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(71) Applicants:
- **China Petroleum & Chemical Corporation**
  Beijing 100728 (CN)
- **Research Institute Of Petroleum Processing, Sinopec**
  Beijing 100083 (CN)

(72) Inventors:
- **LIN, Jianmin**
  Beijing 100083 (CN)
- **ZHANG, Yongguang**
  Beijing 100083 (CN)
- **ZHANG, Jianrong**
  Beijing 100083 (CN)
- **LI, Hang**
  Beijing 100083 (CN)
- **LI, Shuai**
  Beijing 100083 (CN)

(74) Representative: **Bublak, Wolfgang**
Bardehle Pagenberg
Prinzregentenplatz 7
81675 München (DE)

(54) DIESEL COMPOSITION AND PROCESS FOR IMPROVING OXIDATION STABILITY OF BIODIESEL

(57) The present invention discloses a diesel composition, which comprises a base diesel and an additive composition, **characterized in that** said base diesel comprises biodiesel, and said additive composition comprises component (a) and component (b), wherein said component (a) is an arylamine-type antioxidant, and said component (b) is one or more polyamines or derivatives thereof. The diesel composition of the present invention has a superior oxidation stability.

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Description

Technical Field

[0001] The present invention relates to a diesel composition and a method of increasing the oxidation stability of biodiesel.

Background Art

[0002] With the accelerated dieselization of vehicles all over the world, the demand for diesel will be larger and larger, furthurmore, as petroleum resources are drying up day by day and people are more and more conscious of environmental issues, countries worldwide are greatly promoted to expedite the development of alternative fuels for diesel engine. Therefore, biodiesel, which is very environmentally-friendly and renewable, attracts much attention all over the world.

[0003] Biodiesel (BD100), also called fatty acid methyl ester, is obtained by transesterrification of oils from oil crops, such as soybeans and rapeseeds, the fruits of oil plants, such as *Elaeis* and *Pistacia chinesis Bunge,* and oil water plants, such as algae as well as animal fats, used cooking oils thrown away by restaurants or families, and the like with alcohols (methanol, ethanol), and is a clean biofuel. Biodiesel has three advantages of being renewable, clean and safe, and is strategically significant to the agricultural structure adjustment, energy safety and protection of the ecological environment. At present, China is a net importer of petroleum and has limited petroleum reserves, and importing petroleum in huge quantity threatens the energy safety in China; thus, the study on and production of biodiesel is practically significant in China.

[0004] However, because of the starting materials and processing steps, some biodiesels have very poor oxidation stability, causing great difficulties in their use and storage. Biodiesels having poor oxidation stability tends to produce the following aging products: 1) insoluble polymers (gelatines and fatlute), which will cause clogging of engine filters and coking of jet pumps, and result in an increased smoke discharge and difficulty in start-up; 2) soluble polymers, which can form resin-like materials in engines, and may possibly result in flameout and difficulty in start-up; 3) aging acids, which will erode metal parts in engines; 4) peroxides, which will cause aging and embrittlement of rubber parts, resulting in fuel leak.

[0005] The European biodiesel standard EN 14214:2003, the Australian biodiesel standard (Draft 2003), the New Zealand biodiesel standard NZS 7500:2005, the Brazilian biodiesel standard ANP255 (2003), the Indian biodiesel standard IS 15607:2005, the South African biodiesel standard SANS 1935:2004 and the Chinese national standard GB/T 20828-2007 for the biodiesel (BD100) for blended fuel diesel engines all prescribe that the oxidation stability of biodiesel is shown by an induction period of not shorter than 6 hours at 110°C, as measured by the EN 14112:2003 method.

[0006] As generally known, olefins, diolefins and non-hydrocarbons, such as sulphides and nitrides, in petroleum diesel (usually known as diesel, petroleum diesel being introduced here is to be distinguished from biodiesel) produce a series of oxidation intermediate products in the presence of oxygen, and generate insoluble precipitates by condensation. Such insoluble particles generated during the storage of petroleum diesel will influence the properties of the fuel, resulting in the clogging of filter systems, and causing the parts of fuel systems to malfunction, such that the atomization of the oil sprayed will be affected, leading to incomplete combustion, and even the formation of excess carbon deposit in engines to clog spray nozzles. Since the oxidation stability of biodiesel is inferior to that of petroleum diesel, the above problems will be worse if biodiesel is blended with petroleum diesel. The most obvious manifestation is that the stability of a biodiesel-containing blended fuel is inferior to that of petroleum diesel.

[0007] The above problems can be solved or mitigated by the addition of additives. One way is to add antioxidants in pure biodiesel to delay its oxidation, hence mitigating the harms made by the aging products; the other way is to add stabilizers in petroleum diesel or a biodiesel-containing blended fuel to improve the stability of the blended fuel. A stabilizer is capable of terminating, weakening or interfering with various oxidation reactions to inhibit oil deterioration and then improve the stability.

[0008] CN 1742072A discloses a process for increasing the storage stability of biodiesel, comprising adding a stock solution comprising 15-60 wt.% 2,4-di-tert-butylhydroxy toluene dissolved in biodiesel, into the biodiesel to be stabilized until the 2,4-di-tert-butylhydroxy toluene reaches a concentration of 0.005-2 wt.% with respect to the total solution of biodiesel.

[0009] CN 1847368A discloses a method of increasing the oxidation stability of biodiesel, comprising adding a bisphenol-type antioxidant, such as 4,4'-methylenebis[2,6-di-tert-butylphenol] or 2,2'-methylenebis[6-tert-butyl-4-methylphenol], to the biodiesel to be stabilized in a quantity of 10-20000 ppm (w/w).

[0010] CN 1847369A discloses a method of increasing the oxidation stability of biodiesel, comprising adding a primary antioxidant having a melting point of less than or equal to 40 °C to the biodiesel to be stabilized in an amount of from 10 to 20000 ppm (w/w), where the primary antioxidant comprises alkylphenol.

[0011] US2007/113467A1 discloses a fuel composition having an improved oxidation stability, which comprises biodiesel and at least one antioxidant selected from the group consisting of propyl gallate, 1,2,3-trihydroxybenzene, 2,6-di-tert-butyl-p-methylphenol, butylated hydroxyanisole, dilauryl thiodipropinate, tocopherol, and quinoline derivatives.

[0012] CN 101144040A and CN 101353601A disclose methods of improving the oxidation stability of biodiesel by using an arylamine-type antioxidant.

[0013] The above methods of increasing the oxidation stability of biodiesel by using conventional antioxidants are effective in some degree, but require a relatively large amount of antioxidants, and in the meantime do not have a satisfactory effect of improving the stability of a biodiesel-containing blended fuel.

Contents of the Invention

[0014] One of the object of the present invention is to provide a diesel composition with an improved oxidation stability of biodiesel or a superior stability and a method of improving the oxidation stability of biodiesel in order to remove the above-mentioned disadvantages of the prior art of requiring a large amount of antioxidant and having a poor effect of improving the stability of a biodiesel-containing blended fuel.

[0015] The present invention provides a diesel composition comprising a base diesel and an additive composition, **characterized in that** said base diesel comprises biodiesel, and said additive composition comprises component (a) and component (b), wherein said component (a) is an arylamine-type antioxidant, and said component (b) is one or more polyamines or derivatives thereof.

[0016] The present invention further provides a method of increasing the oxidation stability of biodiesel, comprising adding, in a biodiesel-containing base diesel, an additive, wherein said additive is the additive composition provided by the present invention.

[0017] The diesel composition of the present invention has a superior oxidation stability, and component (a) and component (b) surprisingly show synergism, i.e., a much better antioxidative effect than a single antioxidant. Component (b) can be regarded as a co-antioxidant, which surprisingly greatly enhances the effect of the antioxidant. Thus, in reaching the same oxidation stability, the amount of component (a) in the biodiesel composition can be reduced considerably, and in particular when component (a) is expensive or is toxic or corrosive in some degree. It is of great significance to reduce the amount of component (a). Especially, when it simultaneously comprises component (a), component (b) and component (c), the diesel composition of the present invention has a remarkably improved antioxidative property due to the significant synergism of the components.

Specific Embodiments

[0018] In the diesel composition according to the present invention, the amount of additive can be selected from a relatively wide range, such as 50-10000 ppm, preferably 80-8000 ppm, and more preferably 100-5000 ppm, on the basis of the amount of the base diesel.

[0019] The weight ratio of said component (b) to said component (a) is 0.01-100: 1, preferably 0.02-50: 1, more preferably 0.05-10: 1, even more preferably 0.2-5:1.

Component (a)

[0020] Component (a) is at least one arylamine-type antioxidant which may be at least one selected from the group consisting of a substituted naphthylamine, a substituted diphenylamine, a substituted p-phenylene diamine, and a substituted quinoline.

[0021] Said substituted naphthylamine includes, but is not limited to, one or more of the following:

phenyl-α-naphthylamine;
phenyl-β-naphthylamine (antioxidant D);
N-p-methoxyphenyl-α-naphthylamine (antioxidant 102);
p-hydroxyphenyl-β-naphthylamine (antioxidant D-OH);
aldo-α-naphthylamine (antioxidant AP);
2-hydroxy-1,3-bis-[p-(β-naphthylamine)phenoxy] propane (antioxidant C-49);
dimethyl-bis-[p-(β-naphthylamine)phenoxy] silane (antioxidant C-41);
diethyl-bis-[p-(β-naphthylamine)phenoxy]silane (antioxidant C-41-ethyl);
2,2'-bis-[p-(β-naphthylamine)phenoxy] diethyl ether (antioxidant C-41- ethyl ether).

[0022] Said substituted naphthylamine is preferably phenylnaphthylamine, such as one or more of phenyl-α-naphthylamine, phenyl-β-naphthylamine, and N-p-methoxyphenyl-α-naphthylamine, particularly preferably phenyl-α-naphthylamine.

[0023] Said substituted diphenylamine includes, but is not limited to, one or more of the following:

4,4'-diaminodiphenylamine (antioxidant APA);
p-p'-dimethoxydiphenylamine;
N,N,N',N'-tetraphenyldiamine methane (antioxidant 350);
N,N'-diphenylethylene diamine;
N,N'-diphenylpropylene diamine;
N,N'-di-o-tolylethylene diamine;
2-hydroxy-1,3-bis-(p-anilinephenoxy) propane (antioxidant C-47);
2,2'-bis-(p-anilinephenoxy)- diethyl ether (antioxidant H-1);
dimethyl-bis-(p-aniline-phenoxy)-silane (antioxidant C-1);
p-iso-propoxydiphenylamine (antioxidant ISO);
p,p'-diiso-propoxydiphenylamine (antioxidant DISO);
4,4'-bis-(a,a'-dimethylbenzyl)diphenylamine (antioxidant KY-405);
p-hydroxydiphenylamine (antioxidant A03920);
di-(1,1,3,3-tetramethylethyl) diphenylamine (antioxidant ODA);
4,4'-dioctyldiphenylamine;
4,4'-diiso-octyldiphenylamine;
4,4'-diheptyldiphenylamine;
4,4'-dinonyldiphenylamine;
octylated diphenylamine (a mixture of mono-octylated diphenylamine and di-octylated diphenylamine, antioxidant OD);
octyl/butyldiphenylamine (antioxidant L-57);
styrenated diphenylamine (antioxidant DFL, DFC-34); and
a mixture of alkylated diphenylamines, wherein the alkyl may be one or more of heptyl, octyl and nonyl, wherein examples of its industrial products are Pennox A and Pennox A-"S" by Pennwalt, US, Wytox ADP and ADP-X by National polychem (an US company), Agerite Stalite, Agerite Stalite S, Agerite Nepa, and Agerite Gel by Vanderbilt, US, Polylite and Antioxidant 445 by Uniroyal, US, and the antioxidant product under the code name T534 in China.

[0024] The substituted diphenylamine-type antioxidant is preferably an alkylated diphenylamine or a mixture thereof, particularly preferably an alkylated diphenylamine with an alkyl radical having between 4 and 10 carbon atoms, or a mixture thereof, such as, one or more of 4,4'-dioctyldiphenylamine, 4,4'-diiso-octyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dinonyldiphenylamine, octylated diphenylamine(a mixture of mono-octylated diphenylamine and di-octylated diphenylamine), octyl/butyldiphenylamine, and commercial antioxidant T534.

[0025] Said substituted p-phenylene diamine-type antioxidant can be a product obtained by substitution of the hydrogen atom(s) of the amino group(s) ($-NH_2$) in the p-phenylene diamine with one or more of alkyl, aryl, aralkyl, alkylaryl, hydrocarbylacyl, hydrocarbylsulfonyl and hydrocarbylacyloxy. When two hydrogen atoms of the amino groups are substituted, they may be hydrogen on the same amino group or on two different amino groups. Moreover, when there are more than two substituents, the substituents may be the same or different. In other words, said substituted p-phenylene diamine-type antioxidant can be one or more of mono-alkyl substituted p-phenylene diamine, mono-aryl substituted p-phenylene diamine, mono-alkylaryl substituted p-phenylene diamine, mono-arylalkyl substituted p-phenylene diamine, mono-hydrocarbylacyl substituted p-phenylene diamine, mono-hydrocarbylsulfonyl substituted p-phenylene diamine, mono-hydrocarbylacyloxy substituted p-phenylene diamine, N-alkyl-N'-alkyl substituted p-phenylene diamine, N-aryl-N'-alkyl substituted p-phenylene diamine, N-alkyl-N'-alkylaryl substituted p-phenylene diamine, N-aryl-N'-alkyl substituted p-phenylene diamine, N-arylalkyl-N'-alkyl substituted p-phenylene diamine, N-arylalkyl-N'-aryl substituted p-phenylene diamine, N-arylalkyl-N'-hydrocarbylacyl substituted p-phenylene diamine, N-arylalkyl-N'-hydrocarbylsulfonyl substituted p-phenylene diamine, N-arylalkyl-N'-hydrocarbylacyloxy substituted p-phenylene diamine, N-aryl-N'-hydrocarbylacyl substituted p-phenylene diamine, N-alkyl-N'-hydrocarbylsulfonyl substituted p-phenylene diamine, N-alkyl-N'-hydrocarbylacyloxy substituted p-phenylene diamine, N-aryl-N'-hydrocarbylacyl substituted p-phenylene diamine, N-alkyl-N'-hydrocarbylsulfonyl substituted p-phenylene diamine, N-alkyl-N'-hydrocarbylacyloxy substituted p-phenylene diamine, N-alkylaryl-N'-hydrocarbylacyl substituted p-phenylene diamine, N-alkylaryl-N'-hydrocarbylsulfonyl substituted p-phenylene diamine, N-alkylaryl-N'-hydrocarbylacyloxy substituted p-phenylene diamine, N,N-bis-alkyl substituted p-phenylene diamine, N,N-bis-aryl substituted p-phenylene diamine, N,N-bis-alkylaryl substituted p-phenylene diamine, N,N-bis-arylalkyl substituted p-phenylene diamine, N,N-bis-hydrocarbylsulfonyl substituted p-phenylene diamine, N,N-bis-hydrocarbylacyl substituted p-phenylene diamine, and N,N-bis-hydrocarbylacyloxy substituted p-phenylene diamine. Each substituent preferably has 1 to 20 carbon atoms, and in terms of an alkyl radical, it preferably has 4 to 10 carbon atoms.

[0026] Specifically, said substituted p-phenylene diamine-type antioxidant includes, but is not limited to, one or more of the following:

N-phenyl-N'-cyclohexyl-p-phenylene diamine (antioxidant 4010);
N,N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine (antioxidant 4020);
N,N'-bis-(1,4-dimethylamyl) p-phenylene diamine (antioxidant 4030);
N-p-tolyl-N'-(1,3-dimethylbutyl) p-phenylene diamine (antioxidant 4040);
N,N'-diheptyl-p-phenylene diamine (antioxidant 788);
N-isopropyl-N'-phenyl-p-phenylene diamine (antioxidant 4010NA);
N-isopropyl-N'-p-tolyl-p-phenylene diamine (antioxidant methy14010NA);
N,N'-xylyl-p-phenylene diamine (antioxidant PPD-A);
N,N'-diphenyl-p-phenylene diamine (antioxidant H);
N,N'-di-(β-naphthyl) p-phenylene diamine (antioxidant DNP);
N,N'-di-sec-butyl-p-phenylene diamine (antioxidant U-5);
N,N'-dioctyl-p-phenylene diamine (antioxidant 88);
N,N'-bis-(1-methylheptyl) p-phenylene diamine (antioxidant 288);
N,N'-bis-(1-ethyl-3-methylamyl) p-phenylene diamine (antioxidant 8L);
N,N'-bis-(1,4-dimethylbutyl) p-phenylene diamine (antioxidant 66);
N-octyl-N'-phenyl-p-phenylene diamine (antioxidant 688);
N-isobutyl-N'-phenyl-p-phenylene diamine (antioxidant 5L);
N,N'-dimethyl-N,N'-bis-(1-methylpropyl) p-phenylene diamine (antioxidant 32);
N-(p-toluene sulfonyl)-N'-phenyl-p-phenylene diamine (antioxidant TPPD);
N-(3-methylpropenylacryloxo-2-hydroxypropyl)-N'-phenyl-p-phenylene diamine (antioxidant G-1);
N-(3-anilinophenyl)methylacrylamide;
N-hexyl-N'-phenyl-p-phenylene diamine.

[0027] In the present invention, the substituted p-phenylene diamine-type antioxidant is preferably one or more dialkyl p-phenylene diamines wherein the hydrogen atoms of the amino groups therein are substituted by two alkyl radicals, two aryl radicals or one alkyl radical and one aryl radical, and particularly preferably one or more substituted dialkyl p-phenylene diamines, wherein the two amino groups therein are independently substituted with an alkyl radical having 4 to 10 carbon atoms or an aryl radical having 6 to 15 carbon atoms, such as, one or more of N,N'-diheptyl-p-phenylene diamine, N,N'-di-sec-butyl-p-phenylene diamine, N,N'-bis-(1-ethyl-3-methylamyl) p-phenylene diamine, N,N'-bis-(1,4-dimethylbutyl) p-phenylene diamine, N,N'-dioctyl-p-phenylene diamine, and N,N'-bis-(1-methylheptyl) p-phenylene diamine.

[0028] The substituted quinoline-type antioxidant includes, but is not limited to the following:

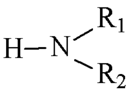
6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (antioxidant AW);
6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline (antioxidant PMQ);
6-dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline (antioxidant DD);
2,2,4-trimethyl-1,2-dihydroquinoline polymer (antioxidant RD, antioxidant124);
a product of low-temperature reaction of a diphenylamine with acetone (antioxidant BAS);
a product of high-temperature reaction of a diphenylamine with acetone (antioxidant BLE);
a product of reaction of a diphenylamine with acetone and aldehyde (antioxidant BXA);
a product of reaction of phenyl-β-naphthylamine with acetone (antioxidant APN, antioxidant AM).

[0029] The arylamine antioxidant is preferably a substituted p-phenylene diamine-type arylamine antioxidant.

[0030] In the present invention, the component (a) is most preferably one or more of N,N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine, N-octyl-N'-phenyl-p-phenylene diamine, N,N'-diheptyl-p-phenylene diamine, N,N'-di-sec-butyl-p-phenylene diamine, N,N'-dioctyl-p-phenylene diamine, N,N'-bis-(1-methylheptyl) p-phenylene diamine, N,N'-bis-(1-ethyl-3-methylamyl) p-phenylene diamine and N,N'-bis-(1,4-dimethylbutyl) p-phenylene diamine.

Component (b)

[0031] Said polyamine is an organic amine having the structure shown by the structural formula (A):



$$H-N(R_1)(R_2)$$

(A)

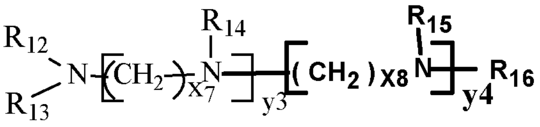
wherein R_1 and R_2 are each independently H, a hydrocarbyl having from 1 to 30 carbon atoms or a hydrocarbyl having from 1 to 30 carbon atoms and bearing a group selected from carbonyl, hydroxyl, carboxyl, ester group, acyl, alkoxy, nitro, cyano, halo, amine group or amino, wherein said hydrocarbyl having from 1 to 30 carbon atoms and a group selected from carbonyl, hydroxyl, carboxyl, ester group, acyl, alkoxy, nitro, cyano, halo, amine group or amino can be further substituted by a hydrocarbyl having from 1 to 30 carbon atoms or a group selected from carbonyl, hydroxyl, carboxyl, ester group, acyl, alkoxy, nitro, cyano, halo, amine group or amino, or can form a ring,
with the proviso that said organic amine comprises two or more N atoms.

[0032] The polyamine of formula (A) is one or more of the following amines:

an amine of the structural formula:

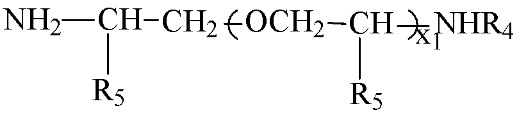
$H_2N\text{-}R_3\text{-}NHR_4$

wherein R_3 is an hydrocarbylene having 1 to 30 carbon atoms or a polyether group, and R_4 is a hydrocarbyl having 1 to 30 carbon atoms or a polyether group, wherein said polyether group includes a group of condensed ethylene oxide or propylene oxide having a number of condensation of between 1 and 30 Preferably, said polyamines includes hexanediamine, N-cocoyl-1,3-propylene diamine, N-oleyl-1,3-propylene diamine, and N-tallow-1,3-propylene diamine;
a polyamine of the structural formula:



$$R_{12}R_{13}N-\left[(CH_2)_{x7}-N(R_{14})\right]_{y3}-\left[(CH_2)_{x8}-N(R_{15})\right]_{y4}-R_{16}$$

wherein R_{12}, R_{13}, R_{14}, R_{15} and R_{16} are each independently H or a hydrocarbyl having 1 to 30 carbon atoms, x7 and x8 are integers from 0 to 10,and y3 and y4 are integers from 0 to 5, wherein one of R_{12} and R_{13} is H, and either R_{12} or R_{13} can form a ring together with R_{14} or R_{15};
a polyether diamine of formula (A1):



$$NH_2-CH(R_5)-CH_2-\left(OCH_2-CH(R_5)\right)_{x1}-NHR_4$$

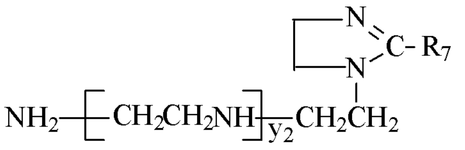
(A1)

wherein x1 is an integer from 1 to 10, R_4 is H or a hydrocarbyl having 1 to 30 carbon atoms, and R_5 is H or methyl. Preferably, said polyether diamine is a polyether diamine with the CAS number 9046-10-0, having a number average molecular weight of 400;
a polyene polyamine of the structural formula:

$H_2N[(CH_2)_{x2}NH]_{y1}R_6$

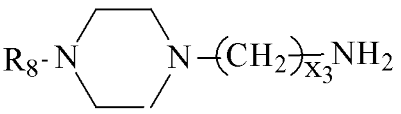
wherein x2 is an integer from 2 to 4, y1 is an integer from 1 to 8, and R_6 is H or a hydrocarbyl having 1 to 30 carbon atoms, and/or a condensate of said polyene polyamine with ethylene oxide and/or propylene oxide, such as one or more of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, propylene diamine, dipropylene triamine, tripropylene

tetramine, tetrapropylene pentamine, pentapropylene hexamine, hexapropylene heptamine, heptapropylene octamine, and N,N'-bis-(3-aminopropyl)-ethylene diamine, or one or more polyene polyamines wherein R_6 is n-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-eicosyl, n-didodecyl; isobutyl, tert-butyl, iso-amyl, neo-amyl, iso-hexyl, iso-heptyl, iso-octyl, iso-nonyl, iso-decyl, iso-dodecyl, iso-tetradecyl, iso-hexadecyl, iso-octadecyl, iso-eicosyl, 9-octadecene, phenylmethyl, phenylethyl or phenylpropyl;
an imidazoline-type polyamine of the formula (A2):



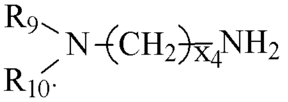
(A2)

wherein y2 is an integer from 0 to 5, and R_7 is a hydrocarbyl having 1 to 24 carbon atoms, and preferably, y2 is an integer from 1 to 3, and R_7 is C_6-C_{20} alkyl or alkenyl;
a piperazine-type polyamine of the formula (A3):



(A3)

wherein R_8 is H, a hydrocarbyl having 1 to 24 carbon atoms or $(CH_2)_{x3}NH_2$, and x3 is an integer from 0 to 5, such as N-(2-aminoethyl) piperazine or N,N'-di-(aminoethyl) piperazine;
a piperidine-type polyamine, which is 4-amino-2,2,6,6-tetramethylpiperidine or 1-(2-aminoethyl) piperidine;
a tertiary amine containing polyamine of the formula (A4), (A5) or (A6):



$$R_9R_{10}N-(CH_2)_{x4}NH_2$$

(A4)

wherein R_9 and R_{10} are hydrocarbyls having 1 to 24 carbon atoms, and x4 is an integer from 0 to 10, such as one or more of N,N-dimethyl-1,3-propylene diamine, N,N-diethyl-1,3-propylene diamine, N,N-dibutyl-1,3-propylene diamine, N,N-dimethyl-1,4-butane diamine, N,N-diethyl-1,4-butane diamine, and N,N-dimethyl-1,6-hexanediamine;

$$N\left[(CH_2)_{x5}NH_2\right]_3 \qquad \text{(A5)}$$

wherein x5 is an integer from 1 to 10, said polyamine being preferably tri-(2-aminoetyl) amine;

$$R_{11}-N\left[(CH_2)_{x6}NH_2\right]_2 \qquad \text{(A6)}$$

wherein R_{11} is a hydrocarbyl having 1 to 24 carbon atoms, and x6 is an integer from 1 to 10, and preferably an integer from 2 to 6, said polyamine being preferably N,N-bis-(3-aminopropyl) methylamine.

[0033] The term "hydrocarbyl" herein refers to hydrocarbon substituents, including aliphatic, alicyclic, aryl and heterocyclic substituents.

[0034] The aliphatic hydrocarbyl may be a saturated hydrocarbyl or unsaturated hydrocarbyl having a double or triple bond, including alkyl, alkenyl, and alkynyl.

[0035] Unless otherwise stated, the term "alkyl" in the present invention refers to linear or branched alkyl typically having 1 to 30, preferably 1 to 18 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-amyl, iso-amyl, 2-methylbutyl, neo-amyl, 3-amyl, n-hexyl, 4-methylamyl, 3-methylamyl, 2-methylamyl, 1-methylamyl, 3,3-dimethylbutyl, 2,2-dimethylbutyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 2-ethylbutyl, 1-methyl-2-methylpropyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl and the like.

[0036] Unless otherwise stated, the term "alkenyl" in the present invention refers to linear or branched alkenyl having a double bond and typically having 2 to 30, preferably 2 to 6 carbon atoms, such as vinyl, 1-propenyl, 1-propyl-2-ene, 2-propenyl, 1-butenyl, 1-butyl-2-ene, 1-butyl-3-ene, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-1-propyl-2-ene, 2-methyl-1-propyl-2-ene, 1-pentenyl, 1-amyl-2-ene, 1-amyl-3-ene, 1-amyl-4-ene, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-1-butyl-2-ene, 2-methyl-1-butyl-2-ene, 3-methyl-1-butyl-2-ene, 1-methyl-1-butyl-3-ene, 2-methyl-1-butyl-3-ene, 3-methyl-1-butyl-3-ene, 1-hexenyl, 1-hexyl-2-ene, 1-hexyl-3-ene, 1-hexyl-4-ene, 1-hexyl-5-ene, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-1-amyl-2-ene, 2-methyl-1-amyl-2-ene, 3-methyl-1-amyl-2-ene, 4-methyl-1-amyl-2-ene, 1-methyl-1-amyl-3-ene, 2-methyl-1-amyl-3-ene, 3-methyl-1-amyl-3-ene, 4-methyl-1-amyl-3-ene, 1-methyl-1-amyl-4-ene, 2-methyl-1-amyl-4-ene, 3-methyl-1-amyl-4-ene, 4-methyl-1-amyl-4-ene, and the like.

[0037] Unless otherwise stated, the term "alkynyl" in the present invention refers to linear or branched alkynyl having a triple bond and typically having 2 to 30, preferably 2 to 6 carbon atoms, such as ethynyl, 1-propynyl, 1-propyl-2-yne, 1-butynyl, 1-butyl-2-yne, 1-butyl-3-yne, 1-pentynyl, 1-amyl-2-yne, 1-amyl-3-yne, 1-amyl-4-yne, 3-methyl-1-butynyl, 1-methyl-1-butyl-2-yne, 1-methyl-1-butyl-3-yne, 2-methyl-1-butyl-3-yne, 1-hexynyl, 1-hexyl-2-yne, 1-hexyl-3-yne, 1-hexyl-4-yne, 1-hexyl-5-yne, 3-methyl-1-pentynyl, 4-methyl-1-pentynyl, 1-methyl-1-amyl-2-yne, 4-methyl-1-amyl-2-yne, 1-methyl-1-amyl-3-yne, 2-methyl-1-amyl-3-yne, and the likeo

[0038] Unless otherwise stated, the term "alicyclic hydrocarbyl" in the present invention refers to saturated cyclohydrocarbyl or unsaturated cyclohydrocarbyl having a double or a triple bond, including cycloalkyl and cycloalkenyl.

[0039] Unless otherwise stated, the "cycloalkyl" is selected from the group consisting of cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and the like. Cyclopropyl, cyclopentyl, cyclohexyl etc. are prefered, and cyclopropyl and cyclohexyl are more preferred.

[0040] Unless otherwise stated, the "cycloalkenyl" is selected from the group consisting of cyclobutenyl, cyclopentenyl, cyclohexenyl, cyclopentadienyl, cyclohexadienyl, cycloheptadienyl, cyclooctadienyl, and the like, of which cyclopentenyl, cyclohexenyl, cyclopentadienyl, cyclohexadienyl etc. are preferred, and cyclopentenyl and cyclopentadienyl are more preferred.

[0041] Unless otherwise stated, the term "aryl" in the present invention refers to any functional groups or substituents derived from simple aromatic rings, such as phenyl, and substituted phenyl (e.g., benzyl, phenylethyl, methoxyphenyl, dinitrophenyl, tert-butoxycarbonylphenyl, and the like), and fused aromatic rings, such as, naphthyl, anthryl, phenanthrenyl, and substituted naphthyl, and the like.

[0042] Unless otherwise stated, the term "heterocyclic substituent" in the present invention comprises a 3-8 membered, saturated cyclic structure containing heteroatoms, or a 3-8 membered, unsaturated cyclic structure containing heteroatoms.

[0043] Said "3-8 membered, saturated cyclic structure containing heteroatoms" refers to a 3-8 membered cyclic structure having no unsaturated bonds in the ring, such as, azacyclopropane (aziridine), 2H-azacyclopropane, diazacyclopropane, azacyclobutane, 1,2-diazacyclobutane, pyrrolidine, imidazolidine, pyrazolidine, hydrogenated pyridone, piperidine , piperazine, ethylene oxide, dioxacyclopropane, thiacyclopropane, oxacyclobutane, 1,2-dioxacyclobutane, thiacyclobutane, tetrahydrofuran, tetrahydrothiophene, 1,3-dioxacyclopentane, 1,3-dithiacyclopentane, tetrahydropyran, 1,4-dioxacyclohexane, 1,3-dioxacyclohexane, 1,3-oxythiacyclohexane, oxyazacyclopropane, oxazole, morpholine and the like.

[0044] Said "3-8 membered, unsaturated cyclic structure containing heteroatoms" refers to a 3-8 membered cyclic structure having unsaturated bonds, such as 3H-diazacyclopropene, azacyclobutadiene, 1,2-diazacyclobutene, pyrrole, dihydropyrrole, imidazole, 4,5-dihydroimidazole, pyrazole, 4,5-dihydropyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, pyridine, 2-pyridone, 4-pyridone, pyridazine, pyrimidine, pyrazine, 1,2,3-triazine, 1,2,4-triazine, 1,3,5-triazine, 1,2,4,5-tetrazine, azacycloheptantriene, 1,2-diazacycloheptantriene, 1,3-diazacycloheptantriene, 1,4-diazacycloheptantriene, azacyclooctatetraene, 1,4-dihydro-1,4-diazacyclooctatriene,1,2-dithiacyclobutene, furan, thiophene, 2,5-dihydrothiophene, 1,2-dithiacyclopentene, 2H-pyran, 2H-pyran-2-one, 3,4-dihydro-2H-pyran, 4H-pyran, 4H-pyran-4-one, 1,4-dioxacyclohexadiene, 1,4-dithiacyclohexadiene, 1,4-oxathiacyclohexadiene, oxacycloheptantriene, thiacycloheptantriene, 1,4-dioxacyclooctatriene, oxazole, 4,5-dihydrooxazole, iso-oxazole, 4,5-dihydroiso-oxazole, 2,3-dihydroisooxazole, 1,2,3-oxdiazole, 1,2,5-oxdiazole, thiazole, 4,5-dihydrothiazole, iso-thiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,3,4-thiadiazole, 2H-1,2-oxazine, 4H-1,2-oxazine, 6H-1,2-oxazine, 2H-1,3-oxazine, 4H-1,3-oxazine, 5,6-dihydro-4H-1,3-oxazine, 6H-1,3-oxazine, 2H-1,4-oxazine, 4H-1,4-oxazine, 2H-1,3-thiazine, 4H-1,3-thiazine, 5,6-dihydro-4H-1,3-thiazine, 6H-1,3-thiazine, 2H-1,4-thiazine, 4H-1,4-thiazine, morpholine, and the like Pyrrole, dihydropyrrole, imidazole, 4,5-dihydroimidazole, pyrazole, 4,5-dihydropyrazole, pyridine, pyridazine, pyrimidine, pyrazine, furan, thiophene, 2,5-dihydrothiophene, 2H-pyran, 2H-pyran-2-one, 3,4-dihydro-2H-pyran, 4H-pyran, 4H-pyran-4-one, 1,4-dioxacyclohexadiene, 1,4-dithiacyclohexadiene, 1,4-oxathiacyclohexadiene, oxazole, 4,5-dihydrooxazole, iso-oxazole, 4,5-dihydroiso-oxazole, 2,3-dihydroiso-oxazole, 1,2,3-oxdiazole, 1,2,5-oxdiazole, thiazole, 4,5-dihydrothiazole, iso-thiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,3,4-thiadiazole etc. are preferred.

[0045] The above-mentioned hydrocarbyl having 1 to 30 carbon atoms may further carry a group selected from the group consisting of carbonyl, hydroxy (-OH), carboxyl (-COOH), ester groups, acyl, alkoxy, nitro, cyano, halo and amino.

[0046] The term "halo" in the present invention refers to fluoro, chloro, bromo, iodo and the like, of which fluoro, chloro and bromo are preferred, and chloro is more preferred.

[0047] The "alkoxy" in the present invention has a linear or branched alkyl and 1 to 30, preferably 1 to 18, carbon atoms, such as, methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, n-pentoxy, iso-pentoxy, 2-methylbutoxy, neo-pentoxy, 3-pentoxy, n-hexoxy, 4-methylpentoxy, 3-methylpentoxy, 2-methylpentoxy, 1-methylpentoxy, 3,3-dimethylbutoxy, 2,2-dimethylbutoxy, 1,1-dimethylbutoxy, 1,2-dimethylbutoxy, 1,3-dimethylbutoxy, 2,3-dimethylbutoxy, 2-ethylbutoxy, 1-methyl-2-methylpropoxy, n-heptoxy, n-octoxy, n-nonyloxy, n-decyloxy, n-undecyloxy, n-dodecyloxy, n-tridecyloxy, n-tetradecyloxy, n-pentadecyloxy, n-hexadecyloxy, n-heptadecyloxy, n-octadecyloxy and the like.

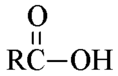
[0048] The "ester group" in the present invention has a linear or branched alkyl and 1 to 30, preferably 1 to 18, carbon atoms, such as, methyl ester group, ethyl ester group, n-propyl ester group, iso- propyl ester group, n-butyl ester group, iso-butyl ester group, sec-butyl ester group, tert-butyl ester group, n-pentyl ester group, iso-pentyl ester group, 2-methylbutyl ester group, neo-pentyl ester group, 3- pentyl ester group, n-hexyl ester group, 4-methylpentyl ester group, 3-methylpentyl ester group, 2-methylpentyl ester group, 1-methylpentyl ester group, n-heptyl ester group, n-octyl ester group, n-nonyl ester group, n-decyl ester group, n-undecyl ester group, n-dodecyl ester group, n-tridecyl ester group, n-tetradecyl ester group, n-pentadecyl ester group, n-hexadecyl ester group, n-heptadecyl ester group, n-octadecyl ester group or the like.

[0049] The "acyl" in the present invention has a linear or branched alkyl and 1 to 30, preferably 1 to 18, carbon atoms, such as, formyl, acetyl, n-propionyl, iso-propionyl, n-butyryl, iso-butyryl, sec-butyryl, tert-butyryl, n-valeryl, iso-valeryl, 2-methylbutyryl, neo-valeryl, 3-valeryl, n-hexanoyl, 4-methylvaleryl, 3-methylvaleryl, 2-methylvaleryl, 1-methylvaleryl, n-heptanoyl, n-octanoyl, n-nonanoyl, n-decanoyl, n-undecanoyl, n-dodecanoyl, n-tridecanoyl, n-tetradecanoyl, n-pentadecanoyl, n-hexadecanoyl, n-heptadecanoyl, n-octadecanoyl and the like.

[0050] Unless otherwise stated, the "hydrocarbylene" in the present invention is formed by removal of one hydrogen atom from the "hydrocarbyl" defined above. Said hydrocarbylene has 1 to 30, preferably 1 to 24 carbon atoms.

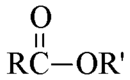
[0051] Said derivatives of polyamines are the reaction products of the ammonolysis reaction of one or more organic acids having 6 to 40 carbon atoms, acyl halides having 6 to 40 carbon atoms, or organic acid alkyl esters having 6 to 40 carbon atoms with the above-mentioned polyamines. Further preferred are the reaction products of the ammonolysis reaction of one or more monofatty acids having 6 to 40 carbon atoms, fatty acyl halides having 6 to 40 carbon atoms, or fatty acid alkyl esters having 6 to 40 carbon atoms with the above-mentioned polyamines. Said ammonolysis reaction refers to a metathetic reaction of one or more of fatty acids, fatty acyl halides and fatty acid alkyl esters with ammonia and/or amine to produce an amide. The reaction product of the above reaction can be used directly as component (b) without being isolated and purified, or the amidate alone therein can be used as component (b) after isolation and purification. Without isolation and purification, the mixture primarily comprises an amidate, and typically further comprises some unreacted starting materials and other reaction products, such as ammonium salts or alcohols. The specific composition of the mixture varies slightly depending on the reaction conditions.

[0052] The amidate according to the present invention is commercially available or obtained through a variety of known amidation reactions. For example, it is obtained by the ammonolysis reaction of an acid of formula (B1) or an ester of formula (B2) with a polyamine of formula (A) in a molar ratio of 1: (0.5-2). In said ammonolysis reaction, said polyamine is present in a stoichiometric amount or a slightly excess amount relative to said acid, acyl halide or ester. For example, an organic monocarboxylic acid of formula (B1) or an organic monocarboxylate of formula (B2) reacts with a polyamine of formula (A) in a molar ratio of 1: (1-2), and the product obtained from the ammonolysis reaction is preferably used directly as component (b) of the present invention without being isolated and purified.



$$R\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(B1)



$$RC(=O)-OR'$$

（B2）

wherein R is a hydrocarbyl having 6 to 40, preferably 8 to 36 carbon atoms.

[0053] In formula (B1), R is a hydrocarbyl having 6 to 40, preferably 8 to 36 carbon atoms. The term "hydrocarbyl" used herein is as defined above, and refers to hydrocarbon substituents, including aliphatic, alicyclic, aryl and heterocyclic substituents. The aliphatic hydrocarbyl may be a saturated hydrocarbyl or unsaturated hydrocarbyl having a double or triple bond. For example, formula (B1) may be a fatty acid, a naphthenic acid, an aromatic acid, or a substituted aromatic acid, and preferably a fatty acid, which may be a monoacid, or a polyacid, such as a diacid. Said acid can be an acid alone or a mixture of acids, such as one or more fatty acids of vegetable oils, e.g., palmitic acid, soybean oil acid, peanut oil acid, rapeseed oil acid, ricinoleic acid, and tall oil fatty acid, and is most preferably one or more liquid acids at normal temperature, e.g. oleic acid, linoleic acid, linolenic acid, dimer oleic acid, dimer linoleic acid, industrial dimer acids, soybean oil acid, peanut oil acid, rapeseed oil acid, ricinoleic acid, and tall oil fatty acid. The substituted aromatic acids are, for example, substituted benzoic acid and/or alkyl substituted salicylic acid, and the like. The fatty acids according to the present invention are C6-C40 fatty acids, preferably one or more of caproic acid, adipic acid, octanoic acid, isooctanoic acid (2-ethylcaproic acid), capric acid, dodecanic acid (lauric acid), tetradecanoic acid, hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), oleic acid, linoleic acid, linolenic acid, ricinolic acid, eicosenoic acid, arachidic acid, erucic acid, docosenoic acid, dimer acids (dimers of oleic acid and/or linoleic acid), oleic acid, linoleic acid, linolenic acid, dimer oleic acid, dimer linoleic acid, industrial dimer acids, soybean oil acid, peanut oil acid, rapeseed oil acid, ricinoleic acid, and tall oil fatty acid.

[0054] In formula (B2), R' is an alkyl having 1 to 5 carbon atoms, preferably methyl, ethyl, propyl, or isopropyl. Formula (B2) is an ester of the acid of formula (B1), preferably a methyl ester of the acid of formula (B1) or a mixture thereof, and particularly preferably a biodiesel.

[0055] Component (b) preferably comprises one or more of the following amidates, wherein the carbonyl moiety of the amide has 6 to 40, preferably 8 to 36, carbon atoms:

$NH_2[(CH_2)_{x2}NH]_{y1}COC_7H_{15}$ (octanoic acid or isooctanoic acid amide),
$NH_2[(CH_2)_{x2}NHh_{y1}COC_8H_{17}$ (nonanoic acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_9H_{19}$ (capric acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{11}H_{23}$ (lauric acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{13}H_{27}$ (tetradecanoic acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{15}H_{31}$ (palmitic acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{17}H_{35}$ (stearic acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{17}H_{33}$ (oleic acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{17}H_{33}O$ (ricinolic acid amide),
$NH_2[(CH_2)_{x2}NH]_{y1}COC_{17}H_{31}$ (linoleic acid amide),and $NH_2[(CH_2)_{x2}NH]_{y1}COC_{21}H_{41}$ (erucic acid amide),

wherein x2 is an integer of from 2 to 4,and y1 is an integer of from 2 to 8, and further preferably, x2 is 2,and y1 is an integer of from 2 to 5. Namely, the further preferred component (b) comprises one or more of the following amidates:

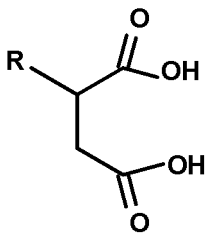
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_7H_{15}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_8H_{17}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_9H_{19}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{11}H_{23}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{13}H_{27}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{15}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{17}H_{35}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}O$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{17}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{21}H_{41}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_7H_{15}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_8H_{17}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_9H_{19}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{11}H_{23}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{13}H_{27}$,

$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{15}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{35}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}O$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{21}H_{41}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_7H_{15}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_8H_{17}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_9H_{19}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{11}H_{23}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{13}H_{27}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{15}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{35}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}O$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{21}H_{41}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{11}H_{23}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{13}H_{27}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{15}H_{31}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{35}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{33}$,
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCOC_{17}H_{31}$,and
$(NH_2CH_2CH_2)_5NHCOC_{17}H_{33}O$.

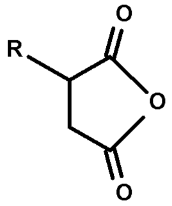
[0056] Said derivatives of polyamines can also be the reaction products of the condensation reaction of the above-mentioned polyamines with C1-C6 aldehyde. The condensation reaction of polyamines with aldehydes is commonly known in the art. The products are predominantly substituted triazines or substituted methanes. The reaction conditions generally include a molar ratio of total polyamines to C1-C6 aldehyde of 1: (0.1-10), preferably 1: 0.2-5, and more preferably 1: 0.3-3, in no presence of a solvent or at the present of a solvent, which is a hydrocarbon solvent, such as hexane, heptane, toluene, or xylene, added for refluxing and separating the reaction water, at a temperature of typically 80-150 °C, for a period of time such that the rection no longer generates water, which is generally from 30 minutes to 10 hours. Said C1-C6 aldehyde is one or more of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, Cyclohexanecarboxaldehyde and an aqueous solution of one or more of them, and preferably one or more of formaldehyde, acetaldehyde, propionaldehyde, Cyclohexanecarboxaldehyde and an aqueous solution of one or more of them. Said formaldehyde may be in the form of a formaldehyde solution or a polyformaldehyde.

[0057] Said derives of polyamines can also be the reaction products of the ammonolysis reaction of an acylating agent containing two acyl groups (C=O) in a molecule and 6-34 carbon atoms with the above-mentioned polyamines in a molar ratio of 1: (0.5-2), wherein said acylating agent containing two acyl groups in a molecule is one or more of a C6-C30 hydrocarbyl substituted organic dicarboxylic acid, a C6-C30 hydrocarbyl substituted anhydride, and a C6-C30 hydrocarbyl substituted half ester. Said ammonolysis reaction refers to a metathetic reaction of one or more of fatty acids, fatty acyl halides and fatty acid alkyl esters with polyamine to produce an amide. The reaction product of the above reaction can be used directly as component (b) without being isolated and purified, or the amidate alone therein can be used as component (b) after isolation and purification. Without isolation and purification, the mixture primarily comprises an amidate, and typically further comprises some unreacted starting materials and other reaction products, such as ammonium salts or alcohols. The specific composition of the mixture varies slightly depending on the reaction conditions.

[0058] In the present invention, the C6-C30 hydrocarbyl substituted organic dicarboxylic acid may be one or more of C6-C30 hydrocarbyl substituted maleic acid, butane dicarboxylic acid (succinic acid), fumaric acid, itaconic acid, citraconic acid, isatoic acid, and phthalic acid; the C6-C30 hydrocarbyl substituted anhydride may be one or more of C6-C30 hydrocarbyl substituted maleic anhydride, succinic anhydride (butane dicarboxylic acid anhydride), itaconic anhydride, citraconic anhydride, isatoic anhydride and phthalic anhydride; the C6-C30 hydrocarbyl substituted half ester may be a partially esterified product of the above C6-C30 hydrocarbyl substituted organic dicarboxylic acid or hydride with an alcohol, preferably a fatty alcohol. That is, a product is obtained by the esterification reaction of one of the two carbonyl groups in the organic dicarboxylic acid or anhydride with the alcohol, while the other carbonyl group does not take part in the esterification reaction. In the present invention, the preferred acylating agent containing two acyl groups in a molecule is one or more of C6-C30 hydrocarbyl substituted succinic acid and C6-C30 hydrocarbyl substituted succinic anhydride. Preferably, the structural formula of the C6-C30 hydrocarbyl substituted succinic acid is shown by formula (B3), and the structural formula of the C6-C30 hydrocarbyl substituted succinic anhydride is shown by formula (B4):



（B3）



（B4）

wherein R is a hydrocarbyl having 6 to 30 carbon atoms. The term "hydrocarbyl" used herein is as defined above, and refers to hydrocarbon substituents, including aliphatic, alicyclic, aryl and heterocyclic substituents. The aliphatic hydrocarbyl may be a saturated hydrocarbyl or unsaturated hydrocarbyl having a double or triple bond. R is preferably an aliphatic hydrocarbyl having 8 to 24 carbon atoms, especially linear alkyl or alkenyl.

[0059] Representative C6-C30 hydrocarbyl substituted organic dicarboxylic acids useful as acylating agents in the present invention may be one or more of nonylsuccinic acid, decylsuccinic acid, dodecylsuccinic acid, tridecylsuccinic acid, tetradecylsuccinic acid, pentadecylsuccinic acid, hexadecylsuccinic acid, octadecylsuccinic acid, nonenylsuccinic acid, decenylsuccinic acid, dodecenylsuccinic acid, tetradecenylsuccinic acid, cetenylsuccinic acid, octadecenesuccinic acid, and docosenylsuccinic acid.

[0060] Representative C6-C30 hydrocarbyl substituted anhydrides useful as acylating agents in the present invention may be one or more of nonylsuccinic anhydride, decylsuccinic anhydride, dodecylsuccinic anhydride, tridecylsuccinic anhydride, tetradecylsuccinic anhydride, pentadecylsuccinic anhydride, hexadecylsuccinic anhydride, octadecylsuccinic anhydride, nonenylsuccinic anhydride, decenylsuccinic anhydride, dodecenylsuccinic anhydride, tetradecenylsuccinic anhydride, cetenylsuccinic anhydride, octadecenesuccinic anhydride, and docosenylsuccinic anhydride.

[0061] The process for preparing the above-mentioned C6-C30 hydrocarbyl substituted succinic anhydride is commonly known in the art, such as the thermal polymerization of a polyolefin having a corresponding chain length with maleic anhydride, or the substitution of a chlorinated hydrocarbon, e.g., a chlorinated polyolefin, with maleic anhydride. Please refer to US3361673, US3676089 and US3172892 for details.

[0062] The above-mentioned hydrocarbyl substituted succinic acid is commercially available or obtainable by a variety of methods known in the art, such as by hydrolysis of the corresponding hydrocarbyl substituted succinic anhydride by treating it with water or water vapor. Specific conditions and operations for hydrolysis are known by the person skilled in the art.

[0063] The ammonolysis reaction of the above-mentioned hydrocarbyl substituted succinic acid and/or succinic anhydride with a polyamine is commonly known in the art, and will not be described herein for details.

[0064] The reaction product of the ammonolysis reaction of a hydrocarbyl substituted succinic acid and/or succinic anhydride with a polyamine is related to both the reaction temperature and the molar ratio of the reactants. Generally speaking, a low reaction temperature (about 100 °C) results in the production of a product with predominant amide; a high reaction temperature (about 150 °C) results in the production of a product with predominant imide. In excess succinic acid and/or succinic anhydride, two or more succinic acid and/or succinic anhydride molecules react with the same polyamine molecule to produce the so-called "double hanging" or "multiple hanging" reaction product. The present invention preferably involves excess polyamine, which results in the production of a "mono-hanging" reaction product.

component (c)

[0065] Preferably, the additive composition of the present invention further comprises component (c), which is a metal deactivator capable of reacting with a metal surface and/or a metal chelator capable of reacting with or binding to a metal or metal ion. The weight ratio of said component (a) to said component (c) is 1: 0-1, preferably 1: 0.01-1, further preferably 1: 1: 0.01-0.5, and even further preferably 1: 0.02-0.2.

[0066] Specifically, said component (c) may be one or more of benzotriazole and derivatives thereof, thiadiazole and derivatives thereof, 8-hydroxyquinoline, ethylene diamine tetracarboxylic acids, hydrazides, β-dines, β-ketone esters, Schiff's bases, and organic polycarboxylic acid and derivatives thereof. Since benzotriazole does not have an excellent solubility in biodiesel, it is generally modified by, basically, introduction thereto of an oil soluble group, such as a long-chain hydrocarbyl, in order to increase its solubility in biodiesel. Thus, said benzotriazole derivatives may be various derivatives having a better solubility in biodiesel than benzotriazole. Specifically, said benzotriazole derivative may be one or more of an ammonium salt formed by benzotriazole and a fatty amine, and a product obtained by the Mannich reaction of benzotriazole, formaldehyde and a fatty amine. Said ethylene diamine tetracarboxylic acids may be ethylene diamine tetraacetic acid (EDTA), said hydrazides may be N-salicylidene-N'-salicyl hydrazide and/or N,N'-diacetyladipoyl dihydrazide. Said β-dine is, for example, acetylacetone, and said β-ketone ester is, for example, octylacetoacetate. Said Schiff's base may be one or more of N,N'-disalicylidene-1,2-ethylene diamine, N,N'-disalicylidene -1,2-propylene diamine, N,N'-disalicylidene-1,2-cyclohexanediamine, and N,N'-disalicylidene-N'-methyldipropylene triamine. Said organic polycarboxylic acid and derivatives thereof may be, for example, one or more of citric acid, tartaric acid, malic acid, succinic acid (butane dicarboxylic acid), maleic acid, phytic acid and derives thereof.

[0067] In the present invention, said component (c) is preferably one or more of benzotriazole, an ammonium salt formed from benzotriazole and a fatty amine, a product obtained by the Mannich reaction of benzotriazole, formaldehyde and a fatty amine (such as the commercially available additive T551), Schiff's base, organic polycarboxylic acids, and a product obtained by the condensation reaction of an organic polycarboxylic acid with a fatty amine or fatty alcohol (i.e., the amide or ester derivatives of organic polycarboxylic acids).

[0068] The additive composition of the present invention may further comprise one or more additional additives, such as flow improvers, cetane number improvers, antistatic agents, preservatives, rust inhibitors, and demulsifiers, if needed.

[0069] The preparation of the additive composition of the present invention is simple, only requiring the mixing of the components for forming the additive composition homogeneously. These components may be mixed directed or in the presence of a solvent, which can be a polar solvent, such as one or more of N,N-dimethylformamide (DMF), 1,4-dioxane, tetrahydrofuran (DHF), dimethyl sulphoxide (DMSO), pyrrolidone and methylpyrrolidone, or a hydrocarbon, in particularly an aromatic, such as benzene, toluene, xylene, an aromatic diluent oil and a mixture thereof, and which can also be a biodiesel or a fatty alcohol, such as iso-octanol.

[0070] The diesel composition of the present invention can be obtained by adding an additive composition according to the present invention into a base diesel, or by adding each of the components of additives according to the present invention into a base diesel, respectively.

[0071] In the diesel composition of the present invention, the base diesel may be a pure biodiesel. Said biodiesel refers to the fatty acid low-carbon alcohol esters produced by the transesterification (alcoholysis) of oils/fats with low-carbon alcohols (such as C_1-C_5 fatty alcohols), and is commonly fatty acid methyl ester, i.e., a product of transesterification of an oil/fat with methanol.

[0072] Said transesterification may be any known or unknown process for the preparation of a biodiesel by the transesterification of an oil/fat with a low-carbon alcohol, such as, acid catalysis, base catalysis, enzyme catalysis, supercritical method and the like. Please refer to CN1473907A, DE3444893, CN1472280A, CN1142993C, CN1111591C and CN1594504A for details.

[0073] Said oil/fat has a generally recognized meaning in the art, is a general term for oils and fats, and comprises fatty acid triglyceride as the main component. Generally, those that are liquid at ambient temperature are called oils, and those that are solid or semi-solid at ambient temperature are called fats. Said oils/fats include vegetable oils and animal fats, and additionally, oil materials from microorganisms and algae, and can even be waste oils/fats, such as used or deteriorated oils/fats including used cooking oils, sewer oils, garbage oils, and acidified oils from oil/fat factories. Said vegetable oils may be oils from both herbs and woody plants, such as peanut oil, corn oil, cottonseed oil, rape seed oil, soybean oil, palm oil, safflower oil, flaxseed oil, coconut oil, oak oil, almond oil, walnut oil, castor oil, sesame oil, olive oil, Tall oil, sunflower oil, curcas oil, tung oil, sorbifolia oil, pistacia oil, and oils from halophytes, e.g., seaside mellow and cyperus beans. Said animal fats may be lard, chicken fat, duck fat, goose fat, mutton fat, horse fat, tallow, whale fat, shark fat, and the like.

[0074] In the biodiesel composition of the present invention, the base diesel may further comprise one or more additional diesels selected from the group consisting of petroleum diesel, Fischer-Tropsch synthetic diesel, hydrocracked biodiesel, and an oxygen-containing diesel concoction, wherein the ratio of the volume of said biodiesel to the volume of said additional diesels is preferably 1: 2-99.

[0075] Said patroleum diesel refers to a fuel for compression-ignited internal-combustion engines, obtained by subjecting a crude oil (petroleum) to various refining processes in a refinery, such as normal pressure-deduced process, catalytic cracking, catalytic reforming, carbonizing, hydrorefining, and hydrocracking, to produce a fraction having a distillation range between 160°C and 380 °C, and then formulating the fuel such that it will meet the national standard GB 252 for light diesels or the national standard GB 19147 for automobile diesels.

[0076] Fischer-Tropsch synthetic diesel primarily refers to GTL diesel (Gas To Liquid) or CTL diesel (Coal To Liquid) produced from natural gas or coal as the starting material, by Fischer-Tropsch (F-T) synthestic method, or BTL diesel (Biomass To Liquid) produce from plant fibers by Fischer-Tropsch synthetic method. Fischer-Tropsch synthetic diesel is substantially free of sulphur and aromatic hydrocarbon, and is a very clear fuel. However, it has a very poor lubricity. Though it has a greatly improved lubricity after being mixed with biodiesel, the oxidation stability of the blended oil may be deteriorated. Thus, a biodiesel-containing blended fuel requires the addition of antioxidants, too.

[0077] Hydrocracked biodiesel, also called second generation biodiesel, refers to the reaction products produced by the hydrogenation and cracking of animal fats and vegetable oils, which reaction products primarily comprise C_8-C_{24} alkanes, in particular C_{12}-C_{20} n-alkanes. Such hydrocracked biodiesel has a high hexadecane value but a low sulphur content and aromatic hydrocarbon content, and, when used as a fuel for diesel engines or as a blending component thereof, can greatly decrease the discharge of contaminants from diesel engines.

[0078] An oxygen-containing diesel blending component refers to an oxygen-containing compound or a mixture thereof that can be blended with various fuels for diesel engines to meet some standards or requirements. They are generally alcohols and ethers, or mixtures thereof. The alcohols may be, for example, C_1-C_{18} fatty alcohols, preferably C_1-C_{12} monofatty alcohols, such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, lauryl alcohol and various isomers thereof. The ethers may be dimethylether, methyl tert-butylether, ethyl tert-butylether, C_6-C_{14} fatty alcohol polyoxyvinylether, C_6-C_{14} fatty alcohol polyoxypropene ether, C_6-C_{14} alkylphenol polyoxyvinylether, C_6-C_{14} alkylphenol polyoxypropene ether, polyoxymethylene dimethylether ($CH_3O(CH_2O)_xCH_3$, wherein x=1-8) and mixtures thereof.

[0079] In the present invention, when the base diesel is a biodiesel-containing blended fuel, said diesel compositon can be obtained by directly mixing the additives, biodiesel and additional diesels, or by first mixing the additives and biodiesel, and then blending them with the additional diesels. The additive components can be directly mixed with the ingredients of the base diesel, or can be premixed to obtain a mixture of additives which is subsequently mixed with the base diesel or the ingredients thereof. The additive components, the biodiesel and the additional diesels are mixed in an order which is not particularly defined, and namely, they can be mixed in various orders. The mixing can be performed at various conditions producing no detrimental effects on the additive composition and diesel composition, such as at ambient temperature.

[0080] The method of increasing the oxidation stability of biodiesel, according to the present invention, comprises blending an additive into a biodiesel-containing diesel component, wherein said additive is the above-mentioned additive composition of the present invention.

[0081] The present invention will be further exemplified by the following Examples.

[0082] Preparation Examples 1-6 are used for showing the preparation of the reaction product of the ammonolysis reaction of a polyamine with a monoacylating agent.

Preparation Example 1

[0083] In a 500ml three-necked flask were added 100g lauric acid (0.5mol) and 56.7g tetraethylene pentamine (0.3mol), which were heated and stirred to 130 °C. Nitrogen gas was introduced and bubbled for 5 hours. 8.5g Water-like material was separated. By infrared analysis of the product, it was found out that the product had the characteristic peaks of amido groups ($-CO-NH_2$). Said reaction product was directly used as component (b).

Preparation Example 2

[0084] Preparation Example 2 is the same as Preparation Example 1, except that the reactant contained 141.7g (0.75mol) tetraethylene pentamine. The reaction product was directly used as component (b).

Preparation Example 3

[0085] In a 500ml three-necked flask were added 141g oleic acid (0.5mol), 77.4g N-(2-aminoethyl) piperazine (0.3mol) and 150g toluene, which were heated and stirred with refluxing and water separation for 6 hours. 8.3g Water-like material was separated, which was subjected to reduced pressure distillation to remove toluene and obtain a reaction product. By infrared analysis of the product, it was found out that the product had the characteristic peaks of amido groups. Said reaction product was directly used as component (b).

Preparation Example 4

[0086] In a 250ml three-necked flask were added 100g dimer acid (an acid number of 197mg KOH/g, a YH13-type high-purity dimer acid produced by YUANDA CHEMICALS CO., LTD., Yichun, Jiangxi Province) and 82.0g pentaethylene hexamine (in a molar ratio of the carboxyl of the dimer acid to pentaethylene hexamine of 1: 1, with the carboxyl of the dimer acid calculated on the basis of the acid number), which were heated and stirred to 140 °C. Nitrogen gas was introduced and bubbled to separate reaction water for 4 hours to obtain a reaction product. By infrared analysis of the product, it was found out that the product had the characteristic peaks of amido groups. Said reaction product was directly used as component (b).

Preparation Example 5

[0087] In a 250ml three-necked flask were added 100g tall oil fatty acid (an acid number of 190mg KOH/g, produced by Arizona) and 59.4g tri-(2-aminoethyl) amine (in a molar ratio of the carboxyl of the tall oil fatty acid to tri-(2-aminoethyl) amine of 1: 1.2, with the carboxyl of the tall oil fatty acid calculated on the basis of the acid number), which were heated and stirred to 120 °C. Nitrogen gas was introduced and bubbled to remove reaction water for 6 hours to obtain a reaction product. By infrared analysis of the product, it was found out that the product had the characteristic peaks of amido groups. Said reaction product was directly used as component (b).

Preparation Example 6

[0088] In a 250ml three-necked flask were added 100g cottonseed oil biodiesel (produced by Shijiazhuang Refining and Chemical Branch of Sinopec), 24.7g triethylene tetramine and 21.8g N-(2-aminoethyl) piperazine (in a molar ratio of the fatty acid methylester of the biodiesel to triethylene tetramine to N-(2-aminoethyl) piperazine of about 1: 0.5: 0.5), which were heated to 120 °C. Nitrogen gas was introduced and bubbled with methanol for 8 hours to obtain a reaction product. Said reaction product was directly used as component (b).

[0089] Preparation Examples 7-10 are used for showing the synthesis of the condensation product of a polyamine with an aldehyde.

Preparation Example 7

[0090] In a 500ml three-necked flask were added 56.7g tetraethylene pentamine (0.3mol), 38.7g N-(2-aminoethyl) piperazine (0.3mol) and 100g toluene, which were heated and stirred with refluxing. 42.0g formaldehyde solution having a concentration of 36 wt.% (0.5mol) was dropwisely added into the three-necked flask over a period of 2 hours. Refluxing and water separation were performed until no water was discharged (about 2 hours). After toluene was removed by reduced pressure distillation, 101g residue was obtained, which was blended with 105g aromatic diluent oil having a distillation range of 159-185 °C to form a diluent. Said diluent was directly used as component (b).

Preparation Example 8

[0091] In a 500ml three-necked flask were added 69.6g pentaethylene hexamine (0.3mol), 9.0g polyformaldehyde (0.3mol, formaldehyde) and 80g toluene, which were heated and stirred with refluxing and water separation until no water was discharged (about 5 hours). After toluene was removed by reduced pressure distillation, 73g residue was obtained, which was blended with 73g aromatic diluent oil having a distillation range of 159-185 °C to form a diluent. Said diluent was directly used as component (b).

Preparation Example 9

[0092] In a 500ml three-necked flask were added 43.8g triethylene tetramine (0.3mol), 72.6g N-dodecyl-1,3-propylene diamine (0.3mol), 18.0g polyformaldehyde (0.6mol, formaldehyde) and 125g toluene, which were heated and stirred with refluxing and water separation until no water was discharged (about 5 hours). After toluene was removed by reduced pressure distillation, 124g residue was obtained, which was blended with 120g aromatic diluent oil having a distillation range of 159-185 °C to form a diluent. Said diluent was directly used as component (b).

Preparation Example 10

[0093] In a 500ml three-necked flask were added 56.7g tetraethylene pentamine (0.3mol), 43.5g N,N-bis-(3-aminopropyl) methylamine (0.3mol) and 110g toluene, which were heated and stirred with refluxing. 29.2g formaldehyde solution having a concentration of 36 wt.% (0.35mol) was dropwisely added into the three-necked flask over a period of 1 hour. Refluxing and water separation were then performed until no water was discharged (about 3 hours). The reaction product was directly used as component (b).

[0094] Preparation Examples 11-15 are used for showing the synthesis of the acylated product of a polyamine.

Preparation Example 11

[0095] In a 500ml three-necked flask were added 56.7g tetraethylene pentamine (0.3mol), 96.5g hexadecenylsuccinic anhydride (0.3mol) and 136.5g xylene, which were heated and stirred with refluxing and water separation for 5 hours. About 5g water was separated, resulting in a mixture comprising about 50 wt.% of an ammonolysis reaction product comprising predominantly hexadecenylsuccinimide. The mixture was directly used as component (b).

Preparation Example 12

[0096] In a 500ml three-necked flask were added 46.4g pentaethylene hexamine (0.2mol), 25.8g N-(2-aminoethyl) piperazine (0.2mol), 56.8g dodecenylsuccinic acid (0.2mol) and 130g toluene, which were heated and stirred with refluxing and water separation for 6 hours. Toluene was removed by reduced pressure distillation, resulting in 121g ammonolysis reaction product comprising predominantly dodecenylsuccinic amide. Said ammonolysis reaction product was further blended with 123g aromatic diluent oil having a distillation range of 159-185 °C to form a diluent. Said diluent was directly used as component (b).

Preparation Example 13

[0097] In a 500ml three-necked flask were added 100g dodecenylsuccinic acid half ester (an additive product with the trade name T747, produced by Lushun Chemical Plant, with an acid number of about 180mg KOH/g), 46.9g triethylene tetramine (in a molar ratio of triethylene tetramine to the carboxyl of the dodecenylsuccinic acid half ester of 1: 1, calculated on the basis of the acid number of T747), and 150g aromatic diluent oil having a distillation range of 159-185 °C, which were heated and stirred. Nitrogen gas was used for bubbling to remove reaction water at 110°C for 5 hours. About 5g water was separated. The resultant product was directly used as component (b).

Preparation Example 14

[0098] In a 500ml three-necked flask were added 56.7g tetraethylene pentamine (0.3mol), 79.8g dodecenylsuccinic anhydride (0.3mol), and 136.5g aromatic diluent oil having a distillation range of 159-185 °C, which were heated and stirred. Nitrogen gas was used for bubbling to remove reaction water at 150 °C for 5 hours. About 5g water was separated, resulting in a mixture comprising about 50 wt.% of an ammonolysis reaction product comprising predominantly mono-dodecenylsuccinimide. The mixture was directly used as component (b).

Preparation Example 15

[0099] The process of Preparation Example 14 was conducted, except that 28.4g tetraethylene pentamine (0.15mol) was used for replacing 56.7g tetraethylene pentamine (0.3mol), and 108.2g aromatic diluent oil having a distillation range of 159-185 °C was used for replacing 136.5g aromatic diluent oil having a distillation range of 159-185 °C. A mixture comprising about 50 wt.% of an ammonolysis reaction product comprising predominantly bis-dodecenylsuccinimide was obtained. Said mixture was directly used as component (b).

[0100] The following Examples are used for showing the preparation of the additives in the diesel composition of the present invention.

Examples 1-9

[0101] Examples 1-9 demonstrate the preparation of the additive composition of the present invention, wherein component (b) was a polyamine.

[0102] Components (a), (b) and (c) were mixed according to the weight ratios shown in Table 1.

Table 1

Example	component (a)	component (b)	component (c)	a:b:c (weight ratio)
Example 1	N,N'-di-sec-butyl-p-phenylene diamine	Tri-(2-aminoethyl) amine	-	1:4:0
Example 2	Antioxidant 88	N-cocoyl-1,3-propylene diamine	-	1:1.2:0

(continued)

Example	component (a)	component (b)	component (c)	a:b:c (weight ratio)
Example 3	N,N'-di-sec-butyl-p-phenylene diamine	Tetraethylene pentamine	-	1:1:0
Example 4	N,N'-di-sec-butyl-p-phenylene diamine	Tetraethylene pentamine	N,N'-disalicylidene -1,2-propylene diamine	1:1:0.06
Example 5	Antioxidant 4020	N,N-dimethyl-1,3-propylene diamine	-	2:1:0
Example 6	N,N'-bis-(1-methyl-heptyl) p-phenylene diamine (antioxidant 288)	Polyether diamine -(CAS No. 9046-10-0)		1:2:0
Example 7	Antioxidant 88	N-(2-aminoethyl) piperazine	-	1:0.2:0
Example 8	Antioxidant 688	N,N-bis-(3-amino-propyl) methylamine	-	1:0.5:0
Example 9	N,N'-di-sec-butyl-p-phenylene diamine	N-(2-aminoethyl) piperazine	-	1:8:0

[0103] Either component (a) or component (b) alone was used as a biodiesel antioxidant, was combined, according to the process of the present invention, with an organic amine beyond the scope of the amine of the present invention as component (b), forming the following comparative examples of the present invention:

Comparative Example a1: N,N'-di-sec-butyl-p-phenylene diamine;
Comparative Example b1: tri(2-aminoethyl) amine;
Comparative Example a2: antioxidant 88;
Comparative Example b2: N-cocoyl-1,3-propylene diamine;
Comparative Example b3: tetraethylene pentamine;
Comparative Example a3: antioxidant 4020;
Comparative Example b4: N,N-dimethyl-1,3-propylene diamine;
Comparative Example a4: N,N'-bis-(1-methylheptyl) p-phenylene diamine;
Comparative Example b5: polyether diamine (CAS No. 9046-10-0);
Comparative Example a5: antioxidant 688;
Comparative Example b6: N-(2-aminoethyl) piperazine;
Comparative Example b7: N,N-bis- (3-aminopropyl) methylamine;
Comparative Example 1: a combination of N,N'-di-sec-butyl-p-phenylene diamine with N,N-dimethylcyclohexylamine in a weight ratio of 1: 1;
Comparative Example 2: a combination of N,N'-di-sec-butyl-p-phenylene diamine with N,N,N',N'-tetramethyl-1,4-butane diamine in a weight ratio of 1: 1;
Comparative Example 3: a combination of N,N'-di-sec-butyl-p-phenylene diamine with triethylene diamine (TEDA) in a weight ratio of 1: 1.

Examples 10-17

[0104] The following Examples demonstrate the preparation of the additive composition of the present invention, wherein component (b) was a polyamine derivative produced by the amination reaction of a monofatty acid or ester with a polyamine.

[0105] Components (a), (b) and (c) were mixed according to the weight ratios shown in Table 2.

Table 2

Example	component (a)	component (b)	component (c)	a:b:c
Example 10	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 1	-	2:1:0
Example 11	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 2	-	2:1:0
Example 12	Antioxidant 88	Preparation Example 3	-	1:3:0
Example 13	Antioxidant 288	Preparation Example 3	-	1:2:0
Example 14	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 4	-	1:1:0
Example 15	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 4	N,N'-disalicylidene -1,2-propylene diamine	1:1:0.0 6
Example 16	Antioxidant 688	Preparation Example 5	-	3:1:0
Example 17	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 6	-	1:5:0

Comparative Example b8: Preparation Example 1;
Comparative Example b9: Preparation Example 2;
Comparative Example b10: Preparation Example3;
Comparative Example b11: Preparation Example 4;
Comparative Example b12: Preparation Example 5;
Comparative Example b13: Preparation Example 6.

Examples 18-24

[0106] Examples 18-24 demonstrate the preparation of the additive composition of the present invention, wherein component (b) was a polyamine derivative produced by the amination reaction of an aldehyde with a polyamine.

[0107] Components (a), (b) and (c) were mixed according to the weight ratios shown in Table 3.

Table 3

Example	component (a)	component (b)	component (c)	a:b:c
Example 18	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 7	-	2:1:0
Example 19	Antioxidant 88	Preparation Example 8	-	1:3:0
Example 20	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 9	-	1:1:0
Example 21	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 9	Tartaric acid	1:1:0.2
Example 22	Antioxidant 288	Preparation Example 10	-	3:1:0
Example 23	4,4'-dioctyldiphenyl amine	Preparation Example 7	-	2:1:0
Example 24	Antioxidant 688	Preparation Example 9	-	1:1:0

Comparative Example b14: Preparation Example 7;
Comparative Example b15: Preparation Example 8;
Comparative Example b16: Preparation Example 9;
Comparative Example b17: Preparation Example 10;
Comparative Example a6: 4,4'-dioctyldiphenylamine.

Examples 25-31

[0108] Examples 25-31 demonstrate the preparation of the additive composition of the present invention, wherein component (b) was a polyamine derivative produced by the amination reaction of a diacylating agent with a polyamine.

[0109] Components (a), (b) and (c) were mixed according to the weight ratios shown in Table 4.

Table 4

Example	component (a)	component (b)	component (c)	a:b:c
Example 25	Antioxidant 88	Preparation Example 11	-	2:1:0
Example 26	4,4'-dioctyldiphenyl amine	Preparation Example 11	-	2:1:0
Example 27	Antioxidant 288	Preparation Example 13	-	1:4:0
Example 28	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 12	-	1:1:0
Example 29	N,N'-di-sec-butyl-p-phenylene diamine	Preparation Example 12	N,N'-disalicylidene -1,2-propylene diamine	1:1:0.06
Example 30	Antioxidant 688	Preparation Example 14	-	1:1:0
Example 31	Antioxidant 688	Preparation Example 15		1:1:0

Comparative Example b18: Preparation Example 11;
Comparative Example b19: Preparation Example 12;
Comparative Example b20: Preparation Example 13;
Comparative Example b21: Preparation Example 14;
Comparative Example b22: Preparation Example 15.

Property Tests

[0110] In the following tests, the cottonseed oil biodiesel and rapeseed oil biodiesel were the products provided by Shijiazhuang Refining and Chemical Branch of Sinopec, the sewer oil biodiesel and acidified oil biodiesel were both provided by Longyan Zhuoyue New Energy Development Co., Ltd, Fujian, and the petroleum diesel was the diesel of Beijing Standard B produced by Sinopec Yanshan Branch.

(1) Test on the oxidation stability of a biodiesel composition comprising pure biodiesel as base diesel

[0111] The oxidation stability of the biodiesel was tested by measuring its induction period at 110 °C using the EN14112: 2003 method (Rancimat method) with an instrument of model 743 for measuring the oxidation stability of a fat or oil from Metrohm Schweiz AG. The longer the induction period is, the better the antioxidative property of the diesel composition; vice versa, the shorter the induction period is, the poorer the antioxidative property of the diesel composition. The results of the test were shown in Tables 5 to 8.

Table 5

Biodiesel	Source of Additive	Amount Added/ (mg/kg)	Induction Period at 110°C/(hr)
Cottonseed Oil Biodiesel	-	-	1.0
	Example 1	500	21.4
	Comparative Example a1	100	3.1
	Comparative Example a1	500	9.8
	Comparative Example b1	400	1.1
	Comparative Example b1	500	1.6
	Example 2	550	17.6
	Comparative Example a2	250	5.9
	Comparative Example a2	550	9.3
	Comparative Example b2	300	0.9
	Comparative Example b2	550	1.9
	Example 3	400	18.4
	Comparative Example a1	200	5.4
	Comparative Example a1	400	9.0
	Comparative Example b3	200	1.0
	Comparative Example b3	400	3.1
	Comparative Example 1	400	0.9
	Example 4	412	20.5
	Example 5	600	20.9
	Comparative Example a3	400	8.5
	Comparative Example a3	600	10.1
	Comparative Example b4	200	0.9
	Comparative Example b4	600	3.0
	Example 6	750	22.1
	Comparative Example a4	250	5.4
	Comparative Example a4	750	11.1
	Comparative Example b5	500	1.5
	Comparative Example b5	750	3.1

(continued)

Biodiesel	Source of Additive	Amount Added/ (mg/kg)	Induction Period at 110°C/(hr)
Sewer Oil Biodiesel	-	-	0.9
	Example 3	600	25.1
	Comparative Example a1	300	6.7
	Comparative Example a1	600	10.9
	Comparative Example b3	300	1.0
	Comparative Example b3	600	4.2
	Comparative Example 2	600	1.2
	Comparative Example 3	600	0.4
	Example 7	600	20.4
	Comparative Example a2	600	10.2
	Comparative Example b6	100	1.0
	Comparative Example b6	600	0.9
	Example 8	750	29.8
	Comparative Example a5	500	9.0
	Comparative Example a5	750	12.8
	Comparative Example b7	250	1.1
	Comparative Example b7	750	4.9
	Example 9	720	21.3
	Comparative Example a1	720	12.2
	Comparative Example b6	720	2.9

[0112] As can be seen from the data in Table 5, component (a) was a common antioxidant, which improved the oxidation stability of biodiesel in some degree, component (b) had no antioxidative effect or a relatively poor antioxidative effect when used alone, and component (a) and component (b) used alone were both listed as comparative examples of the present invention. The oxidation stability of the biodiesel compositions of the present invention were significantly improved. A biodiesel composition comprising a combination of component (a) with component (b) produced a much better effect than the sum of the effects produced by biodiesel compositions comprising component (a) or component (b) alone. Thus it can be seen that components (a) and (b) surprisingly produced an evident synergistic effect. The effect was further enhanced by the addition of an optional component (c).

[0113] Upon comparison of Example 3 with Example 4, it can be seen that the oxidation stability of a biodiesel composition comprising the optional component (c) was further enhanced.

[0114] Upon comparison of Comparative Examples 1, 2 and 3 with Example 3, it can be seen that the combination of an amine-type compound beyond the scope of the present invention as component (b) with an antioxidant of component (a) did not produce any synergism, and on the contrary, led to disappearance of the antioxidative effect, indicating the presence of antagonism. Component (b) in Comparative Example 1 was a mono-tertiary amine, and components (b) in Comparative Examples 2 and 3 were di-tertiary amines, in which the nitrogen atom was not linked to the hydrogen atom in the molecular structure.

Table 6

Biodiesel	Source of Additive	Amount Added/ (mg/kg)	Induction Period at 110°C/(hr)
Cottonseed Oil Biodiesel	-	-	1.0
	Example 10	450	18.9
	Comparative Example a1	450	9.2
	Comparative Example b8	150	0.8
	Comparative Example b8	450	2.8
	Example 11	450	20.9
	Comparative Example b9	150	0.8
	Comparative Example b9	450	3.0
	Example 12	600	16.8
	Comparative Example a2	600	9.8
	Comparative Example b10	450	0.8
	Comparative Example b10	600	2.9
	Example 13	600	21.4
	Comparative Example a4	600	9.3
	Comparative Example b10	400	0.8
	Example 14	600	19.2
	Example 15	618	22.8
	Comparative Example a1	600	11.1
	Comparative Example b11	400	0.8
	Comparative Example b11	600	3.0
Sewer Oil Biodiesel	-	-	0.9
	Example 10	600	25.4
	Comparative Example a1	400	7.5
	Comparative Example b8	200	1.0
	Comparative Example b8	600	3.9
	Example 16	400	18.2
	Comparative Example a5	300	6.8
	Comparative Example a5	400	8.3
	Comparative Example b12	100	1.0
	Comparative Example b12	400	3.3
	Example 17	600	17.7
	Comparative Example a1	100	3.4
	Comparative Example a1	600	10.9
	Comparative Example b13	500	0.9
	Comparative Example b13	600	1.8

[0115] As can be seen from the data in Table 6, component (a) was a common antioxidant, which improved the oxidation stability of biodiesel in some degree, component (b) had no antioxidative effect or a relatively poor antioxidative effect when used alone, and component (a) and component (b) used alone were both listed as comparative examples of the present invention. The biodiesel composition of the present invention had a significantly improved oxidation stability, showing that a biodiesel composition comprising a combination of component (a) with component (b) produced a much better effect than the sum of the effects produced by biodiesel compositions comprising component (a) or component (b) alone. Thus it can be seen that components (a) and (b) surprisingly produced an evident synergistic effect. The effect was further enhanced by the addition of an optional component (c).

[0116] Upon comparison of Example 10 with Example 11, it can be seen that the reaction product resulting from excess amine during the preparation of component (b) produced a slightly better effect. Upon comparison of Example 14 with Example 15, it can be seen that the oxidation stability of a biodiesel composition comprising the optional component (c) was further enhanced.

Table 7

Biodiesel	Source of Additive	Amount Added/ (mg/kg)	Induction Period at 110°C/(hr)
Cottonseed Oil Biodiesel	-	-	1.0
	Example 18	450	19.9
	Comparative Example a1	300	7.2
	Comparative Example a1	450	9.2
	Comparative Example b14	150	1.0
	Comparative Example b14	450	2.9
	Example 19	400	16.2
	Comparative Example a2	100	4.9
	Comparative Example a2	400	8.0
	Comparative Example b15	300	0.8
	Comparative Example b15	400	1.7
	Example 20	600	20.2
	Example 21	660	25.0
	Comparative Example a1	600	11.1
	Comparative Example b16	300	1.0
	Comparative Example b16	600	3.2
	Example 22	600	22.9
	Comparative Example a4	600	9.3
	Comparative Example b17	150	0.9
	Comparative Example b17	600	3.3
	Example 23	450	6.3
	Comparative Example a6	300	3.1
	Comparative Example a6	450	4.0
	Example 24	600	18.6
	Comparative Example a5	300	6.5
	Comparative Example a5	600	10.7

(continued)

Biodiesel	Source of Additive	Amount Added/ (mg/kg)	Induction Period at 110°C/(hr)
Acidified Oil Biodiesel	-	-	0.9
	Example 18	600	25.4
	Comparative Example a1	400	7.5
	Comparative Example a1	600	10.3
	Comparative Example b14	200	1.0
	Comparative Example b14	600	3.8
	Example 19	400	20.3
	Comparative Example a2	100	4.5
	Comparative Example a2	400	8.6
	Comparative Example b15	300	1.9
	Comparative Example b15	400	3.0
	Example 23	600	8.5
	Comparative Example a6	400	4.7
	Comparative Example a6	600	5.8
	Comparative Example b14	200	1.2
	Comparative Example b14	600	3.8

[0117] As can be seen from the data in Table 7, component (a) was a common antioxidant, which improved the oxidation stability of biodiesel in some degree, and component (b) did not improve the antioxidative effect of biodiesel or had a very poor antioxidative effect when used alone in a small amount. The biodiesel composition of the present invention had a significantly improved oxidation stability. A biodiesel composition comprising a combination of component (a) with component (b) produced a much better effect than the sum of the effects produced by biodiesel compositions comprising component (a) or component (b) alone. Thus it can be seen that components (a) and (b) surprisingly produced an evident synergistic effect.

[0118] Upon comparison of Example 21 with Example 20, it can be seen that the oxidation stability of a biodiesel composition comprising the optional component (c) was further enhanced.

Table 8

Biodiesel	Source of Additive	Amount Added/(mg/kg)	Induction Period at 110 °C/(hr)
Rapeseed Oil	-	-	1.2
	Example 25	600	23.8
	Comparative Example a2	400	8.1
	Comparative Example a2	600	10.4
	Comparative Example b18	200	1.4
	Comparative Example b18	600	3.6
	Example 26	600	9.3
	Comparative Example a6	400	4.2
	Comparative Example a6	600	6.0
	Example 27	750	22.1
	Comparative Example a4	150	3.9
	Comparative Example a4	750	9.1
	Comparative Example b20	600	1.4
	Comparative Example b20	750	2.6
	Example 28	700	27.9
	Example 29	721	31.2
	Comparative Example a1	350	7.9
	Comparative Example a1	700	14.4
	Comparative Example b19	350	1.5
	Comparative Example b19	700	5.2
	Example 30	700	28.6
	Comparative Example a5	350	7.0
	Comparative Example a5	700	13.3
	Comparative Example b21	350	1.3
	Comparative Example b21	700	5.6
	Example 31	700	17.7
	Comparative Example b22	350	1.1
	Comparative Example b22	700	4.2
Sewer oil Biodiesel	-	-	0.9
	Example 27	750	29.2
	Comparative Example a4	150	4.2
	Comparative Example a4	750	12.1
	Comparative Example b20	600	3.5
	Comparative Example b20	750	4.9
	Example 28	750	24.8
	Comparative Example a1	400	7.5
	Comparative Example a1	600	10.9
	Comparative Example b19	600	3.7

[0119] As can be seen from the data in Table 8, component (a) was a common antioxidant, which improved the oxidation stability of biodiesel in some degree, and component (b) had no antioxidative effect or a relatively poor antioxidative effect when used alone. The biodiesel composition of the present invention had a significantly improved oxidation stability. A biodiesel composition comprising a combination of component (a) with component (b) produced a much better effect than the sum of the effects produced by biodiesel compositions comprising component (a) or component (b) alone. Thus it can be seen that components (a) and (b) surprisingly produced an evident synergistic effect. The effect was further enhanced by the addition of an optional component (c).

[0120] Upon comparison of Example 28 with Example 29, it can be seen that the oxidation stability of a biodiesel composition comprising the optional component (c) was further enhanced.

[0121] Upon comparison of Example 30 with Example 31, it can be seen that when component (b) was mono-alkenylsuccimide ("mono-hanging"), the combination of it with an antioxidant produced a better antioxidative effect than the combination of it with an antioxidant, when component (b) is bi-alkenylsuccimide ("double hanging").

[0122] The above oxidation stability data of additives were all obtained after three months from the production of the biodiesels. The effect of the present invention was more significant when a sewer oil biodiesel freshly produced (within one week) was used in the tests. Results were shown in Table 9.

Table 9

Biodiesel	Source of Additive	Amount Added/(mg/kg)	Induction Period at 110 °C/ (hr)
Freshly Produced Sewer Oil Biodiesel	-	-	2.1
	Example 3	500	39.8
	Comparative Example a1	250	13.1
	Comparative Example a1	500	19.7
	Comparative Example b3	250	3.8
	Comparative Example b3	500	6.3
	Example 9	720	44.9
	Comparative Example a1	80	5.1
	Comparative Example a1	720	22.7
	Comparative Example b6	640	5.9
	Comparative Example b6	720	6.2

[0123] As can be seen from Table 9, the freshly produced biodiesel was more susceptible to the antioxidant formulation of the present invention. It can be seen from Example 9 and its Comparative Examples that the use of a polyamine-type compound in the present invention greatly reduced the amount of an arylamine-type antioxidant which has some toxicity and dyeability, but produced a greatly improved effect than the arylamine-type antioxidant.

(2) Tests on the antioxidative property and oxidation stability of a blended diesel composition comprising biodiesel and petroleum diesel as base diesel, wherein the biodiesel was sewer oil biodiesel

[0124] The induction periods of the diesel compositions, petroleum diesel and blended diesels at 110 °C were independently measured by the Pr EN15751:2008 method were measured with using a tester of model 743 for measuring the oxidation stability of a fat or oil from Metrohm Schweiz AG. The longer the induction period is, the better the antioxidative property of the diesel composition; vice versa, the shorter the induction period is, the poorer the antioxidative property of the diesel composition. The results of the test were shown in Tables 10 to 13.

[0125] The amount of total insolubles (unit: mg/100 mL) in the blended diesel compositions was measured using the SH/T 0175 method, so as to assess the stability of the diesel compositions. The larger the amount of total insolubles is, the poorer the stability; vice versa, the smaller the amount of total insolubles is, the better the stability. The results of the test were shown in Tables 10 to 13.

Table 10

Base Diesel	Source of Additive	Amount Added (mg/kg)	Oxidation Stability, Induction Period (110°C)/hr	Stability, Total Insolubles (mg/100 mL)
Petroleum Diesel	-	-	>50	0.5
Petroleum Diesel: Biodiesel= 80: 20 (volume) (B20)	-	-	5.8	>10
	Example 3	200	>50	3.1
	Comparative Example a1	200	34.2	6.4
	Comparative Example b3	200	7.9	>10
	Example 5	300	>50	2.0
	Comparative Example a3	200	36.1	4.8
	Comparative Example b4	100	5.6	>10

Table 11

Base diesel	Source of Additive	Amount Added (mg/kg)	Oxidation Stability, Induction Period (110°C)/hr	Stability, Total Insolubles (mg/100 mL)
Petroleum Diesel	-	-	>50	0.5
Petroleum Diesel: Biodiesel= 85:15 (volume) (B15)	-	-	7.2	8.8
	Example 14	200	>50	1.5
	Comparative Example a1	200	32.1	5.1
	Comparative Example b11	200	6.6	9.0

Table 12

Base Diesel	Source of Additive	Amount Added (mg/kg)	Oxidation Stability, Induction Period (110 °C)/hr	Stability, Total Insolubles (mg/100 mL)
Petroleum Diesel	-	-	>50	0.5

(continued)

Base Diesel	Source of Additive	Amount Added (mg/kg)	Oxidation Stability, Induction Period (110 °C)/hr	Stability, Total Insolubles (mg/100 mL)
Petroleum Diesel: Biodiesel= 85: 15 (volume) (B15)	-	-	4.2	8.8
	Example 20	200	>50	2.5
	Comparative Example a1	200	32.1	5.1
	Comparative Example b16	200	4.6	9.0
	Example 20	90*	>50	4.8
* The amount of additive was calculated as 90 mg/kg in the blended fuel which was obtained by blending a biodiesel, in which the additive of Example 20 had been added in an amount of 600 mg/kg, with petroleum diesel in a ratio of 15: 85 by volume.				

Table 13

Base Diesel	Source of Additive	Amount Added (mg/kg)	Oxidation Stability, Induction Period (110°C)/hr	Stability, Total Insolubles (mg/100 mL)
Petroleum Diesel	-	-	>50	0.5
Petroleum Diesel: Biodiesel= 85: 15 (volume) (B15)	-	-	4.5	8.9
	Example 28	200	>50	1.3
	Comparative Example a1	200	41.8	5.4
	Comparative Example b19	200	4.6	8.7
	Example 28	90*	>50	3.4
* The amount of additive was calculated as 90 mg/kg in the blended fuel which was obtained by blending a biodiesel, in which the additive of Example 31 had been added in an amount of 600 mg/kg, with petroleum diesel in a ratio of 15: 85 by volume.				

[0126] As can be seen from the results of Tables 10 to 13, the blended fuels comprising biodiesel all had deteriorated oxidation stability and stability than petroleum diesel. However, the biodiesel composition comprising a mixture of component (a) and component (b) as additive had significantly improved oxidation stability and stability, and components (a) and (b) exhibited synergism, i.e., a significantly enhanced effect, compared with the use of one of them alone.

Claims

1. A diesel composition, which comprises a base diesel and an additive composition, **characterized in that** said base diesel comprises biodiesel, and said additive composition comprises component (a) and component (b), wherein said component (a) is an arylamine-type antioxidant, and said component (b) is one or more polyamines or derivatives thereof.

2. The diesel composition according to claim 1, wherein the weight ratio of said component (b) to said component (a) is 0.01-100:1.

3. The diesel composition according to claim 2, wherein the weight ratio of said component (b) to said component (a) is 0.05-10:1.

4. The diesel composition according to any one of claims 1-3, wherein the arylamine-type antioxidant of component (a) is at least one selected from the group consisting of a substituted naphthylamine, a substituted diphenylamine, a substituted p-phenylene diamine, and a substituted quinoline.

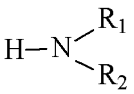
5. The diesel composition according to claim 4, wherein said substituted naphthylamine is one or more selected from the group consisting of phenyl-α-naphthylamine, phenyl-β-naphthylamine, and N-p-methoxyphenyl-α-naphthylamine, said substituted diphenylamine is one or more selected from the group consisting of alkylated diphenylamines with substituents having between 4 and 10 carbon atoms, and said substituted quinoline is one or more selected from the group consisting of 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline , 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-dodecyl-2,2,4-trimethyl-1,2-dihydroquinoline, and 2,2,4-trimethyl-1,2-dihydroquinoline.

6. The diesel composition according to claim 4, wherein the arylamine-type antioxidant of component (a) is one or more selected from the group consisting of di-substituted p-phenylene diamines with substituents having between 4 and 10 carbon atoms.

7. The diesel composition according to claim 6, wherein said arylamine-type antioxidant is N-phenyl-N'-cyclohexyl-p-phenylene diamine, N,N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine, N,N'-bis-(1,4-dimethylamyl)-p-phenylene diamine, N-p-tolyl-N'-(1,3-dimethylbutyl)-p-phenylene diamine, N,N'-diheptyl-p-phenylene diamine, N-isopropyl-N'-phenyl-p-phenylene diamine, N-isopropyl-N'-p-tolyl-p-phenylene diamine, N,N'-xylyl-p-phenylene diamine, N,N'-diphenyl-p-phenylene diamine, N,N'-di-(β-naphthyl)-p-phenylene diamine, N,N'-di-sec-butyl-p-phenylene diamine, N,N'-dioctyl-p-phenylene diamine, N,N'-bis-(1-methylheptyl) p-phenylene diamine, N,N'-bis-(1-ethyl-3-methylamyl) p-phenylene diamine, N,N'-bis-(1,4-dimethylbutyl) p-phenylene diamine, N-octyl-N'-phenyl-p-phenylene diamine, N-isobutyl-N'-phenyl-p-phenylene diamine, N,N'-dimethyl-N,N'-bis-(1-methylpropyl) p-phenylene diamine, N-(p-toluene sulfonyl)-N'-phenyl-p-phenylene diamine, N-(3-methylpropenylacryloxo-2-hydroxypropyl)-N'-phenyl-p-phenylene diamine, N-(3-anilinophenyl) methylacrylamide, or N-hexyl-N'-phenyl-p-phenylene diamine.

8. The diesel composition according to claim 6, wherein said arylamine-type antioxidant is one or more of N,N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine, N-octyl-N'-phenyl-p-phenylene diamine, N,N'-diheptyl-p-phenylene diamine, N,N'-di-sec-butyl-p-phenylene diamine, N,N'-bis-(1-ethyl-3-methylamyl) p-phenylene diamine, N,N'-bis-(1,4-dimethylbutyl) p-phenylene diamine, N,N'-dioctyl-p-phenylene diamine, and N,N'-bis-(1-methylheptyl) p-phenylene diamine.

9. The diesel composition according to any one of claims 1-3, wherein said polyamine is an organic amine having the structure shown by the following formula (A):



(A)

wherein R_1 and R_2 are each independently H, a hydrocarbyl having from 1 to 30 carbon atoms or a hydrocarbyl having from 1 to 30 carbon atoms and bearing a group selected from carbonyl, hydroxyl, carboxyl, ester group, acyl, alkoxy, nitro, cyano, halo, amine group or amino, wherein said hydrocarbyl having from 1 to 30 carbon atoms and a group selected from carbonyl, hydroxyl, carboxyl, ester group, acyl, alkoxy, nitro, cyano, halo, amine group or amino can be further substituted with a hydrocarbyl having from 1 to 30 carbon atoms or bearing a group selected from carbonyl, hydroxyl, carboxyl, ester group, acyl, alkoxy, nitro, cyano, halo, amine group or amino, or can form a ring;

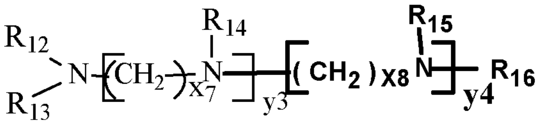
with the proviso that said organic amine comprises two or more N atoms.

10. The diesel composition according to claim 9, wherein the polyamine of formula (A) is one or more of the following amines:

an amine of the structural formula:

$H_2N\text{-}R_3\text{-}NHR_4$

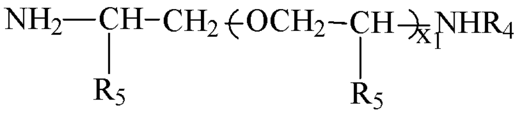
wherein R_3 is an hydrocarbylene having 1 to 30 carbon atoms or a polyether group, and R_4 is a hydrocarbyl having 1 to 30 carbon atoms or a polyether group;
a polyamine of the structural formula:



$$R_{12}R_{13}N\left[(CH_2)_{x7}N(R_{14})\right]_{y3}\left[(CH_2)_{x8}N(R_{15})\right]_{y4}R_{16}$$

wherein R_{12}, R_{13}, R_{14}, R_{15} and R_{16} are each independently H or a hydrocarbyl having 1 to 30 carbon atoms, x7 and x8 are integers from 0 to 10,and y3 and y4 are integers from 0 to 5,
wherein one of R_{12} and R_{13} is H, and either R_{12} or R_{13} can form a ring together with R_{14} or R_{15}.

11. The diesel composition according to claim 9, wherein the polyamine of formula A is a polyether diamine of formula (A1):



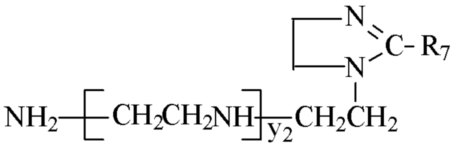
$$NH_2-CH(R_5)-CH_2\left(OCH_2-CH(R_5)\right)_{x1}NHR_4$$

(A1)

wherein x1 is an integer from 1 to 10, R_4 is H or a hydrocarbyl having 1 to 30 carbon atoms, and R_5 is H or methyl;
a polyene polyamine of the structural formula:

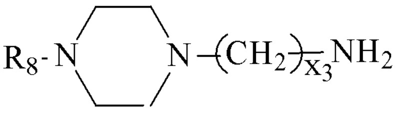
$H_2N[(CH_2)_{x2}NH]_{y1}R_6$

wherein x2 is an integer from 2 to 4, y1 is an integer from 1 to 8, and R_6 is H or a hydrocarbyl having 1 to 30 carbon atoms, and/or a condensate of said polyene polyamine with ethylene oxide and/or propylene oxide;
an imidazoline-type polyamine of the formula (A2);



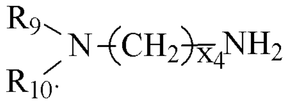
(A2)

wherein y2 is an integer from 0 to 5, and R_7 is a hydrocarbyl having 1 to 24 carbon atoms;
a piperazine-type polyamine of the formula (A3);



(A3)

wherein R_8 is H, a hydrocarbyl having 1 to 24 carbon atoms or $(CH_2)_{x3}NH_2$, and x3 is an integer from 0 to 5;
a piperidine-type polyamine;
a tertiary amine containing polyamine of the formula (A4), (A5) or (A6):



$$\begin{matrix} R_9 \\ R_{10} \end{matrix} > N \left(CH_2 \right)_{x4} NH_2$$

（A4）

wherein R_9 and R_{10} are hydrocarbyls having 1 to 24 carbon atoms, and x4 is an integer from 0 to 10;

$$N \left[\left(CH_2 \right)_{x5} NH_2 \right]_3 \qquad \text{（A5）}$$

wherein x5 is an integer from 1 to 10;

$$R_{11} - N \left[\left(CH_2 \right)_{x6} NH_2 \right]_2 \qquad \text{（A6）}$$

wherein R_{11} is a hydrocarbyl having 1 to 24 carbon atoms, and x6 is an integer from 1 to 10, and preferably an integer from 2 to 6.

12. The diesel composition according to claim 11, wherein the amine of the structural formula $H_2N\text{-}R_3\text{-}NHR_4$ is hexanediamine, N-cocoyl-1,3-propylene diamine, N-oleyl-1,3-propylene diamine, or N-tallow-1,3-propylene diamine; the polyene polyamine of the structural formula $H_2N[(CH_2)_{x2}NH]_{y1}R_6$ is one or more of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, propylene diamine, dipropylene triamine, tripropylene tetramine, tetrapropylene pentamine, pentapropylene hexamine, hexapropylene heptamine, heptapropylene octamine, and N,N'-bis(3-aminopropyl)-ethylene diamine, or one or more polyene polyamines wherein R_6 is n-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-eicosyl, n-didodecyl, iso-butyl, tert-butyl, iso-amyl, neo-amyl, iso-hexyl, iso-heptyl, iso-octyl, iso-nonyl, iso-decyl, iso-dodecyl, iso-tetradecyl, iso-hexadecyl, iso-octadecyl, iso-eicosyl, 9-octadecene, phenylmethyl, phenylethyl or phenylpropyl; a polyamine represented by the formula is a polyether diamine with the CAS number 9046-10-0 and having a Mn of 400; a polyamine represented by the formula (A2) is an imidazoline-type polyamine wherein y2 is an integer from 1 to 3, and R_7 is C_6-C_{20} alkyl or C_6-C_{20} alkenyl; the piperazine-type polyamine of the formula (A3) is N-(2-aminoethyl)piperazine or N,N'-di-(aminoethyl)piperazine, said piperidine-type polyamine is 4-amino-2,2,6,6-tetramethylpiperidine or 1-(2-aminoethyl)piperidine; the tertiary amine containing polyamine of the formula (A4) is one or more of N,N-dimethyl-1,3-propylene diamine, N,N-diethyl-1,3-propylene diamine, N,N-dibutyl-1,3-propylene diamine, N,N-dimethyl-1,4-butylene diamine, N,N-diethyl-1,4-butylene diamine, N,N-dimethyl-1,6-hexanediamine; the tertiary amine containing polyamine of the formula (A5) is tri-(2-aminoethyl) amine; the tertiary amine containing polyamine of the formula (A6) is N,N-bis-(3-aminopropyl) methylamine.

13. The diesel composition according to any one of claims 1-3, wherein said derivatives of polyamines are the reaction products of the ammonolysis reaction of one or more organic acids having 6 to 40 carbon atoms, acyl halides having 6 to 40 carbon atoms, or organic acid alkyl esters having 6 to 40 carbon atoms with the above-mentioned polyamines.

14. The diesel composition according to claim 13, wherein said derivatives of polyamines are the reaction products of the ammonolysis reaction of one or more fatty acids having 6 to 40 carbon atoms, fatty acyl halides having 6 to 40 carbon atoms, or fatty acid alkyl esters having 6 to 40 carbon atoms with the above-mentioned polyamines.

15. The diesel composition according to claim 14, wherein said fatty acid is one or more selected from the group consisting of caproic acid, adipic acid, octanoic acid, isooctanoic acid (2-ethylcaproic acid), capric acid, dodecanic acid, tetradecanoic acid, hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), oleic acid, linoleic acid, linolenic acid, ricinolic acid, eicosenoic acid, arachidic acid, erucic acid, docosenoic acid, dimer acids (dimers of oleic acid and/or linoleic acid), oleic acid, linoleic acid, linolenic acid, industrial dimer acids, soybean oil acid, peanut oil acid, rapeseed oil acid, ricinoleic acid, and tall oil fatty acid; said fatty acyl halide is an acyl halide of the above-mentioned fatty acid; said fatty acid alkyl ester is a C1-C5 alkyl ester of the above-mentioned fatty acid, in particular biodiesel.

16. The diesel composition according to any one of claims 1-3, wherein said derivatives of polyamines are the reaction products of the condensation reaction of said polyamines with C1-C6 aldehyde.

17. The diesel composition according to claim 16, wherein conditions for said condensation reaction include a molar ratio of total polyamines to C1-C6 aldehyde of 1: (0.1-10), and a reaction temperature of 80-150 °C, wherein said C1-C6 aldehyde is one or more of formaldehyde, acetaldehyde, propionaldehyde, cyclo-caproaldehyde, and an aqueous solution of one or more of them.

18. The diesel composition according to any one of claims 1-3, wherein said derives of polyamines are the reaction products of the ammonolysis reaction of an acylating agent containing two acyl groups in a molecule with the above-mentioned polyamines in a molar ratio of 1: (0.5-2), wherein said acylating agent containing two acyl groups in a molecule is one or more of a C6-C30 hydrocarbyl substituted organic dicarboxylic acid, a C6-C30 hydrocarbyl substituted anhydride, and a C6-C30 hydrocarbyl substituted half ester.

19. The diesel composition according to claim 18, wherein said acylating agent is one or more of maleic acid, succinic acid, fumaric acid, itaconic acid, citraconic acid, isatoic acid, phthalic acid, maleic anhydride, succinic anhydride, itaconic anhydride, citraconic anhydride, isatoic anhydride and phthalic anhydride, and the half esters thereof, all of which are substituted by C6-C30 hydrocarbyl.

20. The diesel composition according to claim 18, wherein said acylating agent is one or more of C6-C30 hydrocarbyl substituted succinic acid, C6-C30 hydrocarbyl substituted succinic anhydride, and the half esters thereof.

21. The diesel composition according to claim 18, wherein said acylating agent is one or more of nonylsuccinic acid, decylsuccinic acid, dodecylsuccinic acid, tridecylsuccinic acid, tetradecylsuccinic acid, pentadecylsuccinic acid, hexadecylsuccinic acid, octadecylsuccinic acid, nonenylsuccinic acid, decenylsuccinic acid, dodecenylsuccinic acid, tetradecenylsuccinic acid, cetenylsuccinic acid, octadecenesuccinic acid, docosenylsuccinic acid, nonylsuccinic anhydride, decylsuccinic anhydride, dodecylsuccinic anhydride, tridecylsuccinic anhydride, tetradecylsuccinic anhydride, pentadecylsuccinic anhydride, hexadecylsuccinic anhydride, octadecylsuccinic anhydride, nonenylsuccinic anhydride, decenylsuccinic anhydride, dodecenylsuccinic anhydride, tetradecenylsuccinic anhydride, cetenylsuccinic anhydride, octadecenesuccinic anhydride, docosenylsuccinic anhydride, and the half esters thereof.

22. The diesel composition according to any one of claims 1-3, wherein said diesel composition further comprises component (c), which is a metal deactivator capable of reacting with a metal surface and/or a metal chelator capable of reacting with or binding to a metal or metal ion.

23. The diesel composition according to claim 22, wherein the weight ratio of said component (a) to said component (c) is 1: 0.01-1.

24. The diesel composition according to claim 22, wherein said component (c) is one or more of benzotriazole, an ammonium salt formed by benzotriazole and a fatty amine, a product obtained by the Mannich reaction of benzotriazole, formaldehyde and a fatty amine, Schiff's base, and organic polycarboxylic acids.

25. The diesel composition according to claim 24, wherein said Schiff's base may be N,N'-disalicylidene-1,2-propylene diamine; said organic polycarboxylic acid is tartaric acid.

26. The diesel composition according to any one of claims 1-3, wherein said additive composition is present in an amount of 50-10000 ppm, relative to the amount of the base diesel.

27. The diesel composition according to any one of claims 1-3, wherein said base diesel further comprises one or more additional diesels selected from the group consisting of petroleum diesel, Fischer-Tropsch synthetic diesel, hydrocracked biodiesel, and an oxygen-containing diesel concoction, wherein the ratio of the volume of said biodiesel to the volume of said additional diesels is 1: 0-99.

28. A method of increasing the oxidation stability of biodiesel, comprising adding, in a biodiesel-containing base diesel, an additive composition according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/000950

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, CNPAT, CNKI: diesel, biodiesel, biofuel, fatty acid ester, fatty acid methyl ester, fatty acid ethyl ester, antioxidant, amine, aromatic amine, diamine, polyamine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO2009029373A1(ALBEMARLE CORP) 05 March 2009 (05.03.2009) examples 1-2, paragraphs [0022]-[0032] of description, claims 1-24	1-8, 22-28
X	US6083288A(BP AMOCO CORP) 04 July 2000 (04.07.2000) claims 1-25	1-8, 22-28
X	CN101319155A(BEIJING SIBOLE SCI & TECHNOLOGY DEV CO LTD) 10 December 2008 (10.12.2008) examples 1-6, claims 1-5	1-8, 22-28
A	EP1568757A1(ETHYL CORP)31 August 2005(31.08.2005) paragraphs [0011]-[0021], [0028]-[0031]of description, claims 1-13	1-28
A	WO2007145738A1(CHEMTURA CORP et al.)21.December 2007(21.12.2007) examples 1-3, claims 1-15	1-28

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search 27 August 2010 (27.08.2010)	Date of mailing of the international search report **08 Oct. 2010 (08.10.2010)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer WANG Tao Telephone No. (86-10)62084750

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2010/000950

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/000950

A. CLASSIFICATION OF SUBJECT MATTER

C10L 1/24 (2006.01) i
C10L 10/04 (2006.01) i
C10L 1/183 (2006.01) i

Form PCT/ISA /210 (extra sheet) (July 2009)

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