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(54) Compounds containing amide linkages from mono- and polycarboxylic acids in the same molecule and lubricants and fuels containing same.

(57) Lubricant and fuel additives having excellent dispersant properties have amide linkages, in the same molecule, derived from mono- and polycarboxylic acids. The additives are produced by reacting (1) at least one fatty monocarboxylic acid, (2) at least one alkenyl- or alkylsuccinic acid and anhydride and (3) at least one polyamine.

EP 0 186 473 A2

COMPOUNDS CONTAINING AMIDE LINKAGES FROM MONO- AND POLYCARBOXYLIC ACIDS IN THE SAME MOLECULE AND LUBRICANTS AND FUELS CONTAINING SAME

The invention relates to dispersant additives and to fuel and lubricant compositions containing them. In particular, it relates to certain amides made from polyamines, monocarboxylic acid and polycarboxylic acid.

It is known that in the normal use of organic industrial fluids, such as lubricating oils, transmission fluids, bearing lubricants, power transmitting fluids and the like, oxidizing conditions are encountered which may result in the formation of sludge, lacquers, corrosive acids and the like. These products are undesirable in that they produce oxidation residues or heavy contaminants which may cause normal breakdown of the fluid, leading eventually to severe damage to the parts of the equipment being lubricated.

In the lubrication of modern engines, oil compositions must be able to prevent acids, sludge and other solid contaminants from remaining near the moving metal parts. Poor piston travel and excessive engine bearing corrosion may result unless the oil can prevent sludge and oxidation products from depositing in the engine. Bearing corrosion is another serious problem in gasoline engines which operate at an oil temperature of about 149°C (300°F) or higher.

The most desirable way of decreasing the effect of these problems is to add to the base organic fluid a detergent or dispersant additive capable of dispersing the solid particles to prevent them from interfering with the normal operation of the equipment, thereby leaving the metal surfaces relatively clean. Today, with modern equipment operating under increasingly strenuous conditions, it is desirable to develop new detergents which have improved dispersant properties, which are soluble in the fluid medium to which they are added, and which are themselves stable therein.

U.S. Patent 3,714,045 discloses lubricant compositions containing lubricants and a polyimide produced by reacting (1) a heteropolymer produced by reacting an olefin with maleic anhydride in the presence of a free-radical initiator with (2) a primary arylamine.

U.S. 3,936,480 discloses the reaction of a polyalkylenesuccinic acid anhydride with diphenylolpropane of the formula I and tetraethylenepentamine, pyridine or triethylenetetramine. It should be noted, however, that in all cases wherein diphenolpropane is reacted, a catalyst is used. This is an absolute necessity when a phenolic OH is present, because there will be no reaction with the anhydride without it.

U.S. 3,868,330 discloses a lubricant or fuel composition containing an additive amount of at least one oil-soluble high molecular weight compound made by chlorinating

(1) a mixture of a C_{50} monocarboxylic acid and a low molecular weight polycarboxylic acid, e.g., succinic acid; or

(2) a mixture of a C_{50} ethyleneically unsaturated aliphatic hydrocarbon, a low molecular weight monocarboxcylic acid and a low molecular weight polycarboxylic acid.

This invention provides a reaction product prepared by reacting (1) at least one fatty monocarboxylic acid containing 10 to 20 carbon atoms, (2) at least one alkenyl- or alkylsuccinic acid or anhydride, where the alkenyl group is derived from a mixture of C_{12} to C_{24}, preferably C_{14} to C_{24}, olefins and (3) at least one polyamine of the formula

$RNH[R^1NH]_x$--H

wherein R is a hydrocarbyl group containing 1 to 5 carbon atoms, R^1 is a C_1 to C_5 alkylene group and x is 1 to 9.

This invention also provides a process for making a dispersant for fuel and lubricating compositions comprising reacting (1) at least one fatty monocarboxylic acid containing 10 to 20 carbon atoms, (2) at least one alkenyl- or alkylsuccinic acid or acid anhydride where the alkenyl or alkyl group is derived from a mixture of C_{12} to C_{24} olefins and (3) at least one polyamine of the formula

$RNH[R^1NH]_x$--H

wherein R and R^1 have the definitions given above.

The present invention further provides a lubricant or liquid fuel comprising a major proportion of a lubricant or liquid fuel and a dispersant amount of a product obtained by the process described hereinabove.

The preferred method of preparing the reaction products of this invention involves reacting one of the two types of acids with the amine at from about 100°C to about 175°C, preferably about 150°C to about 175°C, then reacting this product with the other acid at the same temperature.

The two types of acids will be used in such amounts that one type will supply from about 30% to about 90% by weight of the required amount and the other type will supply the complementary amount. The quantity of polyamine will be chosen such that the acids react therewith to form amide or imide groups with at least 40% by weight of the available amino groups. Preferably from about 30% to about 60% of the amino groups are left unreacted, but an effective dispersant is obtained when 60% of the amino groups is reacted with the acid mixture.

Another method that can be used to form the product involves reacting the amine with a mixture of the acids. The same temperature mentioned for the preferred method may be used for both acid-amine reactions. Further, the final product is made by using the same relative proportions of acid mentioned above, and the percentage of reacted amino groups in a given product will be the same.

The useful fatty monocarboxylic acids have the formula

R - COOH

where R is a hydrocarbyl group containing 10 to 20 carbon atoms. Among the saturated members covered by the formula are capric, lauric, myristic, palmitic, stearic and arachidic and tall oil fatty acids. The unsaturated members include oleic, linoleic, linolenic, eleostearic and ricinoleic acids.

The preferred polycarboxylic acids and anhydrides contemplated have the formula II or III where R is an alkenyl or alkyl group derived from a mixture of C_{14} to C_{24} monomers. Polyamines include triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, etc. to nonaethylenedecamine, and the methylene, propylene, butylene and amylene counterparts.

The additive compositions of the present invention impart valuable properties, as hereinbefore indicated, to liquid hydrocarbon combustion fuels, including the distillate fuels, i.e., gasolines and fuel oils. The fuel oils that may be improved in accordance with the present invention are hydrocarbon fractions having an initial boiling point of at least about 38°C (100°F) and an end-boiling point no higher than about 399° (750°F), and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It is to be understood, however, that this term is not restricted to straight run distillate fractions. The distillate fuel oils can be straight run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well-known commercial methods, such as, acid or caustic treatment, hydrogenation, solvent refining, clay treatment etc.

The distillate fuel oils are characterized by their relatively low viscosities, pour points, and the like. The principal property which characterizes the contemplated hydrocarbons, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 38°C (100°F) and about 399°C (750°F). Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Contemplated among the fuel oils are Nos. 1, 2 and 3 fuel oils used for heating and as diesel fuel oils, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications as set forth in A.S.T.M. Specifications D396-48T. Specifications for diesel fuels are defined in A.S.T.M. Specification D975-48T. Typical jet fuels are defined in Military Specification MIL-F-5624B.

The gasolines that are improved by the additive compositions for this invention are mixtures of hydrocarbons having an initial boiling point falling between about 24°C (75°F) and about 57°C (135°F) and an end-boiling point falling between about 121°C (250°F) and about 232°C (450°F). As is well known in the art, motor gasoline can be straight run gasoline or, as is more usual, it can be a blend of two or more cuts of materials including straight run stock, catalytic or thermal reformate, cracked stock, alkylated natural gasoline, and aromatic hydrocarbons. The concentration of additive in the fuel will range from bout 0.00001% to about 0.1% by weight of the composition.

The additive is effective in lubricant compositions for the purposes disclosed in ranges from about 0.1% to about 10.0% by weight of the total lubricant composition. Preferred is from about 1.0% to 5.0%. In general, the additives of this invention may also be used in combination with other additive systems in conventional amounts for their known purpose. The use of additive concentrations of borated alcohols in premium quality automotive and industrial lubricants further improves upon such fluids' fuel economy characteristics. The non-metallic compositions described herein are useful at said moderate concentrations and do not contain any potentially undesirable phosphorus, corrosive sulfur or metallic salts.

The lubricants contemplated for use herein include both mineral oil and synthetic hydrocarbon or hydrocarboxy oils of lubricating viscosity, mixtures of mineral oils and such synthetic oils, and greases prepared therefrom. The synthetic hydrocarbon oils include long chain alkanes such as cetanes, and olefin polymers such as trimers and tetramers of octene and decene. Such synthetic hydrocarbon oils can be mixed with other synthetic oils, including (1) ester oils such as pentaerythritol esters of monocarboxylic acids having 2 to 20 carbon atoms, (2) polyglycol ethers, and (3) polyacetals. Especially useful among the synthetic esters are those made from polycarboxylic acids and monohydric alclohols. More preferred are the ester fluids made from pentaerythritol, and an aliphatic monocarboxylic acid containing from 1 to 20 carbon atoms, or mixtures of such acids.

The following example is offered as a specific illustration of the invention.

EXAMPLE

A mixture of 189g (1.0 mole) of tetraethylenepentamine and 712.5g (2.5 moles) of tall oil fatty acids was heated to about 175°C and was stirred over a three hour period, evolving 45.0 g (2.5 moles) of water. A typical tall oil fatty acid contains about 45-50% oleic acid, 45-50% linoleic acid and 1-6% rosin acids. Subsequently, 106 grams (0.25 mole) of mixed C_{11} to C_{24} alkenylsuccinic anhydride derived from ethylene polymerization were added and the mixture was stirred for one hour at 175°C under reduced pressure to aid in the removal of water. The final product was obtained by filtration.

The deposit-forming tendencies of a fuel were determined in an 8-hour engine test. This accelerated test, when run on fuels that contain no detergents, produces an amount of deposit equivalent to the amount observed in 4,000 miles of operation in field tests on taxicab fleets. In accomplishing the test, a Ford 4.9 liter (300 C.I.D.) engine was equipped with notched rings to increase the amount of blowby and with a glass throttle body section. The engine was operated for 8 hours, using the fuel under test, at alternate idling and running cycles. In the idle cycle the engine was run for 5 minutes at idling speed of 400 rpm with no load. Then for 1 minute the engine was run at a speed of 2,500 rpm under a load of 30 BPH and a manifold pressure of 31.7 kPa (9.4 in. of mercury). During the running cycle the blowby and part of the exhaust were released into the carburetor air intake during the idling cycle. After 8 hours of operation at alternate run and idle, the carburetor was examined and rated for amount of deposit in the throttle throat. The fuel used was a gasoline comprising 40% catalytically cracked component, 40% catalytically reformed component and 20% alkylate, the overall mixture having a boiling range of about 35-210°C. The results are shown in the following table.

TABLE

Ford 4.9 Liter (300 C.I.D.) Carburetor Cleanliness Test

Composition	Conc. gm/1000 liters (Lbs/1000 Bbls.)	% Reduction In Deposits
Base Fuel	0 0	0
Base Fuel Plus Example 1 Product	7.1 (2.5)	60
Base Fuel Plus Example 1 Product	14.3 (5.0)	85

Claims

1. A product formed by reacting (1) at least one fatty monocarboxylic acid containing 10 to 20 carbon atoms, (2) at least one alkenyl- or alkylsuccinic acid or acid anhydride thereof, where the alkenyl or alkyl group is derived from a mixture of C_{12} to C_{24} olefins and (3) at least one polyamine of the formula

$RNH[R^1NH]_x$--H

wherein R is a hydrocarbyl group containing 1 to 5 carbon atoms, R^1 is a C_1 to C_5 alkylene group and x is 1 to 9.

2. The product of claim 1 wherein the fatty monocarboxylic acid is selected from capric, lauric, myristic, palmitic, stearic, arachidic, oleic, linoleic, linolenic, eleostearic, ricinoleic acids and mixtures thereof.

3. The product of any one of the preceding claims wherein the polyamine is selected from triethylenetetramine, tetraethylenepentamine, pentaethylenedexamine, nonethylenedecamine and the methylene, propylene, butylene and amylene counterparts thereof.

4. The product of any one of the preceding claims wherein the alkenyl- or alkylsuccinic acid or anhydride has the formula II or III where R is an alkenyl or alkyl group derived from a mixture of C_{16} to C_{24} monomers.

5. The product of any one of the preceding claims wherein the fatty monocarboxylic acid comprises between about 30 and about 90 percent by weight of the total amount of monocarboxylic and alkenyl-, or alkylsuccinic acids or acid anhydride reacted.

6. The product of any one of the preceding claims wherein the quantity of polyamine selected is one wherein at least 40% by weight of the available amino groups therein are reacted with the acids.

7. The product of any one of the preceding claims wherein the reaction is conducted by reacting one of acids (1) and (2) with amine (3) at a temperature of from 100° to 175°C and then reacting this product with the other acid at the same temperature.

8. The product of any one of the preceding claims wherein the reaction is conducted by reacting amine (3) with a mixture of acids (1) and (2) at a temperature of from 100°C to 175°C.

9. A process for making a dispersant for fuel and lubricating compositions comprising reacting (1) at least one fatty monocarboxylic acid containing 10 to 20 carbon atoms, (2) at least one alkenyl- or alkylsuccinic acid or acid anhydride, where the alkenyl or alkyl group is derived from a mixture of C_{12} to C_{24} olefins and (3) at least one polyamine of the formula

$RNH[R^1NH]_x$--H

wherein R is a hydrocarbyl group containing 1 to 5 carbon atoms, R^1 is a C_1 to C_5 alkylene group and x is 1 to 9.

10. The process of claim 9 wherein the fatty monocarboxylic acid is selected from the group consisting of copric, lauric, myristic, palmitic, stearic, arachidic, oleic, linoleic, linolenic, eleostearic, ricinoleic acids and mixtures thereof.

11. The process of any one of claims 9 & 10 wherein the polyamine is selected from the group consisting of triethylenetetramine, tetraethylenepentamine, pentaethylenedexamine, nonethylenedecamine and the methylene, propylene, butylene and amylene counterparts thereof.

12. The process of any one of claims 9, 10 and 100 wherein the alkenyl- or alkylsuccinic acid or anhydride has the formula II or III wherein R is an alkenyl or alkyl group derived from a mixture of C_{16} to C_{24} monomers.

13. The process of any one of claims 9-12 wherein the fatty monocarboxylic acid comprises between about 30 and about 90 percent by weight of the total amount of monocarboxylic and alkenyl-, or alkylsuccinic acids or acid anhydride reacted.

14. The process of any one of claims 9-13 wherein at least 40% by weight of the polyamine available amino groups therein are reacted with the acids.

15. The process of any one of claims 9-14 wherein the reaction is conducted by reacting one of acids (1) and (2) with amine (3) at a temperature of from 100° to 175°C and then reacting this product with the other acid at the same temperature.

16. The process of any one of claims 9-15 wherein the reaction is conducted by reacting amine (3) with a mixture of acids (1) and (2) at a temperature of from 100° to 175°C.

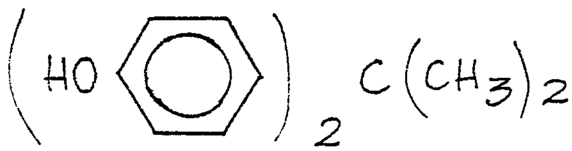
17. A fuel conposition comprising a major proportion of a

liquid fuel and a dispersant amount of the product of any one of claims 1-8.

18. The fuel composition of claim 17 wherein the dispersant constitutes 0.00001% to 0.1% by weight of the composition.

19. A lubricant composition comprising a major proportion of a liquid lubricant and a dispersant amount of the product of any one of claims 1-8.

20. The lubricant composition of claim 19 wherein the dispersant constitutes 1.0% to 5.0% by weight of the composition.



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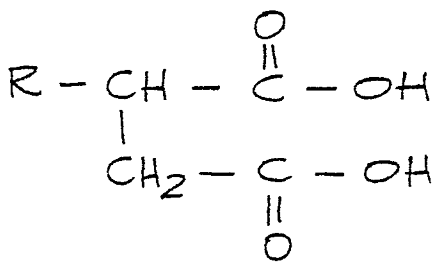

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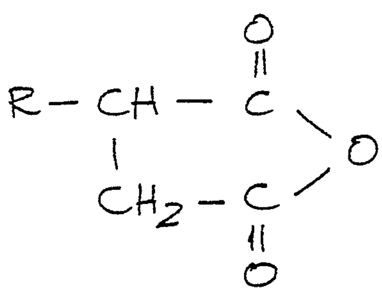

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