This invention relates to new anticorrosion agents consisting of the monamides of dimerized fatty acids. Among the compounds embraced by the present invention are the monamides of dimerized dienoic and trienoic fatty acids and primary or secondary amines having an N-substituent containing at least six carbon atoms. The compounds of this invention are particularly useful for imparting corrosion inhibiting characteristics and other valuable properties to various compositions such as, for example, mineral oil compositions.

As is well known in the art, "straight" or "uncompounded" mineral oils are often deficient in one or more respects for the particular use to which they are put. For example, a high resistance to rust or corrosion is important in the case of fuels or lubricants which contact metal surfaces in the presence of water. Fuels or lubricants for internal combustion engines and for gas or steam turbines are examples of materials which may desirably have incorporated therein additives or improvement agents which impart corrosion inhibiting properties thereto.

Failure to provide sufficient resistance to rust or corrosion by a particular mineral oil may result in extensive wear or damage to costly, finely-machined, moving parts and/or damage to storage and transport facilities, etc.

To overcome this and other deficiencies of uncompounded mineral oils, various agents known as "addition agents," "additives," or "improvement agents" are commonly incorporated in the particular mineral oil to be used.

An object of this invention is to provide new chemical compounds which remedied the above-mentioned deficiencies and which have valuable industrial uses. A further object is to provide a process for the preparation of said new chemical compounds. An additional object is to provide new mineral oil composition containing the above-mentioned chemical compounds and having improved rust and corrosion inhibiting characteristics.

These and other objects are achieved by the present invention which includes monamides of primary or secondary amines having an N-substituent containing at least 6 carbon atoms and dimers of unsaturated fatty acids containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule. These monoamides may be in the form of the acid amide or alternatively, may be in the form of a substantially neutral salt of the acid amide. The invention also includes processes for preparing the described monamides as well as mineral oil compositions containing the same.

In general, the compounds of this invention may be defined by the following generic formula:

\[ \text{where} \]

\[ Z = \text{acyl residue of a dimerized polyolefinic fatty acid}, \]

where \( n \) is an integer of from 10 to 42, where \( z \) is an even integer of from 6 to 10, where \( R_1 \) is a radical containing at least 6 carbon atoms selected from the group consisting of aliphatic, aromatic, aliphatic-aromatic and aromatic-aliphatic radicals, where \( Z \) is an organic radical, preferably of the same kind as \( R_1 \), or hydrogen, where \( Z \) is hydrogen, or a salt-forming metal and \( y \) is an integer equal to the valence of \( Z \). The invention also includes preparation of compounds of the type denoted above and mineral oil compositions containing the same.

The dimerized acids referred to above are dimers, i.e., binomolecular addition products, of conjugated or nonconjugated polyolefinic (dieneic to trienoic), fatty acids having from 6 to 22 carbon atoms before dimerization. Such dimerized fatty acids may be prepared by known methods. Briefly, one method of preparation of said dimerized acids involves subjecting the monomer of a polyolefinic fatty acid of the type described to heat treatment at about 300° C. to about 360° C. from about three to about eight hours under said conditions to about 400 pounds steam pressure. The dimer acid is recovered from the reaction mixture by distillation.

A second method for preparing the dimerized acids involves heating the methyl ester of the polyolefinic fatty acid at about 300° C. for several hours in an inert atmosphere, e.g., carbon dioxide. The resulting dimerized ester is then separated by distillation and saponified. The dimerized acid is then prepared from the saponified product by acidification with a mineral acid, such as hydrochloric acid.

In general, dimerized acids suitable for purposes of this invention are those prepared from polyolefinic monocarboxylic acids having the generic formula:

\[ \text{where} \]

\[ n \] is an integer of from 5 to 21 and \( x \) is 3 or 5. As will be evident, such monomeric acids contain from 6 to 22 carbon atoms and may contain 2 or 3 ethylenic linkages as the ratio of carbon to hydrogen increases (i.e., as \( x \) increases from 3 to 5). Dimerized acids corresponding to the addition products of the foregoing acids therefore may be defined by the generic formula:

\[ \text{where} \]

\[ n \] is an integer of from 10 to 42, and where \( x \) is an even integer from 6 to 10. These dimeric acids are therefore dibasic acids having from 12 to 44 carbon atoms.

Representative of the class of dimerized acids suitable for the purposes of this invention are dimers of dienoic acids such as sorbic (hexadienoic), palmotolic (hexadeca-dienoic), linoleic (octadecadienoic), linolenic (nona-decadienoic) and elcosinic (elcosadienoic) acids. Dimers of trienoic acids, for example, such as linolenic and eleostearic (octadecatrienoic) acids also may be used. The dienoic and trienoic acids containing 18 carbon
atoms, and especially those having conjugated olefinic linkage are distinctly preferred. It is not necessary that both of the unsaturated fatty acid molecules of the bimolecular addition product be identical. Dimers of mixed composition, such as those obtained by dimerizing mixtures of dienoic, trienoic, or dienoic and trienoic acids obtained from naturally occurring drying oils are quite satisfactory. A wide variety of primary and secondary amines which do not adversely affect the oil-solubility of the monoamide can be used in the preparation of the agents of this invention. Primary and secondary amines having a substituent containing at least 6 carbon atoms definitely assist the oil-solubility of the additives. In general, amines suitable for the purposes of this invention are primary or secondary monoaminoes or mixtures thereof having the generic formula:

\[ R_1 \quad \text{H-N-R_2 } \]

where \( R_1 \) and \( R_2 \) are as defined above. Particularly suitable amine contain aliphatic N-substituents, including saturated, unsaturated, aromatic acyclic and polycyclic substituents containing more than 6 carbon atoms.

Illustrative of suitable primary amines are the alkyl amines such as hexyl, octyl, decyl, dodecyl, tetradecyl, octadecyl, eicosyl and hexacosyl amines. Although amines having substituent chains containing more than 26 carbon atoms may be used, the shorter chain amines are preferred for reasons of commercial availability. Primary alkenyl amines such as heptenyl, nonenyl, undecenyl, pentadecenyl and pentacosyl are also satisfactory. Examples of suitable primary cycloaliphatic amines are cyclohexyl amines, cyclooctyl amines, primary, polycyclic or polynuclear aliphatic amines, such as rosin amines, or the amine of abietic acid are also satisfactory. Monocyclic aromatic amines, such as aniline, as well as polycyclic or polynuclear aromatic amines such as diphenyl amine and alpha- and betanaphthylamines also have utility in the present invention. Benzylamine and beta-phenethylamine are illustrative of suitable aromatic-aliphatic amines, just as toluidine and xylidine are exemplary of suitable aliphatic-aromatic amines.

Secondary amines corresponding to all of these classes of amines are also utilized to advantage and include not only secondary amines having identical substituents such as diocytalamine, dioctenylamine, dicyclohexylamine, N,N-diphenylamine, dibenzylamine, and N,N-ditolylamine, but also secondary amines having different substituents from the same class, such as N,N-octahexadecylamine and N,N-phenylalphaphenylethylamine, as well as secondary amines whose substituents are selected from different classes such as N,N-octyphenylamine, monomethyl aniline, N,N-phenylcyclohexylamine. Among the numerous classes of amines suitable for the purposes of this invention, the commercial mixtures of high molecular weight amines derived according to conventional methods from naturally occurring substances, such as cocanut oil, palm oil, animal fats, rosin and the like, are distinctly preferred.

The various amines described above are representative of the class of amines having from one to two N-substituents, at least one of which contains at least six carbon atoms.

The reaction by which the compounds of this invention are prepared involves partial amidation of a dicarboxylic acid with a primary or secondary amine. This reaction is entirely conventional and is carried out according to known procedures and according to known conditions. Therefore, the reaction need only be described briefly.

In this connection, the dimerized acid and amine are admixed in equimolecular proportions. The reactants may be reacted directly with each other or in the form of a solution or dispersion containing the reactants. It is particularly preferred to dissolve the reactants in a mineral oil solvent and to carry out the reaction with the reactants in solution, since localized heating is avoided. Moreover, the product resulting from this procedure is in the form of a mineral oil concentrate containing a substantial proportion, e. g., from one per cent up to the limit of solubility, of the additive. The resulting concentrate may then be blended with the desired vehicle in the desired proportions. Solution of the additive in the ultimate carrier therefore is often greatly facilitated by this expedient.

While the amidation reaction discussed above normally takes place to some degree even at relatively low temperatures, it is desirable to employ heat of a degree at least equal to the boiling point of water, i. e., 212° F., in order to eliminate the water of reaction, and in order to force the reaction to completion. It is preferred that temperatures of not substantially in excess of 350° F. be employed, since decomposition of the product may result. A preferred procedure involves terminating the reaction when the temperature of the reaction mixture reaches a degree not substantially above about 250° F., and allowing the product to cool.

While heat is important in effecting the reaction for the reasons indicated above, it is to be noted that no extraneous source of heat may be necessary when primary amines are reacted. In such instances the heat of reaction is often sufficient of itself to provide a temperature of 250° F. or higher.

Normally, the reaction is complete after about 15 to 30 minutes, or after substantially all of the water of reaction has been removed.

The products of the above-described reaction are the acid amides of dimerized polyolefinic fatty acids. The reaction products normally vary in appearance from waxy solids or semi-solids to viscous, tacky liquids. The color of the products normally varies from straw-colored to dark.

The neutral salts of the acid amides may be conveniently prepared by reacting the acid amide with an alkali metal alcoholate. The resulting alkali metal salt may be used as such, or alternatively other metal salts may be prepared by metallation of the alkali metal salt of the acid amide with a salt of the desired metal. This procedure is described in greater detail in U. S. Patent 2,458,425. Illustrative of metals which provide desirable metallic salts according to this invention are: sodium, lithium, potassium, bariun, calcium, magnesium, strontium, lead, copper, iron, nickel, mercury, zinc, bismuth, aluminum, chromium, tin, manganese, silver and cadmium.

Examples I to V, following, are representative of the mode of preparation of the various compounds of this invention. It is understood that the examples are by way of illustration only and are not intended as limiting.

**EXAMPLE I**

The dimeric acid employed in this example was Emery's M-461-R dimer acid, manufactured by Emery Industries, Inc., Cincinnati, Ohio. M-461-R dimer acid is a commercial form of a dimeric polymer consisting essentially of dilinoleic acid (the dimer of 9,11-decadienoic acid):
The commercial dimer acid had the following physical properties:

**Physical state.** Straw-colored, viscous liquid

**Molecular weight (approx.).** 560

**Neutral equivalent.** 298-310

**Iodine value.** 80-95

**Dimer content (approx.).** percent... 85

**Trimer and higher (approx.).** do... 12

**Monomer (approx.).** do... 3

The compound of this example was prepared by mixing 56 parts by weight of the M-461-R dimer acid with 31.3 parts by weight of "Armeen S." The latter is a commercial mixture of long-chain, primary amines having a molecular weight of about 313. The mixture is composed primarily of octadecadienyl amine and octadecenyl amine and is manufactured by Armour & Company of Chicago, Ill.

The reaction mixture reached a temperature of above 250° F. without application of extraneous heat. After the reaction was complete, i.e., after about 20 minutes, the product was allowed to cool. The product obtained according to this example contained a major proportion of the acid amides of dillinoic acid and 18-carbon, primary, alkyl amine. This product was a waxy solid of amber color.

**EXAMPLE II**

To 56 parts by weight of Emery's M-461-R dimer acid were added 31.0 parts by weight of "Armeen T," a commercial mixture of octadecenyl amine, octadecyl amine and hexadecylamine (manufactured by Armour & Company, of Chicago, Ill.), acid mixture having a molecular weight of about 310. The reaction proceeded vigorously with the evolution of heat, the temperature of the mixture rising above 250° F. without the application of external heat. After about 20 minutes, the mixture was allowed to cool. The product obtained according to this example contained a major proportion of the acid amides of dillinoic acid and primary, alkyl and alkyl mono- amines having from 16 to 18 carbons in the substituent chain. The product was a solid, waxlike substance of amber color.

**EXAMPLE III**

Emery's M-461-R dimer acid in the proportion of 56 parts by weight was added to and stirred with ten parts by weight of cyclohexylamine. The reaction mixture reached a temperature of above 250° F. without application of extraneous heat. After the reaction was complete, i.e., after about 20 minutes, the product was allowed to cool. The product obtained was a mixture of the acid amides of cyclohexylamine and dillinoic acid. In appearance the product was a viscous, waxy, tacky, semisolid.

**EXAMPLE IV**

Dicyclohexylamine in the proportion of 18 parts by weight was added to 56 parts by weight of Emery's M-461-R dimer acid with stirring. This reaction required heating. After the reaction was complete, i.e., after a temperature of 250° F. had been reached, the mixture was allowed to cool. The product of this reaction was a dark, viscous, tacky liquid and contained predominantly a mixture of the acid amides of dillinoic acid and dicyclohexylamine.

**EXAMPLE V**

Fifty-six parts by weight of Emery's M-461-R dimer acid were stirred with 32 parts by weight of resin amine D, manufactured by Hercules Powder Company, of Wilmington, Delaware, and containing essentially the primary amine of abietic acid, and having a molecular weight of about 320. The reaction proceeded vigorously in an exothermic fashion. After the reaction was complete, i.e., after the temperature had reached about 250° F., the mixture was allowed to cool. An amber, viscous liquid comprising predominantly a mixture of the acid amides of the amine of abietic acid and dillinoic acid was obtained.

Acid amides of other dimerized polyolefinic fatty acids and other disclosed amines can be obtained in substantially identical fashion. The neutral salts of these acid amides can be obtained in the manner disclosed above.

The reaction products resulting from the above-described procedures, either alone in the form of a solution concentrate, may be incorporated in the desired vehicle. Where the vehicle is a mineral lubricating oil, e.g., a turbine oil, the reaction products are employed in a minor proportion, sufficient to confer rust and corrosion inhibiting properties upon the latter. Normally, from about 0.02 per cent to about 1.0 per cent of the additive by weight of the composition is sufficient for this purpose, although greater proportions may be employed, if desired. Examples of various mineral oils which are benefited by the compounds of this invention are gasoline, kerosene, diesel fuel, furnace oil, motor oils, lubricating greases, and turbine oils. The invention further includes mineral oil compositions, where the solvent component is not employed as a fuel or lubricant, but merely as a solvent vehicle.

Examples of this type of composition are light naphtha and like oil solvents containing the novel compounds of this invention.

The following example will serve to illustrate more clearly the preparation of the novel mineral oil compositions included in this invention as well as the desirable results obtained by their use.

**EXAMPLE VI**

To each of five samples of a highly refined, highly paraffinic, turbine oil having a gravity of between 30.5° to 32.5° API and a viscosity of about 150 Saybolt Universal seconds at 100° F. was added 0.25 per cent by weight of one of the products prepared in the foregoing Examples I to V. A sixth sample of the untreated turbine oil was utilized as a control or blank. Each of the six samples mentioned was then tested according to the provisions of ASTM corrosion test D-665-47 T, procedure A. Following this test, three of the oil samples were further subjected to the "Film Tenacity" test.

**ASTM corrosion test.**—This test is that specified in the ASTM: Standards of Petroleum Products and Lubricants, November 1948, and is designated as ASTM-D-665-47 T. In brief, procedure A of this test involves placing a 300 ml. sample of the oil in a 400 ml. beaker which is, in turn, immersed in a temperature bath maintained at a temperature of 140° F. The beaker is fitted with a cover provided with openings for a stainless steel, motor-driven stirrer and for insertion of a standard steel test bar having a diameter of 0.30 inch and a length of approximately 5.5 inches which has been carefully cleaned and polished according to a prescribed procedure just prior to the test. The stirrer is started and when the oil sample in the beaker reaches a temperature of 140° F., the test bar is lowered through the proper opening and is suspended from the beaker cover. After thirty minutes, 50 ml. of the oil are removed and re- placed with 30 ml. of distilled water. Stirring is then continued for 48 hours with the temperature maintained at 140° F. At the end of this period the steel bar is removed and examined for rust spots.

**Film tenacity test.**—This test is designed to evaluate corrosion resistance of the film of the oil composition as applied to steel surfaces. It is carried out immediately after the ASTM corrosion test described above. If the steel test bar used in the ASTM test shows no evidence of rusting, it is suspended in the mouth of a 300 ml. flask and is allowed to drain. The beaker containing the oil sample is removed from the constant temperature bath and is replaced with a clean beaker containing 300 ml. distilled water. With the stirrer operating, the temperature of the water in the beaker is allowed to reach 140° F.
When the test bar has drained for a period of thirty minutes it is inserted in the beaker as above. Stirring is continued for 24 hours, after which the test bar is removed and examined for rust spots.

It will be seen that this test is quite drastic, since throughout its operation the steel test bar is protected from the rust only by a thin residual film of the oil being tested. It not only evaluates the protection against rusting provided by the composition, but also indicates the tenacity with which a film of the composition adheres to the metal surface.

The results of the foregoing tests are presented in Table A below:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Base Stock</th>
<th>Additive</th>
<th>Percent by Weight</th>
<th>ASTM Corrosion Test</th>
<th>Film Tenacity Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Turbine Oil</td>
<td>Acids of Dimers of Linoleic Acid and &quot;Armanol&quot;*</td>
<td>0.05</td>
<td>No Rust...</td>
<td>No Rust.</td>
</tr>
<tr>
<td>2</td>
<td>...</td>
<td>Acids of Dimers of Linoleic Acid and &quot;Armanol&quot;*</td>
<td>0.05</td>
<td>...</td>
<td>Do.</td>
</tr>
<tr>
<td>3</td>
<td>...</td>
<td>Acids of Dimers of Linoleic Acid and &quot;Armanol&quot;*</td>
<td>0.05</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>...</td>
<td>Acids of Dimers of Linoleic Acid and &quot;Armanol&quot;*</td>
<td>0.05</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>5</td>
<td>...</td>
<td>Acids of Dimers of Linoleic Acid and &quot;Armanol&quot;*</td>
<td>0.05</td>
<td>...</td>
<td>No Rust.</td>
</tr>
<tr>
<td>6</td>
<td>...</td>
<td>None</td>
<td>0</td>
<td>Heavy Rust.</td>
<td>...</td>
</tr>
</tbody>
</table>

*Not tested.

Similar improvements are obtainable by the use of monoamides prepared from other of the disclosed primary and secondary amines and from other of the disclosed dimeric amines.

The results reported in Table A indicate that extremely small proportions of the compounds of this invention confer a high resistance to corrosion and an improved film tenacity on the oil composition.

The described novel compounds also can be employed in conjunction with gasoline, furnace oil, diesel fuel, slushing oil, motor oils and other oils. The use of the additives in lubricants is considered particularly advantageous, since the additives are considered to enhance the lubricating qualities of the carrier. As has been indicated, the described monoamides can be incorporated in mineral oil products, such as light naphtha, which are employed neither as a fuel nor as a lubricant. In such instances the compositions find use in the coating art, whereby a metallic article subject to rust or corrosion is brushed, dipped or sprayed with the composition comprising the solvent vehicle and the additive. Subsequent evaporation of the solvent leaves the adherent, corrosion-resistant coating of the additive on the article. The compounds of this invention also find utility as corrosion inhibiting additives for various paints, varnishes, automobile undercoatings and the like. In the use of the agents of this invention in various coating compositions, it may be desirable to employ the compounds in substantially greater concentrations than are normally utilized in fuels and lubricants.

It is to be understood that the improved mineral oil compositions of this invention can be additionally improved by incorporation therein of other known additives in order to confer other desirable properties such as increased resistance to oxidation, increased stability, etc., thereon. Thus, there can be added viscosity improvers, thickeners, bearing corrosion inhibitors, antioxidants, dyes, etc.

Numerous modifications of the invention within the scope of the foregoing description and the appended claims will suggest themselves to those skilled in the art.

What I claim is:

1. A monoamide of an amine having from 1 to 2 hydrocarbon N-substituents at least one of which contains at least 6 carbon atoms and a dimer of an unsaturated fatty acid containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule.

2. The compound of claim 1 where the unsaturated fatty acid contains 18 carbon atoms.

3. A monoamide of a primary aliphatic amine containing from 16 to 18 carbon atoms and a dimer of linoleic acid.

4. A monoamide of cyclohexylamine and a dimer of linoleic acid.

5. A monoamide of dicyclohexylamine and a dimer of linoleic acid.

6. A monoamide of a primary rosin amine and a dimer of linoleic acid.

7. A method of preparing a monoamide of a dimerized unsaturated fatty acid comprising reacting an amine having from 1 to 2 hydrocarbon N-substituents at least one of which contains at least 6 carbon atoms with substantially equimolecular proportions of a dimer of an unsaturated fatty acid containing from 6 to 22 carbon atoms and having from 2 to 3 ethylenic linkages per molecule.

8. The method of claim 7 where the dimer and the amine are reacted in a mineral oil solution.

9. A corrosion inhibiting concentrate for addition to mineral oil compositions comprising a mineral oil solvent and a substantial proportion of a monoamide of an amine having from 1 to 2 hydrocarbon N-substituents at least one of which contains at least 6 carbon atoms and a dimer of an unsaturated fatty acid having from 6 to 22 carbon atoms and containing from 2 to 3 ethylenic linkages per molecule.

10. A mineral oil composition comprising a major amount of a mineral oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of a monoamide of an amine having from 1 to 2 hydrocarbon N-substituents at least one of which contains at least 6 carbon atoms and a dimer of an unsaturated fatty acid having from 6 to 22 carbon atoms and containing from 2 to 3 ethylenic linkages per molecule.

11. The composition of claim 10 where the unsaturated fatty acid contains 18 carbon atoms.

12. The composition of claim 10 where the mineral oil is a lubricating oil.

13. The composition of claim 10 where the mineral oil is a turbine oil.

14. A mineral oil composition comprising a major amount of a turbine oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition of a monoamide of a primary aliphatic amine containing from 16 to 18 carbon atoms and a dimer of linoleic acid.
15. The composition of claim 14 where the monoamide is present in the proportion from about 0.02% to about 1.0% by weight of the composition.

16. A mineral oil composition comprising a major amount of a turbine oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of a monoamide of cyclohexylamine and a dimer of linoleic acid.

17. The composition of claim 16 where the monoamide is present in the proportion from about 0.02% to about 1.0% by weight of the composition.

18. A mineral oil composition comprising a major amount of a turbine oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of a monoamide of dicyclohexylamine and a dimer of linoleic acid.

19. The composition of claim 18 where the monoamide is present in the proportion from about 0.02% to about 1.0% by weight of the composition.

20. A mineral oil composition comprising a major amount of a turbine oil and a minor amount, sufficient to impart corrosion inhibiting properties to the composition, of a monoamide of a primary rosin amine and a dimer of linoleic acid.

21. The composition of claim 20 where the monoamide is present in the proportion from about 0.02% to about 1.0% by weight of the composition.

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