10-ml volumetric flask and dilute to volume with CCl₄. This solution will contain 3.78 mg. of C=O as ester and 6.83 mg. of C=O as amide.

CALCULATION

(a) Calibration procedure

Prepare the calibration data for each of the standard solutions as follows:

(1) Fill the 0.5 mm. sample cell with each standard solution.

(2) Fill the companion, 0.5 mm. reference cell with carbon tetrachloride.

(3) Place the cells in their respective beams of the spectrophotometer.

(4) Set the instrument at 90 percent transmittance at 5.0µ and scan the 5.0–6.5µ region of the spectrum at a slow speed.

(b) Determination of absorbancies and absorption coefficients

(1) From each curve, obtain the following:

(a) The percent transmittances, Tr, at the absorption peaks of the 5.75µ and 6.15µ bands. These are the analytical wavelengths for ester C=O and amide C=O, respectively.

(b) The percent transmittances (Tr) correspond to the baseline energy at 5.75µ and 6.15µ. Using a point technique read Tr value at 5.20µ. The same Tr value is used for both ester and amide C=O.

(2) Obtain the absorbance (A) at each wavelength by calculating the logarithm to the base 10 of Tr divided by Ta:

\[ A = \log \frac{Tr}{Ta} \]

(3) Obtain the absorbancy coefficient by dividing the absorbance at each analytical wavelength of the individual carbonyl bands by the mg. of C=O added.

(4) Prepare a table containing the weights of each of the standards added and the absorbance at their respective wavelengths. A typical calibration table is shown in Table 1.

<table>
<thead>
<tr>
<th>Standard Solution</th>
<th>Ester C=O=5.75µ</th>
<th>Amide C=O=6.15µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Solution</td>
<td>6.94</td>
<td>.929</td>
</tr>
<tr>
<td>Standard Solution</td>
<td>6.90</td>
<td>.303</td>
</tr>
<tr>
<td>Standard Solution</td>
<td>3.78</td>
<td>.235</td>
</tr>
</tbody>
</table>

(5) If the absorbancy coefficient are constant with increasing concentration, average the absorbancy coefficients and use the average for calculating a sample. If the absorbancy coefficients vary with concentration, use the absorbancy coefficient obtained from the standard which has an absorbance closest to that of the sample.

ANALYSIS OF SAMPLE

(a) Procedure

(1) Weigh approximately 0.35 gram of dispersant (may have to be warmed) into a 10 ml. volumetric flask and dilute to the mark with carbon tetrachloride.

(2) Record the spectrum over the range of 5.0–6.5µ.

(3) Read the transmittances, Ta and Tr, corresponding to the absorption peaks and the baseline reference point at 5.20, 5.75 and 6.15µ.

(b) Calculations

(1) Calculate the absorbance for the ester and amide carbonyl at their analytical wavelengths.

(2) Calculate the concentration of ester and amide carbonyl in milligrams by the observed absorbancies using the corresponding absorbancy coefficient.

(3) Calculate the concentrations, in percent, by dividing the milligrams of C=O by the total sample weight in milligrams and multiplying by 100.

(4) Convert this to ester/amide ratio by dividing the percent ester carbonyl by the percent amide carbonyl.
The ester/amide ratio of the product is controlled by three factors. First of all, the ratio of ASA to DEA in the reaction affects the ester/amide ratio. Increasing the amount of DEA leads to a decrease in ester/amide ratio and, hence, to a product that will give excessive bearing weight loss when used in lubricating oil compositions. Decreasing the amount of DEA employed in preparing the reaction product below 0.66 mole of DEA per mole of ASA will lead to a reaction product having insufficient amine or hydroxyl groups to remove all the acid function of the ASA. Carrying the reaction out at any given temperature for longer periods leads to higher ester/amide ratios. Similarly, carrying the reaction out at increased temperatures for a given length of time will lead to increased ester/amide ratios. Thus, the determination of the proper ester/amide ratio involves the interrelation of these three factors. It will be subsequently shown that not only is the ester/amide ratio critical in obtaining an acceptable lubricant dispersant, but the manner in which the ester/amide ratio is achieved is also critical. In other words, two dispersants prepared from the starting materials of this invention and possessing the same ester/amide ratio will possess greatly different properties depending upon whether the ester/amide ratio was obtained by varying the heat and time of the reaction or by varying the ratio of reactants. Dispersants prepared using reactant ratios outside those defined by this invention but having an ester/amide ratio within the range defined in this invention are not satisfactory dispersants. Likewise, dispersants prepared using the preferred reactant ratios but employing too long a reaction time leading to ester/amide ratios above those defined in this invention are unsatisfactory. Thus, in order to have a satisfactory dispersant it is necessary to obtain a product within an ester/amide range of from 0.5 to 1.1, preferably 0.85 to 1.0, and to prepare the dispersant employing a reactant ratio of from 0.66 to 1.5, preferably 0.8 to 0.95, moles of DEA per mole of ASA.

Alkenyl succinic anhydrides suitable for use in preparing these ashless dispersants of the present invention are those having the formula:

\[
\begin{align*}
  R_1 &- C = O \\
  | & \quad | \\
  R_2 &- C = O
\end{align*}
\]

wherein \( R_1, R_2 \) and \( R_4 \) are hydrogen or alkyl radicals of from 1 to 20 carbon atoms. \( R_1 \) is an alkyl or alkenyl substituent, preferably an alkanyl radical having a molecular weight of from about 700 to 1100.

In a preferred embodiment of this invention, \( R_1 \) is an alkenyl radical formed by the polymerization of low molecular weight olefins, and \( R_2 \) and \( R_3 \) and \( R_4 \) are hydrogen.

In a more preferred embodiment of this invention, \( R_1 \) is an alkanyl radical formed by the polymerization of monoolefins containing from 2 to 6 carbon atoms. In a most preferred embodiment of this invention, \( R_1 \) is a polybutene radical having a molecular weight of from 7000 to 11000. Such polybutene radicals are bonded to the succinic anhydride portion of the molecule by merely mixing the desired polybutene with a suitable maleic anhydride and heating this mixture to temperatures in excess of 150° C. Methods of preparing such materials are well known in the art. The following example is illustrative of such methods.

**Example 1**

A reaction vessel equipped with heating means, temperature measuring means, stirring means, a reflux condenser, gas inlet and outlet means and a nitrogen source is flushed with nitrogen and 23.5 parts of polybutene having a molecular weight of 1100 and 1.85 parts of maleic anhydride are added. The reactants are stirred at 215–220° C. for 24 hours, allowed to cool and 11.1 parts of hexane are added. The mixture is allowed to set for about several hours and is then filtered through Celite via a Buchner funnel. Hexane is stripped from the filtered at atmospheric pressure at 175° C. and then the pressure is reduced slowly to about 10–11 mm., holding the temperature at about 170–180° C. for about one hour, during which time maleic anhydride is removed. In an average run, 0.8 parts of hexane and 0.21 part of maleic anhydride are recovered, leaving 22.9 parts of ASA.

Dilution of the reaction product before filtration can be done with solvents other than hexane, such as benzene, xylene, toluene, etc. As will be discussed further, it may be desired to dilute the final ASA–DEA reaction product with oil, e.g., for handling purposes, and if such is the case, that diluent can be used in place of the hexane. If oil diluent is used it would be desirable to strip the unreacted maleic anhydride before filtration. A temperature of about 180–185° C. could be used during the strip to isomerize the maleic acid contaminant to insoluble fumaric acid.

In preparing the final product, it is preferred to use the ASA rather than the acid, although the acid can be used. Use of the acid results in no savings, but requires an additional hydrolysis step from the anhydride. Either product will react with the DEA, but the anhydride reacts with the formation of less water and with a more desirable product, and so is preferred. Of course, the ready availability, to a processor, of one or the other will influence the choice.

In carrying out the reaction between ASA and DEA, DEA is less viscous than the ASA and is preferably added to a solution of the ASA in a water-immiscible solvent. Preferred solvents are hydrocarbon solvents having a boiling point of from about 100–200° C. The more preferred solvents are the aromatic hydrocarbon solvents within this boiling range. A most preferred solvent is xylene. The xylene solvent in this reaction performs an extremely important function. During the reaction of the DEA with the ASA, water is produced. This water is removed from the reaction by azeotropic distillation with the xylene. Consequently, it is preferred that a water immiscible solvent be present during the conduction of the reaction between DEA and ASA. When xylene is used as the water immiscible solvent a preferred quantity is from 50 to 120 parts of xylene per 450 parts of ASA. A more preferred quantity of xylene is from 60 to 90 parts of xylene per 450 parts of ASA, and a most preferred quantity of xylene is from 60 to 70 parts of xylene per 450 parts of ASA.

As stated above, the DEA is added to a solution of the ASA in a water immiscible solvent. The DEA is usually added to the solution of ASA at as high a temperature as can be tolerated without causing excess vaporization of the solvent. When xylene is employed as a solvent the DEA is added at a temperature of from about 140–160° C. Following the addition of the DEA, the reaction temperature is maintained at about 150–200° C. A more preferred reaction temperature range is from about 160–190° C, and a most preferred temperature range is from about 175–185° C. If the temperature is allowed to vary outside these ranges the extent to which the reaction proceeds during the reaction period will vary and a reaction product will be obtained that does not possess the proper ester/amide ratio.

The reaction is carried out at the desired temperature range for a period of from about 30 minutes to 1.5 hours. At the higher end of the temperature range, 30 minutes is usually sufficient to bring the reaction product to the desired ester/amide ratio. At lower temperatures longer periods are required. At the most preferred reaction temperature range of from 175–185° C, a reaction product
3,324,033

having the critical ester/amide ratio is usually obtained in 35 minutes.

The reaction may be carried out in the presence of air or under an inert atmosphere. For safety reasons, the reaction is usually blanketed with an inert atmosphere, such as nitrogen.

It is usually preferred to conduct the reaction at atmospheric pressure, although pressures from both below and above atmospheric may be employed. During the progress of the reaction the water immiscible solvent will continuously vaporize from the reaction mass and be condensed in an overhead condensing system. The vapor will consist of a mixture of the water immiscible solvent together with water. The water immiscible solvent is allowed to return the ester/amide ratio when the water is removed from the reaction zone. In a preferred method of carrying out this reaction the reaction is conducted at atmospheric pressure until about 80 percent of the theoretical quantity of water is removed. Following this, the pressure within the reaction vessel is slowly reduced while maintaining the temperature in the same temperature range as employed during the first 80 percent of the reaction. During the pressure reduction period, both water immiscible solvent and water are withdrawn from the reaction zone, so that when the reaction pressure finally reaches 40 mm of Hg, both water and water immiscible solvent will be substantially removed from the reaction product.

At this point in the process a sample of the product is analyzed using the previously described infrared method to determine the ester/amide ratio.

The following examples illustrate methods of carrying out the process of preparing the dispersants of this invention employing the previously described preferred reaction conditions.

**Example 2**

To a reaction vessel fitted with an agitator, heating means and condensing means was added 458 parts of an ASA wherein the alkenyl radical had a molecular weight of 900 and 64 parts of xylene. These materials were then stirred and heated to 145°C, at which point 35.3 parts of DEA were added. The initial heat of reaction caused the temperature to rise to 156°C. The reaction mass was then heated and, at a temperature of 172°C, xylene began to co-distill together with the water of esterification. Heating was continued for a period of 35 minutes, during which time the temperature rose to 190°C. The pressure was then gradually reduced to 40 mm Hg over a period of 40 minutes while holding the temperature at 180°C, following which the reaction mass was cooled, yielding an ASA–DEA reaction product having an ester/amide ratio determined by the previously described infrared method of 0.85. In order to facilitate handling, a quantity of a 75 SUS neutral oil was added, resulting in a product containing 25 percent neutral oil.

**Example 3**

To a reaction vessel described in Example 2 was charged 545 parts of an ASA wherein the alkenyl radical had a molecular weight of 900 and 81.5 parts of xylene. This material was stirred and heated to 145°C, at which time 41.9 parts of DEA were added. The initial heat of reaction raised the temperature to 156°C. The reaction mass was heated and the water and xylene began to co-distill at 164°C. Heating was continued while the water and xylene was distilled off, resulting in a temperature increase to 182°C, after 36 minutes. The reaction pressure was then gradually reduced to 40 mm Hg over a 40 minute period, during which time the reaction mixture was held at 178–181°C, thus causing the remaining water and xylene to be distilled from the reaction mixture. Following this vacuum operation the product was cooled and analyzed by the previously described infrared method and found to have an ester/amide ratio of 0.9. As in the previous example, the reaction product was diluted with a 75 SUS neutral oil to give a lubricating oil dispersant additive containing about 75 percent of the ASA–DEA reaction product and the remainder, neutral oil.

**Example 4**

To a reaction vessel equipped as in Example 2 was added 4,500 parts of an ASA wherein the ASA was prepared from maleic anhydride and polybutylene having a molecular weight of about 900. Following this, 680 parts of xylene were placed in the reaction vessel. Heat was then applied and the reaction temperature was raised to 145°C. At this point, 346 parts of DEA were added, causing a slight temperature rise. The reaction temperature was then raised to 180°C, causing water and xylene to co-distill from the reaction mass. When the water and xylene separated in the distillation receiver the upper xylene level was returned to the reaction zone. After 45 minutes, the reaction zone was cooled and analyzed by the previously described infrared method.

**Example 5**

To the reaction vessel described in Example 2 was placed 1,198 parts of an ASA wherein the alkenyl group is derived from the polymerization of butene and has a molecular weight of about 1100. To this is added 180 parts of toluene and the reaction mass heated to 125°C, while stirring. Following this, 116.5 parts of DEA are added and the reaction mass heated to about 150°C. Water and toluene co-distill, and for about a half-hour water is withdrawn from the distillate and the toluene in the distillate is recycled to the reaction mass. Following this, the pressure in the reaction vessel is gradually reduced to 50 mm Hg over a 30 minute period while maintaining the reaction mass temperature at 170°C. Infrared analysis of the product obtained shows it to have an ester/amide ratio of 0.5.

**Example 6**

To the reaction vessel of Example 2 was charged 798 parts of an ASA wherein the alkenyl radical is derived from polybutylene having a molecular weight of 700. Following this, 120 parts of chlorobenzene are added to the reactor and the reaction mass is heated to 140°C, while stirring. At this temperature, 95.5 parts of DEA are added and the reaction temperature is then raised to about 175°C. During the following 45 minute period, the chlorobenzene is co-distilled from the reaction mass together with water. Water is drained from the distillate and the chlorobenzene is returned to the reaction zone. During the next 30 minute period, the reaction pressure is gradually reduced to 50 mm Hg and the remaining water and chlorobenzene is distilled therefrom. The product is a viscous oil having an ester/amide ratio of 1.1 by the previously described infrared procedure.

**Example 7**

To the reaction vessel described in Example 2 is added 1,098 parts of an ASA wherein the alkenyl radical is derived from polybutylene having a molecular weight of about 1,000. Following this, 150 parts of chloroxylene are added and the mixture heated to 150°C with stirring. At this temperature, 105 parts of DEA are added and the reaction is heated to 200°C, allowing water and chloroxylene to co-distill. The water is drained from the distillate mass and the chloroxylene returned to the reaction zone. After 15 minutes of such treatment, the pressure is gradually reduced over the subsequent 15 min-
ute period while maintaining the reaction temperature at 200° C., resulting in an ASA-DEA reaction product having an ester/amide ratio of 1.0.

The products of this invention are quite viscous at room temperature. A desirable viscosity range for a detergent-dispersant is about 300–400 SUS at 100° C., and about 10,000 SUS at 160° F. Heating the product before use will allow it to be handled effectively. In the alternative, the product may be diluted with an oil, preferably a non-additive oil. The following table shows the dilution requirements of the product from Example 4.

### Dilution to obtain

<table>
<thead>
<tr>
<th>Oil:</th>
<th>300–400 SUS at 100° C., percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 9 refined oil</td>
<td>23–26</td>
</tr>
<tr>
<td>SL-100 solvent</td>
<td>37–41</td>
</tr>
<tr>
<td>No. 75 oil</td>
<td>37–41</td>
</tr>
<tr>
<td>Humble SEN-100</td>
<td>43–46</td>
</tr>
<tr>
<td>Texaco SEN-5</td>
<td>45–49</td>
</tr>
<tr>
<td>Midcontinent 95–V1</td>
<td>50–54</td>
</tr>
</tbody>
</table>

1. From Western solvents.
2. Solvent refined neutral oil of 100 SUS at 100° F.

The ester/amide ratio as determined by the foregoing method is a critical feature of the present invention. This ester/amide ratio should be maintained within the range of from about 0.5 to 1.1. When the ester/amide ratio is allowed to fall below this range the use of the product as a dispersant in lubricating oil is not feasible because it will result in excessive bearing weight loss, which cannot be tolerated. When the ester/amide ratio is allowed to exceed the preferred range the reaction product when added to lubricating oil will not provide the necessary dispersancy. Furthermore, the dispersant must be prepared using a reactant ratio of from 0.66 to 1.5 moles of DEA per mole of ASA. Deviation from these criteria results in an unsatisfactory product. This is shown by the following tests which compare both dispersancy and bearing weight loss obtained with reaction products made using different reactant ratios and having various ester/amide ratios.

In the test, oil samples were prepared containing 5 weight percent of the condensation products of DEA and ASA. The condensation products were prepared in a process similar to that in Example 2 except that different amounts of DEA were employed per mole of ASA. The condensation products had a range of ester/amide ratios. In addition, two of the dispersants were subjected to a longer reaction time, causing an increase in ester/amide ratio.

In the first part of the test, the oil samples containing 5 weight percent of the various condensation products were subjected to a Polyverform test. In this procedure, 48 liters per hour of air were bubbled through 100 ml. samples of the test oil maintained at 300° F., which contained additionally 0.05 weight percent ferrie oxide (as ferric-2-ethylhexaole) and 0.1 weight percent of lead bromide. The oil also contained a weighed and polished copper-lead bearing. After 48 hours of this treatment, the acid number increase and bearing weight loss were determined.

Following this, a second test blend was prepared using 10 grams of the oil already subjected to the above Polyverform test, 83 grams of new oil, 7 grams of a typical sludge material and 2 grams of water. In this test blend, the concentration of the original condensation product carried over from the Polyverform test is reduced to 0.5 wt. percent. The second test blends were emulsified in a blender for 20 minutes and then centrifuged for 2.5 hours. Following this, the percent light transmittance of the oil was measured. The better the dispersant, the more of the sludge that will remain suspended following the centrifuging and hence the lower the present light transmittance that will be measured. When the above tests were carried out on a series of dispersants prepared by condensing an ASA (molecular weight of alkenyl radical about 900) and DEA employing different reactant ratios under the same reaction conditions, various ester/amide ratios resulted. The following results were obtained.

### Table: Dilution Requirements

<table>
<thead>
<tr>
<th>Test No.</th>
<th>DEA/ASA ratio</th>
<th>Ester/Amine ratio*</th>
<th>Acid No.</th>
<th>Bearing Weight Loss (mg.)</th>
<th>Percent Transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>1.07</td>
<td>1.9</td>
<td>3.5</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>0.99</td>
<td>1.45</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.86</td>
<td>1.0</td>
<td>1.5</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>1.3</td>
<td>0.71</td>
<td>1.15</td>
<td>10.5</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>0.46</td>
<td>1.3</td>
<td>18.8</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>1.12</td>
<td>1.28</td>
<td>18.5</td>
<td>11</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>1.17</td>
<td>1.3</td>
<td>23.5</td>
<td>11</td>
</tr>
</tbody>
</table>

*Determined by infrared method.

As the above test results show, excellent dispersant activity is observed in test numbers 1–5, as evidenced by the very low percent light transmittance. However, test number 5, which exceeded the maximum DEA/ASA ratio of 1.5, exhibited a very high bearing weight loss, making it unacceptable for use in lubricating oils.

Samples 6 and 7 were made using reactant ratios about equal to samples 3 and 5. However, the reaction time was extended for six additional hours, causing an increase in the number of ester carboxyl groups and a decrease in the number of amide carboxyl groups. The criticality of this change in ester/amide ratio is apparent. Sample 6 had a reactant ratio of 1.0 and, from this, would be expected to have about the same properties as sample 3, having an ester/amide ratio of 0.95. However, test number 6 showed a bearing weight loss of 18.5 mg., over three times that of sample 3. This amply demonstrates that both the proper DEA/ASA ratio and ester/amide ratio must be present before the reaction product of ASA and DEA exhibits the properties required for an acceptable dispersant.

The dispersants of this invention are effective in both hydrocarbon and synthetic lubricating oils, including lubricating oil used in spark-ignition engines, turbines and diesel engines. To prepare oil compositions of this invention, an appropriate quantity of from about 0.01 to about 10 weight percent, and preferably from about 1–5 weight percent of a dispersant product of this invention is blended with the base oil. The lubricating oil compositions may contain other materials such as antioxidants, viscosity index improvers, corrosion inhibitors, wear inhibitors, and the like. The following examples illustrate the preparation of lubricant compositions of this invention.

### Examples 8–14

Lubricating oil compositions are prepared by blending a solvent refined crank case lubricating oil having a viscosity index of 95 and an SAE viscosity of 10 with 0.5 weight percent 4,4'-methylenebis(2,6-di-tet-butylphenol), 0.4 weight percent dialkylhydrogen phosphate, 0.1 percent of the n-octylamine salt of 1(octyl)-5-oxic-3-pyrrolidinecarboxylate, and the following concentrations of the indicated dispersant.

<table>
<thead>
<tr>
<th>Dispersant from:</th>
<th>Concentration, weight, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 2</td>
<td>0.01</td>
</tr>
<tr>
<td>Example 3</td>
<td>0.1</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.1</td>
</tr>
<tr>
<td>Example 5</td>
<td>2.0</td>
</tr>
<tr>
<td>Example 6</td>
<td>5.0</td>
</tr>
<tr>
<td>Example 7</td>
<td>6.0</td>
</tr>
<tr>
<td>Example 8</td>
<td>7.0</td>
</tr>
<tr>
<td>Example 9</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Each of the above lubricating oil compositions has greatly improved dispersant qualities.
Lubricating oils are prepared as in Examples 8–14 by blending the indicated oil with 3 weight percent of the product produced following the procedure of Example 3.

A. A dioctyl sebacate having a viscosity of 210° F. of 36.7 SUS, a viscosity index of 159 and a molecular weight of 426.7.
B. A di-(sec-amy1) sebacate having a viscosity at 210° F. of 33.8 SUS, a viscosity index of 133 and a molecular weight of 342.5.
C. A di-(2-ethylhexyl) sebacate having a viscosity at 210° F. of 37.3 SUS, a viscosity index of 152 and a molecular weight of 426.7.
D. A di-(2-ethylhexyl) adipate having a viscosity at 210° F. of 34.2 SUS, a viscosity index of 121 and a molecular weight of 370.6.
E. A diisoctyl azelate having a kinematic viscosity of 3.34 centistokes at -65° F., an ASTM slope from -40° F. to 210° F. of 0.693, a pour point of -85° F., a flash point of 425° F., and a specific gravity at 25° C. of 0.9123.
F. A diisoctyl adipate having a viscosity at 210° F. of 35.4 SUS, a viscosity at 100° F. of 57.3 SUS, a viscosity of 3.980 SUS at -40° F. and a viscosity index of 143.

The above synthetic ester lubricants have greatly improved dispersant qualities. Likewise, other synthetic lubricants such as phosphorus esters and polyalkylene oxides are greatly improved by the use of the dispersant additives of this invention.

1 claim:

1. An ashless dispersant ideally suited for use in lubricating oil, said dispersant being the reaction product of diethanolamine and an alkenyl succinic anhydride wherein the alkenyl substituent is a polybutene having a molecular weight of from about 700 to 1100, said reaction product being further characterized in that from 0.66 to 1.5 moles of diethanolamine are reacted per mole of alkenyl succinic anhydride and the reaction is conducted at a reaction temperature for a time such that the resulting product has an ester-amide ratio of from 0.5 to 1.1.

2. The ashless dispersant of claim 1 wherein from 0.8 to 0.95 mole of diethanolamine are reacted per mole of alkenyl succinic anhydride.

3. The ashless dispersant of claim 2 wherein said ester/amide ratio is from 0.85 to 1.0.

4. The ashless dispersant of claim 3 wherein said reaction product is made in a reaction carried out at a temperature of from about 150 to 200° C.

5. The ashless dispersant of claim 4 wherein said reaction is carried out for a period of from 0.5 to 1.5 hours.

6. The ashless dispersant of claim 5 wherein said reaction is carried out in xylene.

7. A lubricating oil composition containing a dispersing quantity of the ashless dispersant of claim 1.

8. A lubricating oil composition containing a dispersing quantity of the ashless dispersant of claim 2.

9. A lubricating oil composition containing a dispersing quantity of the ashless dispersant of claim 3.

10. A lubricating oil composition containing from 0.05 to 5 weight percent of the ashless dispersant of claim 3.

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