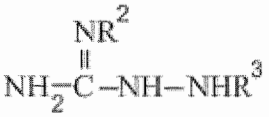
example, because of the need for additional friction modifiers and/or corrosion inhibitors in the low sulfur fuels.

[0005] Conventional quaternary ammonium compounds have been found effective in cleaning up certain fuels but are not effective in other fuels. In addition, such compounds have non-covalently bound anions that may lead to other problems such as deposit formation in the fuel from the anionic part of the compound.

[0006] Certain quaternary ammonium internal salts have been found to be effective where conventional quaternary ammonium salts lack the performance. However quaternary ammonium internal salts may be ineffective in certain petroleum fuels. Accordingly, there is a need for fuel additives, additive concentrates and fuel compositions that provide improved engine performance in a variety of fuels and engines.

[0007] In accordance with the disclosure, exemplary embodiments provide a fuel additive concentrate, a method for cleaning fuel injectors, a method for restoring power to a diesel fuel injected engine, a fuel composition, and a method of operating a fuel injected diesel engine. The additive concentrate includes (a) a hydrocarbyl substituted quaternary ammonium internal salt; and (b) a hydrocarbyl substituted dicarboxylic anhydride derivative selected from a diamide, acid/amide, acid/ester, diacid, amide/ester, diester, and imide. The hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500. A weight ratio of (a) to (b) in the additive concentrate ranges from about 1:20 to about 2:1. The additive concentrate is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula



wherein R^2 is selected from hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^3 is selected from hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

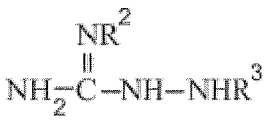
[0007a] In one aspect, there is provided an additive concentrate for a fuel for use in an injected fuel engine comprising

(a) a hydrocarbyl substituted quaternary ammonium internal salt comprising a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C2-C8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is free of non-covalently bonded anion species; and

(b) a hydrocarbyl substituted dicarboxylic anhydride derivative selected from the group

consisting of a diamide, acid/amide, acid/ester, diacid, amide/ester, diester, and imide, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500,

wherein a weight ratio of (a) to (b) in the additive concentrate ranges from about 1:20 to about 2:1, and wherein the additive concentrate is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula



wherein R^2 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^3 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

[0007b] In another aspect, there is provided a diesel fuel composition comprising a major amount of a low sulfur diesel fuel and a minor amount of the additive concentrate as defined above.

[0007c] In another aspect, there is provided a method of cleaning up internal components of a fuel injector for a diesel engine comprising operating a fuel injected diesel engine on a fuel composition as defined above.

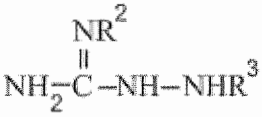
[0007d] In another aspect, there is provided a method of restoring power to a diesel fuel injected engine after an engine dirty-up phase comprising combusting in the engine a diesel fuel composition as defined above, wherein the power restoration is measured by the following formula:

Percent Power recovery = (DU-CU)/DU x 100

wherein DU is a percent power loss at the end of a dirty-up phase without the additive, CU is the percent power loss at the end of a clean-up phase with the fuel additive, and said power restoration is about 49% or greater.

[0008] In another aspect, there is provided a method of improving the injector performance of a fuel injected diesel engine comprising operating the engine on a fuel composition comprising a major amount of fuel and from about 5 to about 500 ppm by weight based on a total weight of the fuel of a synergistic fuel additive comprising (a) a hydrocarbyl substituted quaternary ammonium internal salt comprising a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C_2-C_8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is free of non-covalently bonded anion species; and (b) a

hydrocarbyl substituted dicarboxylic anhydride derivative selected from the group consisting of a diamide, acid/amide, acid/ester, diacid, amide/ester, diester, and imide, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500, wherein a weight ratio of (a) to (b) in the fuel additive ranges from about 1:20 to about 2:1, wherein when the synergistic additive(s) is present in the fuel, at least about 49 % of the power lost during a dirty up phase of a CEC F98-08 DW10 test conducted in the absence of the synergistic additive(s) is recovered and wherein the additive concentrate is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula



wherein R^2 is selected from hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^3 is selected from hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms. In another embodiment, at least 70% of the lost power is recovered. In still another embodiment at least 100% of the lost power is recovered.

[0009] A further aspect of the disclosure provides a method of operating a fuel injected engine comprising combusting in the engine a fuel composition containing a major amount of fuel and from about 5 to about 500 ppm by weight based on a total weight of the fuel of a synergistic fuel additive comprising (a) a hydrocarbyl substituted quaternary ammonium internal salt comprising a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C_2-C_8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is free of non-covalently bonded anion species; (b) a reaction product derived from (i) a hydrocarbyl substituted dicarboxylic acid, anhydride, or ester, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500 and (ii) a polyamine of the formula H_2N-((CHR^1-$(CH_2)_n$-$NH)_m$-H, wherein R^1 is hydrogen, n is 1 and m is 4, wherein a molar ratio of (i) reacted with (ii) ranges from about 0.5:1 to about 2:1; and (c) a metal deactivator selected from the group consisting of tolyltriazole and N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine, wherein a weight ratio of (a) to (b) in the fuel additive ranges from about 1:20 to about 2:1 and a weight ratio of (b) to (c) ranges from 0.5:1 to 5:1, and wherein fuel additive is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula

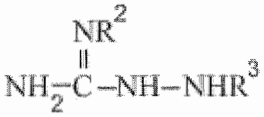
WHAT IS CLAIMED IS:

1. An additive concentrate for a fuel for use in an injected fuel engine comprising

(a) a hydrocarbyl substituted quaternary ammonium internal salt comprising a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C_2-C_8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is free of non-covalently bonded anion species; and

(b) a hydrocarbyl substituted dicarboxylic anhydride derivative selected from the group consisting of a diamide, acid/amide, acid/ester, diacid, amide/ester, diester, and imide, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500,

wherein a weight ratio of (a) to (b) in the additive concentrate ranges from about 1:20 to about 2:1, and wherein the additive concentrate is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula



wherein R^2 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^3 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

~~2. The additive concentrate of claim 1, wherein additive component (a) comprises a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C_2-C_8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is substantially devoid of free anion species.~~

~~3~~2. The additive concentrate of claim ~~2~~1, wherein the hydrocarbyl substituted quaternary ammonium internal salt is derived from the group consisting of acylated polyamines, fatty amide tertiary amines, fatty acid substituted tertiary amines, and fatty ester tertiary amines.

43. The additive concentrate of claim 1, wherein the internal salt is selected from the group consisting of (1) hydrocarbyl substituted compounds of the formula R-NMe_2CH_2COO where R is from C_1 to C_{30}; (2) fatty amide substituted internal salts; and (3) hydrocarbyl substituted imide, amide, or ester internal salts wherein the hydrocarbyl group has 8 to 40 carbon atoms.

~~5~~4. The additive concentrate of claim ~~2~~1, wherein the internal salt is selected from the group consisting of polyisobutenyl substituted succinimide, succinic diester, and succinic diamide internal salts; C_8-C_{40} alkenyl substituted succinic internal salts; oleyl amidopropyl dimethylamino internal salts; and oleyl dimethylamino internal salts.

~~6~~5. The additive concentrate of claim ~~2~~1, wherein additive component (a) comprises an oleyl amidopropyl dimethylamino internal salt.

~~7~~6. The additive concentrate of claim 1, wherein component (b) is derived from a polyamine of the formula H_2N-((CHR^1-$(CH_2)_n$-$NH)_m$-H, wherein R^1 is hydrogen, n is 1 and m is 4, wherein a molar ratio of hydrocarbyl substituted dicarboxylic anhydride reacted with the polyamine ranges from about 0.5:1 to about 2:1.

~~8~~7. The additive concentrate of claim ~~7~~6, wherein a molar ratio of hydrocarbyl substituted dicarboxylic anhydride reacted with the polyamine ranges from about 1:1 to about 1.6:1.

~~9~~8. The additive concentrate of claim 1, further comprising a metal deactivator, wherein the metal deactivator is selected from the group consisting of tolyltriazole and N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine.

~~10~~9. The additive concentrate of claim ~~9~~8, wherein a weight ratio of component (b) to the metal deactivator ranges from about 0.5:1 to about 5:1.

~~11~~10. A diesel fuel composition comprising a major amount of a low sulfur diesel fuel and a minor amount of the additive concentrate of claim 1.

~~12~~11. The diesel fuel composition of claim ~~11~~10, wherein the amount of additive concentrate in the fuel ranges from about 5 to about 500 ppm by weight based on a total weight of fuel.

~~13~~12. The diesel fuel of claim ~~11~~10, wherein the low sulfur diesel is substantially devoid of biodiesel fuel components.

~~14~~13. A method of cleaning up internal components of a fuel injector for a diesel engine comprising operating a fuel injected diesel engine on a fuel composition of claim ~~11~~10.

~~15~~14. A method of restoring power to a diesel fuel injected engine after an engine dirty-up phase comprising combusting in the engine a diesel fuel composition of claim ~~11~~10, wherein the power restoration is measured by the following formula:

Percent Power recovery = (DU-CU)/DU x 100

wherein DU is a percent power loss at the end of a dirty-up phase without the additive, CU is the percent power loss at the end of a clean-up phase with the fuel additive, and said power restoration is about 49% or greater.

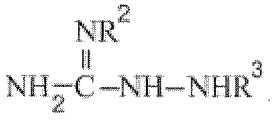
~~16~~15. The method of claim ~~15~~14, wherein the power restoration is measured as percent power recovery relative to the power before the dirty up phase and said power restoration is greater than 100%.

~~17~~16. A method of improving the injector performance of a fuel injected diesel engine comprising operating the engine on a fuel composition comprising a major amount of fuel and from about 5 to about 500 ppm by weight based on a total weight of the fuel of a synergistic fuel additive comprising:

(a) a hydrocarbyl substituted quaternary ammonium internal salt comprising a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C_2-C_8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is free of non-covalently bonded anion species; and

(b) a hydrocarbyl substituted dicarboxylic anhydride derivative selected from the group consisting of a diamide, acid/amide, acid/ester, diacid, amide/ester, diester, and imide, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500,

wherein a weight ratio of (a) to (b) in the fuel additive ranges from about 1:20 to about 2:1, wherein when the synergistic additive(s) is present in the fuel, at least about 49 % of the power lost during a dirty up phase of a CEC F98-08 DW10 test conducted in the absence of the synergistic additive(s) is recovered and wherein the additive concentrate is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula



wherein R^2 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^3 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

~~18~~17. The method of claim ~~17~~16, wherein the engine comprises a direct fuel injected diesel engine.

~~19~~18. The method of claim ~~17~~16, wherein the fuel comprises an ultra-low sulfur diesel fuel.

~~20~~19. The method of claim ~~17~~16, wherein the fuel additive, further comprises a metal deactivator, wherein the metal deactivator is selected from the group consisting of tolyltriazole and N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine.

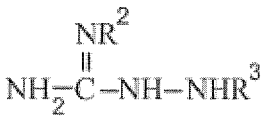
~~21~~20. A method of operating a fuel injected diesel engine comprising combusting in the engine a fuel composition comprising a major amount of fuel and from about 5 to about 500 ppm by weight based on a total weight of the fuel of a synergistic fuel additive comprising:

(a) a hydrocarbyl substituted quaternary ammonium internal salt comprising a reaction product of a hydrocarbyl substituted compound containing at least one tertiary amino group and a halogen substituted C_2-C_8 carboxylic acid, ester, amide, or salt thereof, wherein the reaction product as made is free of non-covalently bonded anion species;

(b) a reaction product derived from (i) a hydrocarbyl substituted dicarboxylic acid, anhydride, or ester, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight ranging from about 450 to about 1500 and (ii) a polyamine of the formula H_2N-((CHR^1-$(CH_2)_n$-$NH)_m$-H, wherein R^1 is hydrogen, n is 1 and m is 4, wherein a molar ratio of (i) reacted with (ii) ranges from about 0.5:1 to about 2:1; and

(c) a metal deactivator selected from the group consisting of tolyltriazole and N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine,

wherein a weight ratio of (a) to (b) in the fuel additive ranges from about 1:20 to about 2:1 and a weight ratio of (b) to (c) ranges from 0.5:1 to 5:1, and wherein the fuel additive is devoid of a reaction product of a hydrocarbyl substituted dicarboxylic acid, anhydride or ester and an amine compound of the formula



wherein R^2 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R^3 is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms.

~~22~~21. The method of claim ~~21~~20, wherein the internal salt is selected from the group consisting of polyisobutenyl substituted succinimide, succinic diamide, and succinic diester internal salts; C_8-C_{40} alkenyl substituted succinimide, succinic diamide, and succinic diester internal salts; oleyl amidopropyl dimethylamino internal salts; and oleyl dimethylamino internal salts.

~~23~~22. The method of claim ~~21~~20, wherein the hydrocarbyl group of the hydrocarbyl-substituted quaternary ammonium internal salt may range from C_8 to C_{40}.

~~24~~23. A fuel additive composition comprising:

a) an oleyl amidopropyl dimethylamino internal salt,

b) a reaction product derived from (i) a hydrocarbyl substituted succinic anhydride, wherein the hydrocarbyl substituent of component (b) has a number average molecular weight of about 950, and (ii) a tetraethylene pentamine, wherein a molar ratio of (i) reacted with (ii) is about 1.6:1, and

c) a metal deactivator selected from the group consisting of tolyltriazole and N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine.