

OXIDATION STABILIZED FUELS HAVING ENHANCED CORROSION RESISTANCE

TECHNICAL FIELD:

[0001] The disclosure is directed to certain diesel fuel additives and to diesel fuels and diesel fuel additive concentrates that include the additive. In particular the disclosure is directed methods for improving the oxidation stability and/or corrosion resistance of diesel and biodiesel fuels.

BACKGROUND AND SUMMARY:

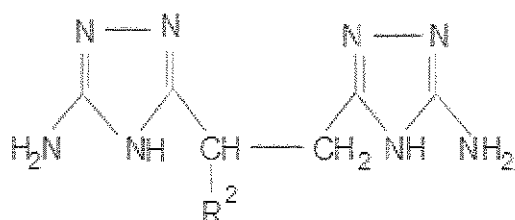
[0001] In order to preserve valuable resources and reduce emissions that may be detrimental to the environment, renewable fuels, made from crops such as oilseed rape, soya, oil palm, sugar cane or maize, have been added to fuels. A goal of using such fuel components is to make transport fuels increasingly environmentally friendly without changing how a vehicle engine works on such fuel.

[0002] Biodiesel components for fuel may be produced from straight vegetable oil, animal oil/fats, tallow and waste oils. Almost all biodiesel components are produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield. Rape, oil palm and soya oil are the most common crops used for biodiesel production. Most commercially available biodiesel fuels are actually biodiesel blends that are properly referenced with the letter B followed by a one- or two-digit number that represents the percentage of biodiesel used in the blend with petroleum diesel fuel. Pure biodiesel is sometimes called "neat" biodiesel and is also referred to as B100. The most common biodiesel blends are B2, B5, B7, B10, B20 and B50. The remaining fraction is petroleum-based diesel fuel, which is often referred to as petrodiesel.

[0003] Vegetable oils and fatty acid methyl esters have a relatively short storage life as they are slowly oxidized by atmospheric oxygen. The resulting oxidation products may be insoluble in the fuel and thus may damage vehicle engines. For this reason oxidation stability of biodiesel containing fuels is an important quality criterion. Until now, use of relatively expensive fuel additive components may be required to meet the oxidation stability standards of biodiesel containing fuels as determined by ASTM D-2274. Hence, methods for effectively

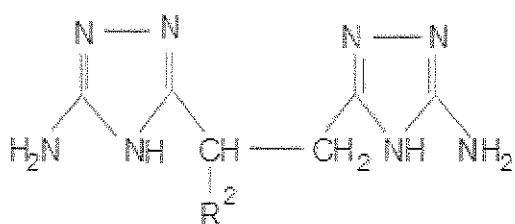
reducing or eliminating the need for relatively expensive fuel components while maintaining the oxidation stability of biodiesel containing fuels are needed.

[0004] In accordance with the disclosure, exemplary embodiments provide methods of improving oxidation stability of biodiesel-containing fuel compositions. The methods provide combining a major amount of middle distillate fuel containing more than about 5 volume percent of at least one biodiesel component with a minor amount of a synergistic mixture of (A) a hydrocarbyl-substituted succinimide dispersant and (B) a compound of the formula:



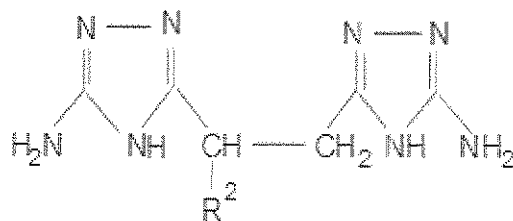
and tautomers and enantiomers thereof. In the formula, R^2 is a hydrocarbyl group having a number average molecular weight ranging from 100 to 5000. The synergistic mixture has a weight ratio of A:B ranging from 2:1 to 10:1.

[0005] Another embodiment of the disclosure provides a method of operating an engine on a middle distillate fuel containing more than about 5 volume percent of at least one biodiesel component. The method includes formulating the fuel with a minor amount of a synergistic mixture of (A) a hydrocarbyl-substituted succinimide dispersant and (B) a compound of the formula:



and tautomers and enantiomers thereof to provide an oxidation resistant fuel composition, wherein R^2 is a hydrocarbyl group having a number average molecular weight ranging from 100 to 5000. The synergistic mixture has a weight ratio of A:B ranging from 2:1 to 10:1. The engine is operated on the fuel composition.

[0006] A further embodiment of the disclosure provides use of a synergistic mixture of (A) a hydrocarbyl-substituted succinimide dispersant and (B) a compound of the formula:



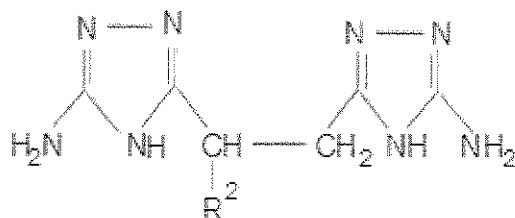
and tautomers and enantiomers thereof, wherein R^2 is a hydrocarbyl group having a number average molecular weight ranging from 100 to 5000. The synergistic mixture has a weight ratio of A:B ranging from 2:1 to 10:1 in a middle distillate fuel containing at least 7 volume percent of at least one biodiesel component to improve the oxidation stability of the fuel according to ASTM D-2274.

[0007] An unexpected advantage of the synergistic mixture of A and B described above, is that a middle distillate fuel containing more than about 5 volume percent biodiesel components may not require the use of relatively expensive metal deactivation agents in order to meet or exceed the oxidation stability criteria for such fuel as determined by ASTM D-2274 in the presence of added copper.

[0008] Additional embodiments and advantages of the disclosure will be set forth in part in the detailed description which follows, and/or can be learned by practice of the disclosure. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0009] In accordance with embodiments of the disclosure, a synergistic fuel additive mixture is provided. The synergistic mixture includes: (A) a hydrocarbyl-substituted succinimide dispersant and (B) a compound of the formula:



and tautomers and enantiomers thereof, wherein R^2 is a hydrocarbyl group having a number average molecular weight ranging from 100 to 5000. The synergistic mixture may have a weight

ratio of A:B ranging from about 2:1 to about 10:1, for example from about 3:1 to about 6:1, more particularly from about 3.5:1 to 5:1.

[00010] As used herein, the term "hydrocarbyl group" or "hydrocarbyl" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

- (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);
- (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
- (3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Hetero-atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, or as a further example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; in some embodiments, there will be no non-hydrocarbon substituent in the hydrocarbyl group.

[00011] As used herein, the term "major amount" is understood to mean an amount greater than or equal to 50 wt. %, for example from about 80 to about 98 wt. % relative to the total weight of the composition. Moreover, as used herein, the term "minor amount" is understood to mean an amount less than 50 wt. % relative to the total weight of the composition.

[00012] "Biorenewable fuel," "biodiesel fuel," and "biodiesel component" as used herein is understood to mean any fuel which is derived from resources other than petroleum. Such resources include, but are not limited to, corn, maize, soybeans and other crops; grasses, such as switchgrass, miscanthus, and hybrid grasses; algae, seaweed, vegetable oils; natural fats; and mixtures thereof. In an aspect, the biorenewable fuel may include monohydroxy alcohols, such

as those having from 1 to about 5 carbon atoms. Non-limiting examples of suitable monohydroxy alcohols include methanol, ethanol, propanol, n-butanol, isobutanol, t-butyl alcohol, amyl alcohol, and isoamyl alcohol.

[00013] “Middle distillate fuel” as used herein may be, for example, a naphtha, kerosene or diesel fuel composition. It may be a heating oil, an industrial gas oil, a drilling oil, an automotive diesel fuel, a distillate marine fuel or a kerosene fuel such as an aviation fuel or heating kerosene. It may in particular be a diesel fuel composition. More particularly, a middle distillate fuel is a fuel that is suitable and/or adapted and/or intended for use in an internal combustion engine; for example an automotive fuel composition, and/or adapted and/or intended for use in an automotive diesel (compression ignition) engine. Such middle distillate fuel may be organically or synthetically derived, for example a petroleum derived or Fischer-Tropsch derived gas oil. A middle distillate fuel may have boiling points within the usual diesel range of from 125 or 150 to 400 or 550° C., depending on grade and use. A density of the middle distillate fuel may range from 0.75 to 1.0 g/cm³, for example, from 0.8 to 0.86 g/cm³, at 15° C. (IP 365) and a measured cetane number (ASTM D613) of from 35 to 80, suitably from 40 to 75 or 70. An initial boiling point of a middle distillate fuel may suitably be in the range 150 to 230° C. and the fuel may have a final boiling point in the range 290 to 400° C. A kinematic viscosity of the middle distillate fuel at 40° C. (ASTM D445) might suitably range from 1.5 to 4.5 mm²/s (centistokes).

[00014] Component A of the synergistic mixture may be a dispersant, such as an amine-containing dispersant. Suitable amine-containing dispersants may include hydrocarbyl-substituted succinimide dispersants. The hydrocarbyl substituent of the dispersant may have a number average molecular weight ranging from about 100 to about 5000, such as about 500 to about 5000 daltons, as determined by GPC.

[00015] As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between an amine and a hydrocarbyl-substituted succinic acid or anhydride (or like succinic acylating agent), and is intended to encompass compounds wherein the product may have amide, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of or contact with an amine and an anhydride moiety.

[00016] Suitable hydrocarbyl-substituted succinic anhydrides may be formed by first reacting an olefinically unsaturated hydrocarbon of a desired molecular weight with maleic anhydride. Reaction temperatures of about 100°C to about 250°C may be used.

[00017] With higher boiling olefinically-unsaturated hydrocarbons, good results may be obtained at about 200°C to about 250°C. This reaction may be promoted by the addition of chlorine.

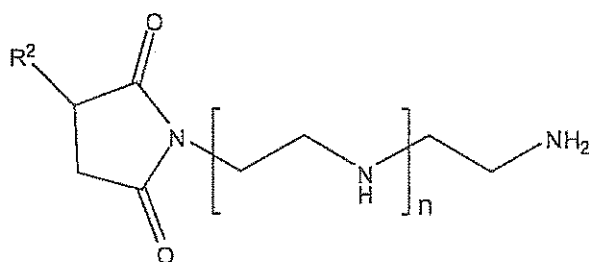
[00018] Typical olefins may include, but are not limited to, cracked wax olefins, linear alpha olefins, branched chain alpha olefins, polymers and copolymers of lower olefins. The olefins may be chosen from ethylene, propylene, butylene, such as isobutylene, 1-octane, 1-hexene, 1-decene and the like. Useful polymers and/or copolymers may include, but are not limited to, polypropylene, polybutenes, polyisobutene, ethylene-propylene copolymers, ethylene-isobutylene copolymers, propylene-isobutylene copolymers, ethylene-1-decene copolymers and the like.

[00019] In an aspect of the disclosed embodiments, the hydrocarbyl substituents of the hydrocarbyl-substituted succinic anhydrides may be derived from butene polymers, for example polymers of isobutylene. Suitable polyisobutenes for use herein include those formed from HR-PIB having at least about 60%, such as about 70% to about 90% and above, terminal vinylidene content. Suitable polyisobutenes may include those prepared using BF_3 catalysts. The average number molecular weight of the hydrocarbyl substituent may vary over a wide range, for example from about 100 to about 5000, such as from about 500 to about 5000, as determined by GPC.

[00020] Carboxylic reactants other than maleic anhydride may be employed such as maleic acid, fumaric acid, malic acid, tartaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, ethylmaleic anhydride, dimethylmaleic anhydride, ethylmaleic acid, dimethylmaleic acid, hexylmaleic acid, and the like, including the corresponding acid halides and lower aliphatic esters. A mole ratio of maleic anhydride to olefin in the reaction mixture may vary widely. Accordingly, the mole ratio may vary from about 5:1 to about 1.5, for example from about 3:1 to about 1:3, and as a further example, the maleic anhydride may be used in stoichiometric excess to force the reaction to completion. The unreacted maleic anhydride may be removed by vacuum distillation.

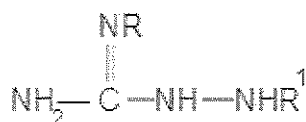
[00021] Any of numerous polyamines can be utilized in preparing the hydrocarbylsubstituted succinimide dispersant. Non-limiting exemplary polyamines may include aminoguanidine bicarbonate (AGBC), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA) and heavy polyamines. A heavy polyamine may comprise a mixture of polyalkylenepolyamines having small amounts of lower polyamine oligomers such as TEPA and PEHA, but primarily oligomers having seven or more nitrogen atoms, two or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures. Additional non-limiting polyamines which may be used to prepare the hydrocarbyl-substituted succinimide dispersant are disclosed in U.S. Pat. No. 6,548,458, the disclosure of which is incorporated herein by reference in its entirety. In an embodiment of the disclosure, the polyamine may be selected from tetraethylene pentamine (TEPA).

[00022] In an embodiment, the dispersant may include compounds of formula (IV):

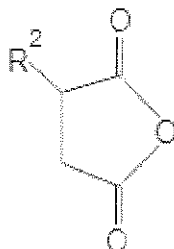


wherein n represents 0 or an integer of from 1 to 5, and R^2 is a hydrocarbyl substituent as defined above. In an embodiment, n is 3 and R^2 is a polyisobutenyl substituent, such as that derived from polyisobutylenes having at least about 60%, such as about 70% to about 90% and above, terminal vinylidene content. Compounds of formula (IV) may be the reaction product of a hydrocarbyl-substituted succinic anhydride, such as a polyisobutenyl succinic anhydride (PIBSA), and a polyamine, for example tetraethylene pentamine (TEPA).

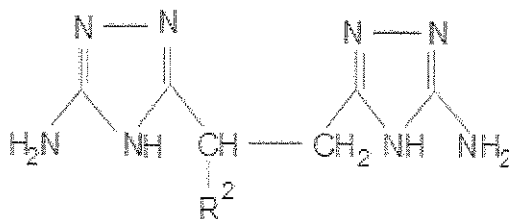
[00023] Component B of the synergistic mixture may be made by reacting an amine compound or salt thereof of the formula



wherein R is selected from the group consisting of a hydrogen and a hydrocarbyl group containing from about 1 to about 15 carbon atoms, and R¹ is selected from the group consisting of hydrogen and a hydrocarbyl group containing from about 1 to about 20 carbon atoms with a hydrocarbyl carbonyl compound of the formula



wherein R² is a hydrocarbyl group having a number average molecular weight ranging from about 200 to about 3000. Without desiring to be bound by theoretical considerations, it is believed that the reaction product of the amine and hydrocarbyl carbonyl compound is an aminotriazole, such as a bis-aminotriazole compound of the formula



including tautomers and enantiomers thereof, having a number average molecular weight ranging from about 200 to about 3000 containing from about 40 to about 80 carbon atoms. The five-membered ring of the triazole is considered to be aromatic. The aminotriazoles are fairly stable to oxidizing agents and are extremely resistant to hydrolysis. It is believed, although it is not certain, that the reaction product is polyalkenyl bis-3-amino-1,2,4-triazole. Such a product contains relatively high nitrogen content, within the range of about 1.8 wt % to about 2.9 wt % nitrogen.

[00024] In other aspects of the present disclosure, the disclosed additive containing the synergistic mixture of A and B may include a fuel soluble carrier. Such carriers may be of various types, such as liquids or solids, e.g., waxes. Examples of liquid carriers include, but are not limited to, mineral oil and oxygenates, such as liquid polyalkoxylated ethers (also known as polyalkylene glycols or polyalkylene ethers), liquid polyalkoxylated phenols, liquid

polyalkoxylated esters, liquid polyalkoxylated amines, and mixtures thereof. Examples of the oxygenate carrier fluids may be found in U.S. Pat. No. 5,752,989, the description of which carriers is herein incorporated by reference in its entirety. Additional examples of oxygenate carrier fluids may include alkyl-substituted aryl polyalkoxylates described in U.S. Patent Publication No. 2003/0131527, published July 17, 2003 to Colucci et. al., the description of which is herein incorporated by reference in its entirety.

[00025] In other aspects, the additive containing the synergistic mixture of A and B may not contain a carrier. For example, some compositions may not contain mineral oil or oxygenates, such as those oxygenates described above.

[00026] One or more additional optional additives may be present in the fuel compositions disclosed herein. For example, the fuel compositions may contain antifoam agents, dispersants, detergents, antioxidants, thermal stabilizers, carrier fluids, metal deactivators, dyes, markers, corrosion inhibitors, biocides, antistatic additives, drag reducing agents, friction modifiers, demulsifiers, emulsifiers, dehazers, anti-icing additives, antiknock additives, surfactants, cetane improvers, corrosion inhibitors, cold flow improvers, pour point depressants, solvents, demulsifiers, lubricity additives, extreme pressure agents, viscosity index improvers, seal swell agents, amine stabilizers, combustion improvers, dispersants, conductivity improvers, marker dyes, organic nitrate ignition accelerators, manganese tricarbonyls compounds, and mixtures thereof. In some aspects, the fuel additive compositions described herein may contain about 10 wt.% or less, or in other aspects, about 5 wt.% or less, based on the total weight of the additive or fuel composition, of one or more of the above additives. Similarly, the fuel compositions may contain suitable amounts of fuel blending components such as methanol, ethanol, dialkyl ethers, and the like.

[00027] When formulating the presently disclosed compositions, the disclosed additives can be employed in amounts sufficient to improve the oxidation stability of a fuel, such as middle distillate fuel containing more than 5 volume percent of at least one biodiesel component, for example B7, B10, B20, B50 and B100 diesel fuel. In some aspects, the fuels may contain a major amount of a fuel and a minor amount of the above-described synergistic additive composition. In an aspect, fuels of the present disclosure may contain, on an active ingredient

basis, an aminotriazole compound (B) as described herein in an amount ranging from about 1 ppm to about 100 ppm, such as from about 20 ppm to about 70 ppm. In another aspect, the presently disclosed fuel compositions may contain, on an active ingredient basis, a dispersant (A) as described herein in an amount ranging from about 50 to about 500 ppm, such as from about 80 ppm to about 200 ppm.

[00028] In aspects where a carrier is employed, the fuel compositions may contain, on an active ingredients basis, an amount of the carrier ranging from about 10 mg to about 1000 mg of carrier per kg of fuel, such as about 25 mg to about 700 mg of carrier per kg of fuel. The active ingredient basis excludes the weight of (i) unreacted components associated with and remaining in the disclosed additives as produced and used, and (ii) solvent(s), if any, used in the manufacture of the disclosed additives either during or after its formation but before addition of a carrier, if a carrier is employed.

[00029] The fuel additives of the present disclosure may be blended into a base fuel individually or in various sub-combinations. In some embodiments, the additive components of the present disclosure may be blended into a fuel concurrently using an additive concentrate, as this takes advantage of the mutual compatibility and convenience afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concentrate may reduce blending time and lessen the possibility of blending errors.

[00030] The diesel fuels of the disclosed embodiments may be applicable to the operation of both stationary diesel engines (e.g., engines used in electrical power generation installations, in pumping stations, etc.) and ambulatory diesel engines (e.g., engines used as prime movers in automobiles, trucks, road-grading equipment, military vehicles, etc.).

[00031] In one embodiment, the biodiesel-containing diesel fuels of the present disclosure may be essentially free, such as devoid, of conventional metal deactivator compounds. The term “essentially free” is defined for purposes of this application to be concentrations having substantially no measurable effect on oxidation stability or insolubles formation according to ASTM D-2274.

[00032] Metal deactivators that may be reduced or eliminated from the biodiesel containing fuels according to the disclosure may include the condensation product of an ortho-hydroxy aromatic aldehyde with an aliphatic amine. A typical example of such metal deactivator is disalicylalalkylenediamine which is prepared by the condensation of two mols of salicylaldehyde with one mol of alkylenediamine. Such metal deactivators include, for example, salicylidene-o-aminophenol, disalicylidene ethylenediamine, disalicylidene propylenediamine, and N,N'-disalicylidene-1,2-diaminopropane.

EXAMPLES

[00033] The following examples are illustrative of exemplary embodiments of the disclosure. In these examples as well as elsewhere in this application, all parts and percentages are by weight unless otherwise indicated. It is intended that these examples are being presented for the purpose of illustration only and are not intended to limit the scope of the invention disclosed herein.

Example 1

[00034] In the following example, a B7 diesel fuel was doped with 2 ppm copper using a copper solution of copper naphthenate having 8 wt.% copper and was oxidized according to ASTM D-2274 to determine the total insolubles in 500 ml of fuel. The maximum insoluble according to ASTM D-2274 in diesel fuel is 2.5 mg/100 ml of fuel. The base B7 fuels containing no added copper had total insolubles of 0.6 mg/100 ml of fuel. Copper was added and the fuels were oxidized according to the ASTM procedure in order to determine the oxidation stability of the fuels containing at least one biodiesel component.

[00035] In all of the runs, the carrier used for the additives (A) and (B) as defined above was a mixture of Aromatic 150 and Aromatic 200. In the following table "MDA" is a conventional metal deactivator as described above. Runs The results are shown in the following table.

Table 1

Run No.	Fuel No.	(A) mg/kg	(B) mg/kg	MDA mg/kg	Carrier mg/kg	Adherent Insolubles mg/100 ml	Filterable Insolubles mg/100 ml	Total Insolubles mg/100 ml
1	1	0	0	0	0	238.7	2.1	240.8
2	2	0	0	0	0	1740	55	1794
3	1	190	0	10	760	3.6	2.2	5.8
4	1	120	30	0	420	0.9	<0.1	0.9
5	2	190	0	0	770	486	64	550
6	2	120	0	0	450	1056	140	1196
7	2	0	30	0	70	0	6.5	6.5
8	2	120	30	0	420	0.3	0.4	0.7
9	2	120	30	0	420	1.63	<0.1	1.63
10	2	60	15	0	210	3.51	<0.1	3.51
11	2	120	30	10	420	1	0	1
12	2	0	0	10	50	0.6	0.2	0.8

[00036] As shown by Runs 4 and 8-9, a combination of component A and B provided a synergistic decrease in the amount of insolubles in oxidized fuel containing 2 ppm copper as compared to the base fuel (Runs 1 and 2). Even at a half-treat rate of components A and B, (Run 10), there was a synergistic decrease in total insolubles in the oxidized fuel compared to the base fuel (Run 2). Run 3 containing component A and an MDA showed significant improvement over the base fuel of Run 1 and adding MDA to components A and B (Run 11) showed no significant improvement over Runs 4 and 8-9 containing no MDA or Run 12 containing MDA alone. Accordingly, MDA may be eliminated from a fuel containing more than 5 volume percent biodiesel components and still be capable of improved oxidation stability when the synergistic mixture of components A and B is used.

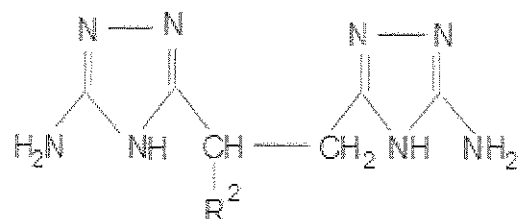
[00037] It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to “an antioxidant” includes two or more different antioxidants. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items

[00038] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00039] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

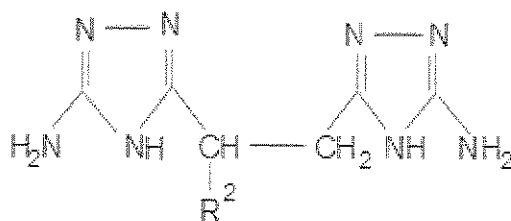
WHAT IS CLAIMED IS:

1. A method of improving oxidation-stability of a biodiesel-containing fuel composition, comprising: combining a major amount of middle distillate fuel containing more than about 5 volume percent of at least one biodiesel component with a minor amount of a synergistic mixture consisting essentially of (A) a hydrocarbyl-substituted succinimide dispersant and (B) a compound of the formula:



- and tautomers and enantiomers thereof, wherein R² is a hydrocarbyl group having a number average molecular weight ranging from 100 to 5000 and wherein a weight ratio of A:B ranges from 2:1 to 10:1.
2. The method of claim 1, wherein component A of the mixture comprises a reaction product of polyalkenyl succinic acid or anhydride with tetraethylene pentamine.
 3. The method of claim 2, wherein the polyalkenyl succinic acid or anhydride is derived from polyisobutylene having a number average molecular weight ranging from 800 to 1100 daltons.
 4. The method of claim 3, wherein the polyisobutylene comprises a high reactivity polyisobutylene having at least 60% or more terminal olefinic double bonds.
 5. The method of any one of claims 1 to 4, wherein the middle distillate fuel comprises from 200 to 600 ppm by weight of the mixture of A and B.
 6. The method of any one of claims 1 to 5, wherein R² is a polyolefin radical having a number average molecular weight of from 200 to 3,000 daltons.

7. The method of any one of claim 1 to 6, wherein the middle distillate fuel is substantially devoid of disalicylidene diaminoalkane compounds.
8. The method of any one of claims 1 to 7, wherein the fuel containing A and B has a total insolubles amount of no more than 2.5 mg/100ml as determined by ASTM D-2274.
9. The method of any one of claims 1 to 8, wherein the middle distillate fuel is substantially devoid of metal deactivators.
10. The method of any one of claims 1 to 9, wherein the weight ratio of A:B in the middle distillate fuel ranges from about 3.5:1 to about 5:1.
11. Use of a synergistic mixture consisting essentially of (A) a hydrocarbyl-substituted succinimide dispersant and (B) a compound of the formula:



- and tautomers and enantiomers thereof, wherein R^2 is a hydrocarbyl group having a number average molecular weight ranging from 100 to 5000 and wherein a weight ratio of A:B ranges from 2:1 to 10:1 in a middle distillate fuel containing at least 7 volume percent of at least one biodiesel component to improve the oxidation stability of the fuel according to ASTM D-2274, wherein the oxidation stability of the fuel according to ASTM D-2274 is less than 2.5 mg/100 ml insolubles compared to the oxidation stability of the fuel without the synergistic mixture having greater than 2.5 mg/100 ml insolubles.
12. Use of the mixture of claim 11, wherein component A of the mixture comprises a reaction product of polyalkenyl succinic acid or anhydride with tetraethylene pentamine, wherein the polyalkenyl succinic acid or anhydride is derived from polyisobutylene having a number average molecular weight ranging from 800 to 1100 daltons.

13. Use of the mixture of claim 12, wherein the polyisobutylene comprises a high reactivity polyisobutylene having at least 60% or more terminal olefinic double bonds.
14. Use of the mixture of any one of claims 11 to 13, wherein the middle distillate fuel comprises from 200 to 600 ppm by weight of the mixture of A and B.
15. Use of the mixture of any one of claims 11 to 14, wherein the middle distillate fuel is substantially devoid of metal deactivators.