POLYESTER QUATERNARY AMMONIUM SALTS

Field of the Invention

[0001] The invention relates to polyester amide quaternary ammonium salts, ~~including amine, amide, and ester salts,~~ processes for making them, and their use as additives, including their use in fuels, such as diesel fuel and fuel oils. The invention particularly relates to the use of polyester amide quaternary ammonium salts as detergents in fuels and the methods of making them.

Background of the Invention

[0002] Hydrocarbon fuels generally contain numerous deposit-forming substances. When used in internal combustion engines (ICEs), deposits tend to form on and around constricted areas of the engine which are in contact with the fuel. In automobile engines deposits can build up on engine intake valves leading to progressive restriction of the gaseous fuel mixture flow into the combustion chamber and to valve sticking. There are two general types of inlet valve deposits, heavy deposits and thin deposits. These different types of deposits affect the performance of the fuel and the engine in slightly different ways. Heavy deposits are carbonaceous and oily in appearance. They cause flow restriction past the valves, which in turn reduces the maximum power of the engine, decreasing fuel economy and increasing emissions. Thin deposits tend to cause problems on starting the engine and increasing emissions.

[0003] As engines become more sensitive to deposits, it has become common practice to incorporate a detergent in the fuel composition for the purposes of inhibiting the formation, and facilitating the removal, of engine deposits, thereby improving engine performance and emissions.

[0004] It is known to use certain polyisobutylsuccinimide-derived quaternized PIB/amine and/or amide dispersants/detergents as additives in fuel compositions. Polyisobutylsuccinimides may also be described as polyisobutylene succinimides. These quaternized dispersants/detergents are derived from traditional PIB/amine and/or amide fuel additive compounds that have pendant tertiary amine sites which can be alkylated, i.e. quaternized, by a quaternizing

agent, such as propylene oxide. Examples of these additives are disclosed in U.S. patent application US 2008/0307698.

[0005] However there is a need for additives that provide the benefits described above while also exhibiting improved viscosity profiles and material handling properties. Such improvements would allow for the use of less diluent materials in the concentrates and additive packages generally used in the commercial products that contain these types of fuel additives, and so in the final fuels as well. Less diluent would be required if the viscosity profiles and material handling properties allowed for additive-containing compositions to be transferred and handled (i.e. pumped, poured, mixed, etc) without having to heat the material more than typical and/or without the need of specialized high viscosity equipment. Improved viscosity profiles and material handling properties would allow for reduced use of diluents, saving cost, reducing waste and so and improving the environmental impact of the materials. This would also allow the use of more concentrated additive packages and intermediate compositions, which can be transported more efficiently, again reducing costs and environmental impact.

Summary of the Invention

[0006] The present invention deals with a new class of detergents which offer significant improvements over traditional PIB/amine detergents, including polyisobutylsuccinimide-derived quaternized detergents. A new class of polyester amide quaternized salts have now been discovered. These polyester amide quaternized salts have polyester-based hydrocarbyl groups and provide improved viscosity profiles and material handling properties compared to polyisobutylsuccinimide-derived quaternized detergents and related materials. The polyester amide quaternized salts of the invention provide equivalent detergency and thermal stability performance as other quaternized detergents but also provide the improved viscosity profiles and material handling properties described above.

[0007] The present invention provides a composition ~~containing~~ comprising a quaternized polyester amide salt ~~derived from~~ which comprises the reaction product of: a polyester amide~~that~~ containsing a tertiary amino group; and a

quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate. ~~suitable for converting the tertiary amino group to a quaternary nitrogen. The quaternizing agent may be a dialkyl sulfate, a benzyl halide, a hydrocarbyl substituted carbonate, a hydrocarbyl epoxide, or some combination thereof.~~ Any of the quaternizing agents described herein, ~~particularly the hydrocarbyl epoxide,~~ may be used in combination with an acid, for example acetic acid.

[0008] The invention provides for quaternized polyester amide salts where the polyester amide used in their preparation is itself the reaction product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having a~~n oxygen or~~ nitrogen atom capable of condensing with said acid and further having a tertiary amino group. ~~The invention further provides for the polyester reactant to be a polyester amide containing a tertiary amino group.~~

[0009] The invention further provides for fuel compositions that include the quaternized polyester amide salts described herein and a fuel which is liquid at room temperature. Additional fuel additives may also be present.

[0010] The invention provides for methods of fueling an internal combustion engine comprising the steps of supplying to the engine a fuel which is liquid at room temperature and a composition comprising one or more of the quaternized polyester amide salts described herein.

[0011] The invention also provides for a process of making a quaternary ammonium salt detergent comprising the steps of reacting (a) a polyester amide containing a tertiary amino group; and (b) a quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate. ~~suitable for converting the tertiary amino group to a quaternary nitrogen. The quaternizing agent may be selected from the group consisting of dialkyl sulfates, benzyl halides, hydrocarbyl substituted carbonates; hydrocarbyl epoxides in combination with an acid or mixtures thereof.~~ The described process results in the quaternized dispersants described herein.

Detailed Description of the Invention

[0012] Various preferred features and embodiments will be described below by way of non-limiting illustration.

The Polyester Quaternary Ammonium Salt Detergent

[0013] The polyester quaternary salts detergents of the invention include quaternized polyester amine, amide, and ester salts. The additives may also be described as quaternary polyester salts. The additives of the invention may be

What is claimed is:

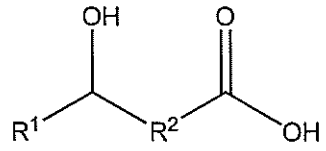
1. A composition comprising a quaternized polyester amide salt which comprises the reaction product of:

a. a polyester amide containing a tertiary amino group; and

b. quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate.~~suitable for converting the tertiary amino group to a quaternary nitrogen.~~

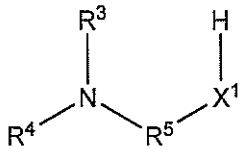
2. The composition of claim 1 wherein the polyester amide comprises the reaction product of a fatty carboxylic acid containing at least one hydroxyl group and a compound having a~~n oxygen or~~ nitrogen atom capable of condensing with said acid wherein said compound contains a tertiary amino group.

3. The composition of claim 2 wherein the fatty carboxylic acid is represented by the formula:



where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms; and

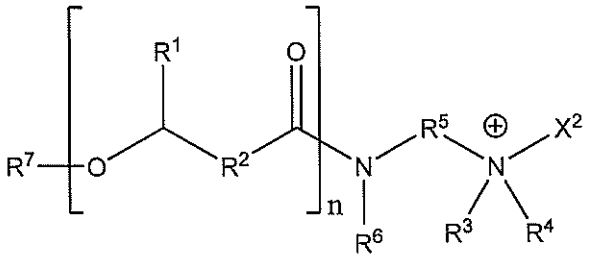
wherein the compound having a~~n oxygen or~~ nitrogen atom capable of condensing with said acid and further having a tertiary amino group is represented by the formula:



where R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene group containing from 1 to 20 carbon atoms; and X^1 is ~~O or~~ NR^6 where R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms;

~~4. The composition of claim 1 wherein the quaternized polyester salt comprises a quaternized polyester amide salt wherein the polyester containing a tertiary amino group used to prepare said quaternized polyester salt comprises a polyester amide containing a tertiary amino group.~~

~~5~~4. The composition of claim 1 wherein the quaternized polyester amide salt comprises a cation represented by the following formula:



where R^1 is a hydrogen or a hydrocarbyl group containing from 1 to 20 carbon atoms and R^2 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^3 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^4 is a hydrocarbyl group containing from 1 to 10 carbon atoms; R^5 is a hydrocarbylene group containing from 1 to 20 carbon atoms; R^6 is a hydrogen or a hydrocarbyl group containing from 1 to 10 carbon atoms; n is a number from 1 to 10; R^7 is hydrogen, a hydrocarbonyl group containing from 1 to 22 carbon atoms, or a hydrocarbyl group containing from 1 to 22 carbon atoms; and X^2 is a group derived from the quaternizing agent.

~~6~~5. The composition of claim 2 wherein the compound having a~~n oxygen or~~ nitrogen atom capable of condensing with said acid and further having a tertiary amino group comprises N,N-diethylethylenediamine, N,N-dimethylethylenediamine, N,N-dibutylethylenediamine, N,N-dimethyl-1,3-

diaminopropane, N,N-diethyl-1,3-diaminopropane, ~~N,N-dimethylaminoethanol, N,N-diethylaminoethanol,~~ or combinations thereof.

~~7~~6. The composition of claim 2 wherein the fatty carboxylic acid containing at least one hydroxyl group comprises: 12-hydroxystearic acid; ricinoleic acid; 12-hydroxy dodecanoic acid; 5-hydroxy dodecanoic acid; 5-hydroxy decanoic acid; 4-hydroxy decanoic acid; 10-hydroxy undecanoic acid; or combinations thereof.

~~8. The composition of claim 1 wherein the quaternizing agent comprises ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or combinations thereof wherein the quaternizing agent is used in combination with an acid.~~

~~9~~7. The composition of any one of claims 1 to 6, further comprising a metal deactivator, a ~~detergent~~ composition other than those of claim 1, a dispersant, a viscosity modifier, a friction modifier, a dispersant viscosity modifier, an extreme pressure agent, an antiwear agent, an antioxidant, a corrosion inhibitor, a foam inhibitor, a demulsifier, a pour point depressant, a seal swelling agent, a wax control polymer, a scale inhibitor, a gas-hydrate inhibitor, or combinations thereof.

~~10~~8. The composition of any one of claims 1 to 7, further comprising an overbased metal containing detergent, a zinc dialkyldithiophosphate, or combinations thereof.

~~11~~9. The composition of any one of claims 1 to 8, further comprising a fuel which is liquid at room temperature.

~~12~~10. The method of fueling an internal combustion engine comprising:

A. supplying to said engine:

i. a fuel which is liquid at room temperature; and

ii. a composition comprising a quaternized polyester amide salt which comprises the reaction product of: (a) a polyester amide containing a tertiary amino group; and (b) quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate.~~suitable for converting the tertiary amino group to a quaternary nitrogen.~~

~~13~~11. A process of making a quaternary ammonium polyester amide salt detergent comprising:

I. reacting (a) a polyester amide containing a tertiary amino group; and (b) quaternizing agent selected from ethylene oxide, propylene oxide, butylene oxide, styrene oxide, or a combination thereof used in combination with an acid; dimethyl oxalate, methyl 2-nitrobenzoate, and methyl salicylate;~~suitable for converting the tertiary amino group to a quaternary nitrogen;~~

thereby obtaining the quaternized dispersant.

~~14~~12. The process of claim ~~14~~ 11 wherein the polyester amide containing a tertiary amino group is prepared by a process comprising:

I. reacting (a)(i) a fatty carboxylic acid containing at least one hydroxyl group and (a)(ii) a compound having a~~n oxygen or~~ nitrogen atom capable of condensing with said acid and further having a tertiary amino group;

thereby obtaining the polyester amide containing a tertiary amino group.