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3,427,245

LUBRICANT ADDITIVE COMPOSED OF A MIXTURE OF AMINE SALTS OF MONOAMIDES AND MONOAMIDES OF ALKENYL SUCCINIC ACIDS
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10 Claims

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ABSTRACT OF THE DISCLOSURE

Mixtures of aliphatic hydrocarbon substituted succinamic acid amine salts, wherein the amine is a secondary amine, are provided for use under extreme corrosion conditions, particularly phosphate lubricants.

This application is a continuation-in-part of application Ser. No. 423,316, filed Jan. 3, 1965, now abandoned.

This invention concerns novel rust inhibitors which provide rust protection in the presence of phosphate esters. More particularly, this invention concerns C-alkenyl substituted succinamic acid salts which provide rust protection in the presence of phosphate esters.

The widespread use of metals subject to corrosion, particularly ferrous metals which are subject to rusting, has encouraged efforts to find methods to prevent the corrosion. Corrosion can occur in a variety of environments. Rusting is a particular problem with ferrous metals when water is present. Rusting can be a problem with containers for corrosive fluids, with bearings or other parts of machinery which must operate in the presence of water, e.g., steam turbines, or with the moving parts of engines where water tends to form or collect.

The rusting problem is extremely severe with materials which promote or enhance rusting, such as phosphate esters which are employed as hydraulic fluids and extreme pressure agents, as well as for other uses. With phosphate esters, the problem of rust protection is further aggravated, because many of the common commercial rust inhibitors are relatively or totally ineffective.

Succinic acid, substituted succinic acids and derivatives have found use as corrosion inhibitors. Illustrative of United States patents disclosing alkenyl succinic acids or derivatives are U.S. Patents Nos. 2,124,628, 2,133,734, 2,279,688, 2,568,876, 2,604,451, 2,779,740 and 2,783,206. Many of the derivatives are concerned with amides or imides of polyalkylene polyamines or amide esters or alkanolamines.

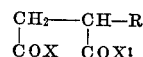
Pursuant to this invention, the partial amine salts of alkenyl succinamides are provided, wherein the alkenyl succinic acid from which the amide is derived is of from 14 to 25 carbon atoms and the amine from which the amide is derived is a secondary amine having two hydrocarbyl groups of from 1 to 10 carbon atoms and being of a total of from 2 to 20 carbon atoms, more usually of from 2 to 16 carbon atoms. (By hydrocarbyl is intended a monovalent organic radical composed solely of carbon and hydrogen, which may be aliphatic, alicyclic or aromatic or combinations thereof, e.g., aralkyl.) Usually, the hydrocarbyl groups will be free of aliphatic unsaturation, olefinic and acetylenic, particularly acetylenic.

The amine used for formation of the salt may be the same or different than the amine used for formation of the succinamide. The amine used for salt formation is also secondary, having hydrocarbyl substituents having a total of from 2 to 20 carbon atoms. The preferred sub-

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stituents for both amines (used in the formation of amide and salt) are lower alkyl of from 1 to 6 carbon atoms, and particularly aryl of from 6 to 10 carbon atoms.

The compounds of this invention have the following formula:



wherein R is an aliphatic hydrocarbon group, (free of acetylenic unsaturation) e.g., alkyl or alkenyl, of from 10 to 21 carbon atoms, one of X and X¹ is an N,N-dihydrocarbyl substituted amino radical and the other is from 5 to 60 mole percent of amine salt and the remainder hydroxyl.

The compositions of this invention are, therefore, mixtures of



wherein R is as defined previously, one of X² and X³ is N,N-dihydrocarbylamino, preferably hydrocarbyl is lower alkyl or aryl, having a total of from 2 to 20 carbon atoms and the other is hydroxyl, and



wherein R is as defined previously and one of X⁴ and X⁵ is N,N-dihydrocarbylamino, preferably lower alkyl or aryl, having a total of from 2 to 20 carbon atoms and the other is



wherein R¹ and R² are hydrocarbyl groups of from 1 to 10 carbon atoms, preferably lower alkyl and aryl, and may be the same or different.

The mole percent of composition (I) is 40 to 95, while that of II is correspondingly 5 to 60. More usually, the mole percent of (I) will be 65 to 95, with the corresponding amount of II being 5 to 35.

Generally, the aliphatic hydrocarbyl radical of the alkenylsuccinic acid will not be a single radical, but a mixture of various radicals within the carbon range indicated. For example, mixtures having relatively equal amount of radicals of from 15 to 21 carbon atoms or from 9 to 21 carbon atoms find use in this invention.

The alkenyl or alkyl group bonded to the succinyl radical is a normal straight chain olefinic radical or alkyl radical. That is, the alkenyl or alkyl radical is derived from an olefin having all of its carbons except for the terminal carbons bonded to only two other carbons, the terminal carbons being bonded to only one carbon. However, the succinyl radical need not be bonded to the 1 carbon of the alkenyl radical, although the 1 position will generally be the position for bonding.

The following is a list of succinamic acids which may be used for the acid-amino salt mixtures of this invention:

N,N-dimethyl n-eicosenylsuccinamic acid
N,N-diethyl n-tetradecenylsuccinamic acid
N,N-diethyl n-pentadecenylsuccinamic acid
N,N-diethyl n-octadecenylsuccinamic acid
N,N-diethyl n-eicosenylsuccinamic acid
N,N-dibutyl n-dodecenylsuccinamic acid
N,N-dibutyl n-tetradecenylsuccinamic acid
N,N-dibutyl n-hexadecenylsuccinamic acid
N,N-dihexyl n-tetradecenylsuccinamic acid
N,N-diphenyl n-dodecenylsuccinamic acid
N,N-diphenyl n-tetradecenylsuccinamic acid
N,N-diphenyl n-hexadecenylsuccinamic acid
N,N-diphenyl n-heptadecenylsuccinamic acid
N,N-diphenyl n-octadecenylsuccinamic acid
N,N-ditolyl n-hexadecenylsuccinamic acid
N,N-dibenzyl n-tetradecenylsuccinamic acid

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N,N-diphenyl n-hexadecenylsuccinamic acid
 N,N-diphenyl n-tetradecenylsuccinamic acid
 N-ethyl, N-propyl n-hexadecenylsuccinamic acid
 N-methyl, N-ethyl n-hexadecenylsuccinamic acid
 N-methyl, N-phenyl n-tetradecenylsuccinamic acid
 N-ethyl, N-phenyl n-octadecenylsuccinamic acid
 N-methyl, N-phenyl n-nonadecenylsuccinamic acid, etc.

The alkenyl succinic acids used in the formation of the succinamic acids are prepared by the reaction of an olefin, preferably an alpha-olefin, with maleic anhydride to form the alkenyl succinic anhydride. This product may then be hydrogenated to form the alkyl succinic anhydride. However, in most instances there would be little if any advantage in the alkyl over the alkenyl succinic anhydride and, to that extent, the hydrogenation step to the alkyl succinic anhydride is considered superfluous for the purposes of this invention. The methods of reacting an olefin with maleic anhydride are well known in the art and do not require exemplification here.

Illustrative of various alpha-olefins which find use are decene-1, undecene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, eicosene-1, heneicosene-1.

When preparing the compounds of this invention the desired alkenylsuccinic anhydride is reacted with a secondary amine having the formula



wherein R^3 and R^4 are hydrocarbyl groups of from 1 to 10 carbon atoms, more usually of from 2 to 8 carbon atoms. Preferably R^3 and R^4 are alkyl or carbocyclic aryl. The alkyl groups will generally be of from 2 to 6 carbon atoms, while the aryl groups will generally be of from 6 to 10 carbon atoms, more usually of from 6 to 8 carbon atoms. The preferred amines used for formation of the salts are the same as those used for preparation of the amide. Usually, the partial salt is obtained by using an excess of the amine when preparing the succinamic acid.

Illustrative of various amines are dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, dinonylamine, didecylamine, methylhexylamine, ethylbutylamine, methyldecylamine, diphenylamine, ditolyeamine, tert-butylphenylmethylamine, N-methylaniline, isopropylphenethylamine, benzylmethylamine, etc. While inert substituents may be present in the secondary amine, it is preferred that the nitrogen substituents be hydrocarbon.

The amines used may be a single amine or a mixture of amines.

The following examples are offered by way of illustration and not by way of limitation.

Example A

Into a reaction flask in a nitrogen atmosphere was introduced 352 g. (1.5 moles) of olefins, derived from cracking wax, in the range of from C_{10} to C_{20} , having an average molecular weight of 230, and 147 g. (1.5 moles) of maleic anhydride and the mixture heated for 10 hours at a temperature in the range of about 180–235° C. At the end of this time, the product was cooled and isolated yielding 355 g. Neutralization equivalent was 216 (Calc. 160) indicating about 70% reaction with the remaining portion being unreacted olefin.

Example B

Into a reaction flask in a nitrogen atmosphere was introduced 362 g. (1.5 moles) of olefins, derived from cracking wax, having from 15 to 20 carbon atoms (242 average molecular weight) and 147 g. of maleic anhydride (1.5 moles) and the mixture heated at a temperature of about 180–250° C. for a period of 3 hours. At the end of this time, 383 g. of a product was isolated. Neutralization equivalent 250 (Calc. 170) indicating about 70% reaction to form the alkenyl succinic anhydride.

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Example I

Into a reaction flask was introduced 33 g. of the product obtained in Example A and 7.3 g. (0.1 mole) 30 mole percent excess) of diethylamine and the mixture heated at 100° C. for 2 hours. At the end of this time, the reaction mixture was cooled and the product isolated. Neutralization equivalent 450.

Example II

Into a reaction flask was introduced 34 g. of the product of Example B and 7.3 g. of diethylamine (0.1 mole) (47 mole percent excess) and the mixture heated at 50° C. for 1 hour. At the end of this time, the reaction product was cooled and the product isolated. Neutralization equivalent, 343.

Example III

Into a reaction flask was introduced 9.2 g. (0.019 mole) of the product obtained in Example B and 4.68 g. (10% excess) of diphenyl amine and the mixture heated at 150° C. The reaction mixture was allowed to cool and the product isolated.

Example IV

Into a reaction flask was introduced 9.2 g. (0.019 mole) of the product obtained in Example B and 5.10 g. (20% excess) of diphenyl amine and the mixture heated at 150° C. The reaction mixture was allowed to cool and the product isolated.

The products of this invention were tested under a variety of severe conditions to demonstrate their excellence in inhibiting rust formation.

The first tests reported are the turbine oil test ASTM D 665–60 and the Emulsibility Test ASTM D 1401–56T, the latter demonstrates the ability of oil and water to separate from each other. Since it is essential that the oil and water separate at a reasonable rate in a turbine, the effect of any additives upon the separation is essential to a determination of their efficacy. The rust test uses both distilled and synthetic sea water on a standard carbon steel specimen. The following table indicates results obtained both as to emulsibility and rusting in distilled water as well as synthetic sea water. The sample used 0.1 weight percent of the succinamic acid in a turbine oil comprising 92% heavy and 8% light turbine oil base, o,o'-di-t-butyl-p-cresol antioxidant, 0.3 weight percent and poly(dimethyl-siloxane) defoamer, 0.005 weight percent.

TABLE I

Succinamic acid, example	Emulsibility		Rust observed	
	Vol., ml.	Time, min.	Distilled water	Synthetic sea water
I.....	3	24	No rust.....	No rust.
II.....	3	10	do.....	Do.
III.....	3	21	do.....	Do.
IV.....	3	18	do.....	Do.

The materials of this invention permit rapid separation between the oil and water, while providing excellent rust protection.

Using tricresyl phosphate in place of the turbine oil in the turbine oil rust test described above, the following results were obtained:

TABLE II

Succinamic acid	Wt. percent	Rust observed	
		Distilled water	Synthetic sea water
I.....	0	Heavy rust.....	Heavy rust.
II.....	1	No rust.....	Few specks.
III.....	4	do.....	No rust.
IV.....	1	do.....	Do.

Using 2 weight percent, the composition of Example I was tested in a grease rusting test (ASTM D 1743–60T).

The test is described as a method for determining the corrosion preventive properties of greases using grease-lubricated tapered roller bearings stored under wet conditions. This method shows correlation between laboratory results and service for grease lubricated aircraft wheel bearings. The grease used was a 15% lithium stearate-bis(2-ethylhexyl) sebacate grease. At the end of the test, no rust was observed, giving the grease the high rating of 1.

Finally, the exemplary composition of Example IV, the partial salt of N,N-diphenylalkenylsuccinamic acid was tested with a variety of commercial phosphate ester hydraulic fluids in the Humidity Cabinet Test (ASTM D 1748). The test employs 100% relative humidity and 120° F. temperature. The following table indicates the results:

TABLE III

Phosphate ester hydraulic fluid	Rust observed in 24 hours	
	Without additive, percent	With 1 wt. percent of Ex. IV
Skydrol.....	100	Trace
Skydrol 500A.....	100	Trace
Skydrol 7000.....	100	Trace
Pydraul AC.....	100	Trace
Pydraul F-9.....	100	Trace

Skydrols=Nonflammable aviation hydraulic fluids—500A is based on dibutyl phenyl phosphate, 7000 is based on octyl diphenyl phosphate. Pydrauls=Nonflammable industrial hydraulic fluids, based on tricresyl phosphate and chlorinated biphenyl.

The above results demonstrate the extraordinary capability of the composition of this invention in protecting ferrous metals from rusting. Not only are the compositions of this invention effective with hydrocarbon materials and fatty acid-salt greases, but they are effective in the presence of the corrosion promoting phosphate esters. Moreover, while providing corrosion protection in the turbine oil test, they are also capable of passing the emulsibility test, essential to their usefulness in a turbine.

The compositions of this invention may be used with a wide variety of lubricating media, including oils of lubricating viscosity, as well as greases. Various base oils which find use include such oils as petroleum lubricating oil: naphthenic base, paraffin base and mixed base; synthetic oils; alkylene polymers and alkylene oxide polymer; esters of organic and inorganic acids; aryl hydrocarbons and ethers; organic silicon compounds, etc.

Various grease thickeners include alkali metal and alkaline earth metal carboxylates, such as lithium hydroxy stearate, complex calcium acetate thickeners, and the sodium salt of tallow acids.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

I claim:

1. A composition of matter useful under extreme corrosion conditions resulting from the presence of phosphate containing lubricants consisting of a mixture of



wherein R is a straight chain aliphatic hydrocarbon group of from 10 to 21 carbon atoms, one of X² and X³ is N,N-dihydrocarbylamino having from 2 to 20 carbon atoms, and the other is hydroxyl, and



wherein R is as defined previously, one of X⁴ and X⁵ is N,N-dihydrocarbylamino having a total of from 2 to 20 carbon atoms and the other is



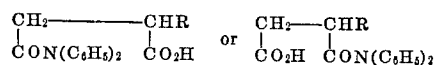
wherein R¹ and R² are hydrocarbyl groups of from 1 to 10 carbon atoms and, wherein the mole percent of (I) is in the range of 40 to 95, while the corresponding mole percent of (II) is in the range of 5 to 60.

2. A composition according to claim 1, wherein said N,N-dihydrocarbylamino is diarylamino, wherein said aryl group is of from 6 to 10 carbon atoms.

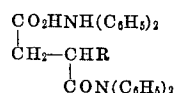
3. A composition according to claim 1, wherein said N,N-dihydrocarbylamino is di(lower alkyl) amino.

4. A composition according to claim 1, wherein R is a mixture of alkenyl groups of from 9 to 21 carbon atoms.

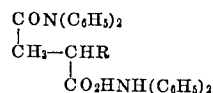
5. A composition of matter having from 40 to 95 mole percent of



and correspondingly from 5 to 60 mole percent of



or



wherein R is a straight chain alkenyl group of from 10 to 21 carbon atoms.

6. In a lubricating oil or grease composition, in an amount which is effective for inhibiting corrosion, a composition according to claim 5.

7. A method of protecting a surface subject to corrosion which comprises applying to said surface an effective amount to inhibit the corrosion of a composition according to claim 1.

8. In a lubricating oil or grease composition, in an amount which is effective for inhibiting corrosion, a composition according to claim 1.

9. In a turbine oil or phosphate lubricating composition, in an amount which is effective for inhibiting corrosion, a composition according to claim 1.

10. A composition according to claim 1, wherein R is terminally attached to the CH of the succinamic acid.

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