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(54) Titre : COMPOSITION DE CARBURANT DIESEL ET PROCEDE D'AMELIORATION DE LA FILTRABILITE DU
CARBURANT DIESEL

(54) Title: DIESEL FUEL COMPOSITION AND A METHOD TO IMPROVE FILTERABILITY OF DIESEL FUEL

(57) **Abrégé/Abstract:**

Disclosed is a stabilized diesel fuel composition comprising a) a diesel fuel with a cetane number less than or equal to 50, b) an effective amount of at least one compound selected from the group consisting of the cetane improvers and c) i) an effective stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds or ii) an effective synergistic stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds and at least one antioxidant compound selected from the group consisting of the aromatic amine antioxidants and the hindered phenolic antioxidants. The cetane improvers are for example nitrate esters. The diesel fuel compositions exhibit improved filterability.

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(54) Title: DIESEL FUEL COMPOSITION AND A METHOD TO IMPROVE FILTERABILITY OF DIESEL FUEL

(57) Abstract: Disclosed is a stabilized diesel fuel composition comprising a) a diesel fuel with a cetane number less than or equal to 50, b) an effective amount of at least one compound selected from the group consisting of the cetane improvers and c) i) an effective stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds or ii) an effective synergistic stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds and at least one antioxidant compound selected from the group consisting of the aromatic amine antioxidants and the hindered phenolic antioxidants. The cetane improvers are for example nitrate esters. The diesel fuel compositions exhibit improved filterability.

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Diesel Fuel Composition and a Method to Improve Filterability of Diesel fuel

The present invention relates to stabilized Diesel fuel compositions that comprise cetane improvers. The stabilized Diesel fuel compositions exhibit improved filterability. The Diesel fuel compositions comprise stabilizers selected from the group consisting of the stable nitroxide
5 compounds and optionally the aromatic amine and hindered phenolic antioxidants. The cetane improvers are, for example, nitrate esters.

The present compositions form reduced insoluble material that may clog fuel lines and filters.

Diesel fuel is the second most used fuel for internal combustion engines. It is used extensively in trucks, buses, and in heavy equipment, as well as in marine and stationary applica-
10 tions. Its use in passenger cars is also growing due to the higher fuel efficiency of compression ignition engines over spark ignition engines.

In Diesel engines, the fuel is ignited during the compression stroke by the heat generated due to the compression of the air in the cylinder. There is a period between when the fuel is injected into the cylinder and when the compression generated heat induces the fuel to burn.
15 This period is known as the ignition delay, and if too long, Diesel knock can occur. Other effects of long ignition delay are power loss, increased carbon monoxide production, and incomplete combustion, which leads to increased hydrocarbons and particulates in the exhaust. Recently, there has been pressure from regulatory agencies to reduce these environmental pollutants.

20 An indication of how well a particular fuel will perform in a compression ignition engine is the cetane number. Poor fuels with a long ignition delay have a low cetane number, while better fuels have higher cetane numbers. Typical values are 40-48 for a commercial Diesel fuel, and greater than 50 for a premium product. In addition to the environmental benefits, a high cetane fuel can decrease engine deposits and facilitate cold temperature starting.

25 Due to increased demand, there has been an increase in the use of cracked materials for Diesel fuel. Unfortunately, catalytic cracker, hydrocracker and coker distillates have low cetane numbers. In some cases the cetane number is below 40, which is the minimum cetane number allowed by Diesel fuel specifications. Additives known as cetane improvers have been developed that will raise the cetane number of a Diesel fuel to acceptable levels.

30 Nitrate ester cetane improvers are disclosed for example in U.S. Patent Specification Nos. 4,705,534, 5,258,049 and 5,482,518.

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Cetane improvers may destabilize Diesel fuel. In a typical thermal stability test, ASTM D6468, the fuel is aged at 150°C (302°F) for either 1.5 or 3.0 hours. Under these conditions, a thermally stable, low cetane number fuel would produce very little deposits. If a commercial cetane improver, such as 2-ethylhexyl, nitrate were added, the fuel quality with respect to combustion would increase, but more deposits would be formed in the thermal stability test. In actual engines, these deposits could lead to plugged fuel lines and clogged fuel filters.

EP-A-0947577 teaches a fuel composition that includes a cetane improver and tertiary alkyl amine thermal stabilizers. U.S. published App. No. 2002/0026743 discloses the use of heterocycles with large hydrocarbyl groups, such as polyisobutenyl succinimide, to increase the thermal stability of a cetane improver in a fuel composition.

Despite efforts to prevent the formation of insoluble material induced by the cetane improver, there remains a need to stabilize Diesel fuels more effectively. The need is greatest for those fuels that are more sensitive to the deleterious effects of the cetane improver.

Surprisingly, it has been found that hindered nitroxide stabilizers are especially suited as additives which increase the thermal stability of Diesel fuels that contain cetane improvers. The hindered nitroxide stabilizers serve to reduce the formation of insoluble material, or deposits in the Diesel fuel and thereby increase filterability and prevent plugging of fuel filters.

U.S. Patent Specification No. 5,711,767 discloses the use of stable nitroxide compounds to reduce gum formation in gasoline. U.S. Patent Specification No. 5,460,634 teaches the use of stable nitroxide compounds to reduce emissions produced by the combustion of fuels.

The present invention pertains to a stabilized Diesel fuel composition comprising

- a) A Diesel fuel with a cetane number less than or equal to 50;
- b) An effective amount of at least one compound selected from the group consisting of the cetane improvers; and
- 25 c) i) An effective stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds or
- ii) An effective synergistic stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds and at least one antioxidant compound selected from the group consisting of the aromatic amine antioxidants and the hindered phenolic antioxidants.
- 30

The additive combination of the stable nitroxide and the antioxidants of component c) is synergistic towards providing thermal stability.

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The Diesel fuel is present as the major constituent, which is present in amounts greater than 50 percent by weight of the total formulation.

- Hydrocarbon based Diesel fuels are comprised in general of mixtures of hydrocarbons which fall within the Diesel fuel boiling range, typically about 160°C to about 370°C, for example a
- 5 90% distillation point between 282°C and 338°C (ASTM D-396 and D-975). The Diesel fuel may have a specification that includes a minimum flash point of 38°C. The Diesel fuels are middle distillate fuels since they comprise the fractions, which distill after gasoline. The Diesel fuels of the invention have a low sulphur content, for example not more than 500 ppm by weight, for instance not more than 100 ppm or not more than 60 ppm by weight sulphur.
- 10 Aromatic content is in the range of 10-50% by volume, for example about 10-35% by volume. Lower sulphur content leads to lower aromatics.

Typical cetane number values are 40-48 for a commercial Diesel fuel. The present Diesel fuels have a cetane number of less than 50. That is, the present Diesel fuels have an inherent cetane number of less than 50 (prior to addition of any cetane improver).

- 15 The cetane improvers are for example selected from the group consisting of peroxides, for example di-t-butylperoxide, thioaldehydes, tertiary alkyl primary amines, perketals as disclosed in U.S. Patent Specification No. 5,011,503, alkylether/peroxide blends as disclosed in U.S. Patent Specification No. 5,520,710, peracids as disclosed in EP-A-0537931, tetrazoles and triazoles as disclosed in U.S. Patent Specification No. 4,632,674, N,N-disubstituted organic nitroxides as disclosed in U.S. Patent Specification No. 4,398,505, organic nitrates,
- 20 and mixtures thereof. The disclosures of the U.S. Patents are hereby incorporated by reference.

- The cetane improvers are in particular organic nitrates, for example nitrate esters, or alkyl nitrates. Nitrate ester cetane improvers are disclosed for example in U.S. Patent Specification
- 25 Nos. 4,705,534, 5,258,049 and 5,482,518, the disclosures of which are hereby incorporated by reference.

- The nitrate esters are for example hydrocarbyl nitrates where hydrocarbyl is a straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkyl of 2 to 24 carbon atoms interrupted by one to three oxygen atoms, straight or branched chain alkenyl of 3
- 30 to 24 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or C₁-C₄alkyl-substituted cycloalkyl of 5 to 12 carbon atoms.

Examples of hydrocarbyl are methyl, ethyl, n-propyl, isopropyl, butyl, amyl, hexyl, heptyl, octyl, isooctyl, 2-ethylhexyl, nonyl, decyl, allyl, cyclopentyl, cyclohexyl, methylcyclohexyl, cyclo-dodecyl, 2-ethoxyethyl and 2-(2-ethoxyethoxy)ethyl.

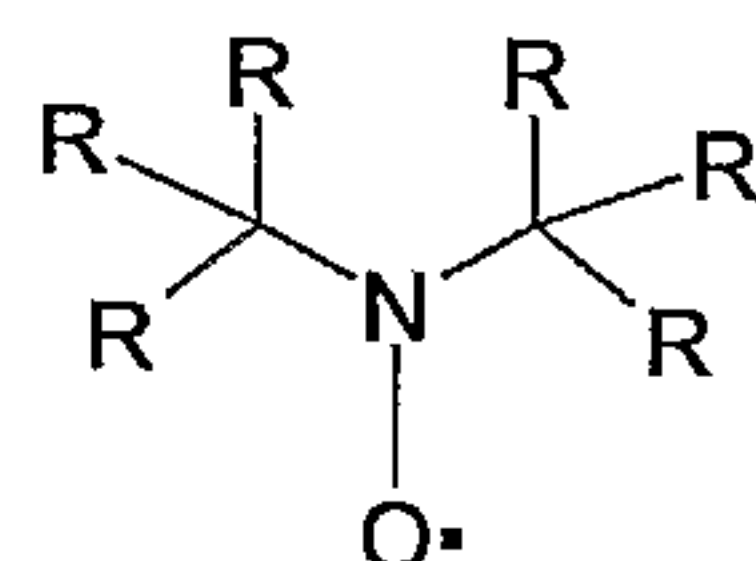
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For example, the preferred nitrate ester is 2-ethylhexyl nitrate.

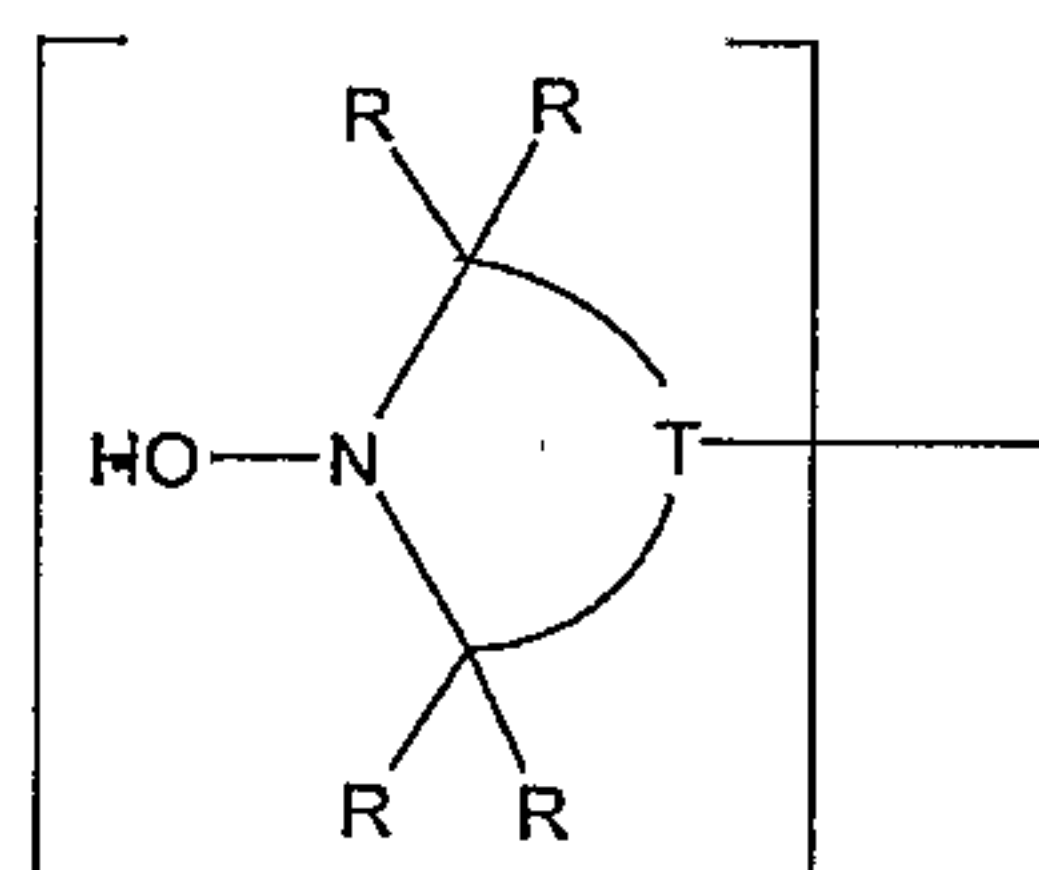
The nitroxides of this invention are for example those disclosed in U.S. Patent Specification Nos. 5,711,767 and 5,460,634, the disclosures of which are hereby incorporated by reference.

- 5 The nitroxide can be of several different classes. Both aromatic and aliphatic (often hindered amine) nitroxides are shown to be effective in the present compositions. The hindered amine nitroxides are particular value, that is compounds with a nitroxyl moiety flanked by two tertiary carbon atoms. The flanking tertiary carbon atoms may be further connected by various bridging groups to form cyclic structures, such as six-membered piperidines, piperazi-
- 10 nes, five membered pyrrolidines and the like.

The nitroxide stabilizers useful in this invention are for example of the formula

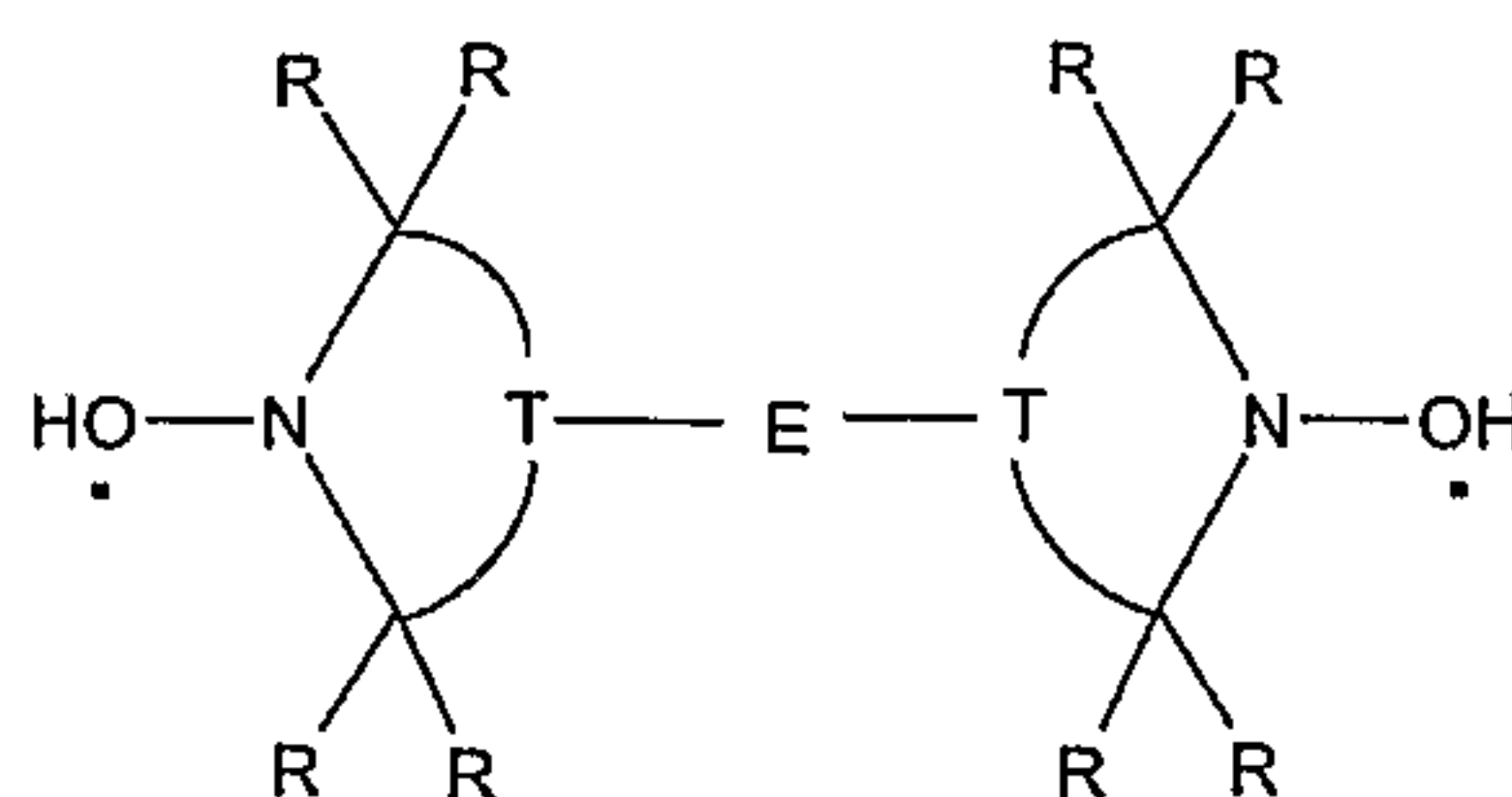


or are compounds that contain one or more groups of the formula



- 15 wherein each R is independently methyl or ethyl and T is a group required to complete a 5- or 6-membered ring.

Two or more nitroxide groups may be present in the same molecule by being linked through the T moiety as exemplified below where E is a linking group.



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The stable nitroxide compounds are for example selected from the group consisting of bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-ethoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-propoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-acetamido-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-*t*-butyl-benzoate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)*n*-butylmalonate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)phthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)isophthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)terephthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)hexahydroterephthalate, *N,N'*-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipamide, *N*-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam, *N*-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)dodecylsuccinimide, 2,4,6-tris-[*N*-butyl-*N*-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-*s*-triazine, 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one), 2-oxyl-1,1,3,3-tetramethyl-2-isobenzazole, 1-oxyl-2,2,5,5-tetramethylpyrrolidine, *N,N*-bis-(1,1,3,3-tetramethylbutyl)nitroxide, *N,N*-diphenylnitroxyl, a mixture of mono- and dialkylated *tert*-butyl/*tert*-octyl-*N,N*-diphenylnitroxyls and a mixture of mono- and dialkylated nonyl-*N,N*-diphenylnitroxyls.

The stable nitroxide compounds are for example bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-ethoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-propoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-acetamido-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine or 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one.

A specific embodiment is where the nitroxide compound is bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate or 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine.

The aromatic amine antioxidants are for example selected from the group consisting of 4-(*p*-toluene-sulphamoyl)diphenylamine, diphenylamine, *N*-allyldiphenylamine, 4-isopropoxydiphenylamine, *N*-phenyl-1-naphthylamine, *N*-(4-*tert*-octylphenyl)-1-naphthylamine, *N*-phenyl-2-naphthylamine, octylated diphenylamine, for example 4,4'-di-*tert*-octyldiphenylamine, 4-*n*-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-*tert*-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, *N,N,N',N'*-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (*o*-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, *tert*-oc-

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tylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyl-diphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isoheptyldiphenylamines, a mixture of mono- and dialkylated tert-butyl-diphenylamines,
 5 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, phenylenediamine and N,N'-di-sec-butyl-phenylenediamine.

The hindered phenolic antioxidants are for example selected from the group consisting of
 10 Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side
 15 chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1-methylundec-1-yl)phenol, 2,4-dimethyl-6-(1-methylheptadec-1-yl)phenol, 2,4-dimethyl-6-(1-methyltridec-1-yl)phenol or mixtures thereof;

Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol or 2,6-di-dodecylthiomethyl-
 20 4-nonylphenol;

Hindered hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate or bis-(3,5-di-tert-butyl-4-hydroxyphenyl)adipate;
 25 Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol or mixtures thereof (vitamin E);

Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amylphenol) or 4,4'-bis(2,6-dimethyl-4-hydroxy-
 30 phenyl)disulphide;

Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butyl-

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phenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane or 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane;

O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydi-benzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxy benzyl)sulphide or isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate;

Hydroxybenzylated malonates, for example dioctadecyl 2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)-malonate, di-octadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate or bis[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate;

Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene or 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol;

Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine or 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate;

Benzylphosphonates, for example dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxy-

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benzylphosphonate, dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate or the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid;

Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide or octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate;

- 5 Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, butanol, n-octanol, isooctanol (a mixture of octanols), octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)-isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethyl-
- 10 hexanediol, trimethylolpropane or 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane;

- Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, isooctanol (a mixture of octanols), octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thio-
- 15 diethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)-isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane or 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane;

- Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, isooctanol (a mixture of octanols), octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodi-
- 20 ethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)-isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane or 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-
- 25 [2.2.2]octane;

- Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, isooctanol (a mixture of octanols), octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate,
- 30 N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane or 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; and

Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide

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or N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Naugard® XL-1 supplied by Uniroyal).

For example, the antioxidant compound is diphenylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyl-diphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, phenylenediamine or N,N'-di-sec-butyl-phenylenediamine.

The effective stabilizing amount of component c) is from about 0.05 ppm to about 10,000 ppm, by weight, based on the weight of the fuel composition. For example component c) is present from about 0.1 ppm to about 1000 ppm, from about 0.2 ppm to about 100 ppm, or from about 0.5 ppm to about 25 ppm. For example, component c) is present from about 0.05 ppm to about 1000 ppm, from about 0.05 ppm to about 100 ppm, or from about 0.05 ppm to about 25 ppm, based on the entire fuel formulation. For instance, component c) is present from about 0.1 ppm to about 10,000 ppm, from about 0.2 ppm to about 10,000 ppm, or from about 0.5 ppm to about 10,000 ppm, based on the weight of the entire fuel formulation.

The ratio of the stable nitroxides to the antioxidants is for example from about 1:99 to about 95:5 parts by weight. For example, the ratio of the stable nitroxides to the antioxidants by weight is from about 1:10 to about 10:1, from about 1:5 to about 5:1, from about 1:3 to about 3:1, or about 1:1 parts by weight. The ratio of the stable nitroxides to the antioxidants is for example about 1:4 parts by weight.

The present stabilized compositions exhibit excellent filterability. Accordingly, provided is a process for improving the filterability and improving the cetane number of a Diesel fuel, which process comprises adding to a Diesel fuel with a cetane number less than or equal to 50,

b) An effective amount of at least one compound selected from the group consisting of the cetane improvers and

c) i) An effective stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds or

ii) An effective synergistic stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds and at least one antioxidant compound selected from the group consisting of the aromatic amine antioxidants and the hindered phenolic antioxidants.

Additional known additives may also be present in the compositions and processes of this invention. Additional additives include for example dispersants, for example hydrocarbyl-substituted succinimides or succinamides and hydrocarbylpolyamines; metallic based combus-

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tion improvers, such as ferrocene, corrosion inhibitors, other antioxidants, such as amine-formaldehyde products, anti-foams, deodorants, anti-wear agents, flow improvers, wax antisealing additives or other operability improvers, cloud point depressants, friction modifiers, solubilizers, anti-rust agents, detergents lubricants, other heat stabilizers, and the like. Other additives may be present from about 5 ppm to about 500 ppm by weight based on the weight of the entire formulation.

The invention is illustrated by the following non-limiting Example. Unless otherwise noted, parts and percentages are by weight.

Example

10 **Diesel Fuel Filterability**

Filterability is determined according to ASTM test method D6468. A Diesel fuel sample is heated under air to 150°C for either 90 or 180 minutes. The fuel is then filtered, and the amount of deposits on the filter paper is measured by reflectivity. The more deposits trapped on the filter, the lower the reflectivity of the filter pad. Too many deposits will clog filters in actual use.

The table below demonstrates results with two different low sulphur Diesel fuels. Percent reflectance is measured on samples heated to 150°C for 90 minutes. Levels are ppm based on the fuel formulation.

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Formulation	2-EHN	Compound 1	Compound 2	Compound 3	Blend 1	Percent Reflectance
A	0	---	---	---	---	94
B	1500	---	---	---	---	69
C	1500	1.4	---	---	---	74
D	1500	10.4	---	---	---	78
E	0	---	---	---	---	95
F	1500	---	---	---	---	73
G	1500	---	1.0	---	---	74
H	1500	---	10.0	---	---	78
I	1500	---	---	1.0	---	80
K	1500	---	---	10.0	---	84
L	1500	---	---	---	1.0	79
M	1500	---	---	---	10.0	84

2-EHN: 2-ethylhexyl nitrate cetane improver;

Compound 1: bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;

5 Compound 2: 1-oxyl-4-hydroxy-2,2,6,6-tetramethylpiperidine;

Compound 3: 1-oxyl-4-n-propoxy-2,2,6,6-tetramethylpiperidine;

Blend 1: 14% Compound 1, 56% by weight mixture of mono- and dialkylated tert-butyl/tert-octyl-diphenylamines, 30% inert aromatic solvent (by weight).

10 Formulations A-D are with Diesel Fuel 1. Formulations E-M are with Diesel Fuel 2. The two fuels are within ASTM D975 specifications (Diesel fuel specifications) according to the present invention.

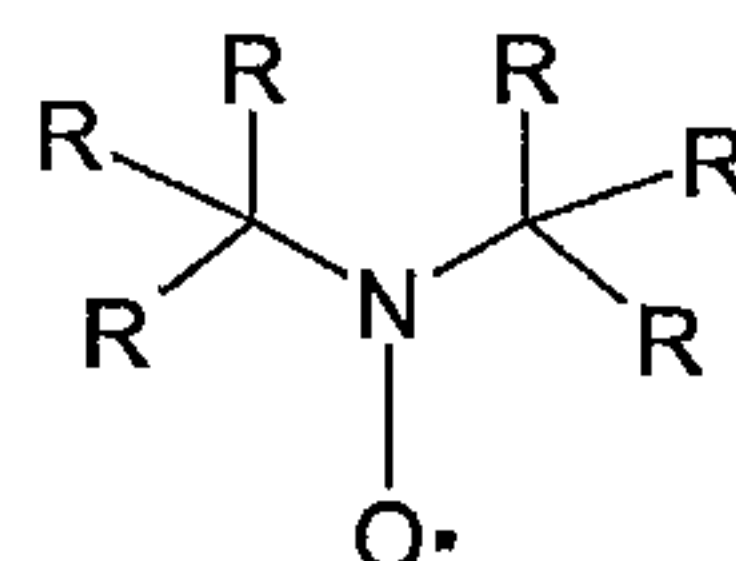
It is seen that the cetane improver significantly reduces the filterability of the Diesel fuel.

15 Even at a level of 1 ppm of added stable nitroxide compound, there is a marked decrease in precipitate as indicated by a measurable increase in filter pad reflectance. Thus, with the use of the nitroxide alone or in combination with antioxidants, there will be a reduced tendency for Diesel fuel to form insoluble material that could plug fuel filters and lines.

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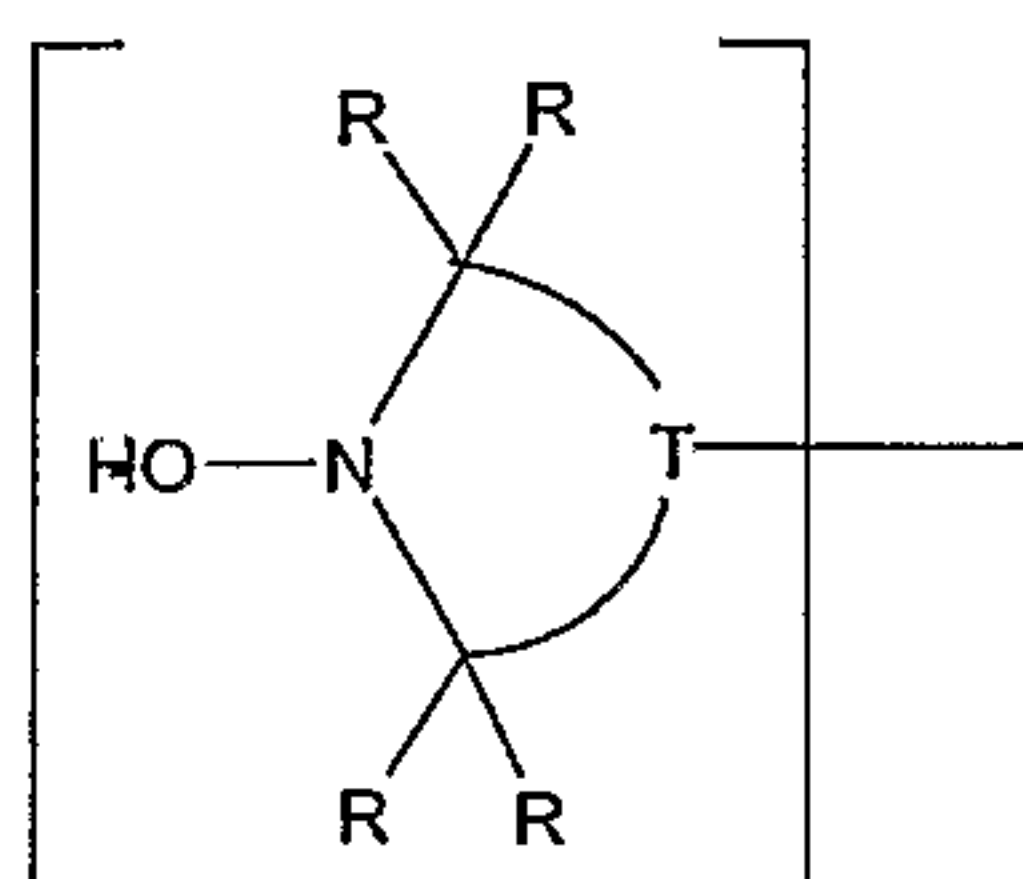
Claims

1. A stabilized Diesel fuel composition comprising
 - a) A Diesel fuel with a cetane number less than or equal to 50;
 - b) An effective amount of at least one compound selected from the group consisting of the cetane improvers; and
 - c) i) An effective stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds; or
 ii) An effective synergistic stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds and at least one antioxidant compound selected from the group consisting of the aromatic amine antioxidants and the hindered phenolic antioxidants.
2. A composition according to claim 1, in which the cetane improvers are selected from the group consisting of the hydrocarbyl nitrates where hydrocarbyl is a straight or branched chain alkyl of 1 to 24 carbon atoms, straight or branched chain alkyl of 2 to 24 carbon atoms interrupted by one to three oxygen atoms, straight or branched chain alkenyl of 3 to 24 carbon atoms, cycloalkyl of 5 to 12 carbon atoms or C₁-C₄alkyl-substituted cycloalkyl of 5 to 12 carbon atoms.
3. A composition according to claim 2, in which hydrocarbyl is selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, butyl, amyl, hexyl, heptyl, octyl, isooctyl, 2-ethylhexyl, nonyl, decyl, allyl, cyclopentyl, cyclohexyl, methylcyclohexyl, cyclododecyl, 2-ethoxyethyl and 2-(2-ethoxyethoxy)ethyl.
4. A composition according to claim 2, in which the hydrocarbyl nitrate is 2-ethylhexyl nitrate.
5. A composition according to claim 1, where the stable nitroxide compounds are of the formula

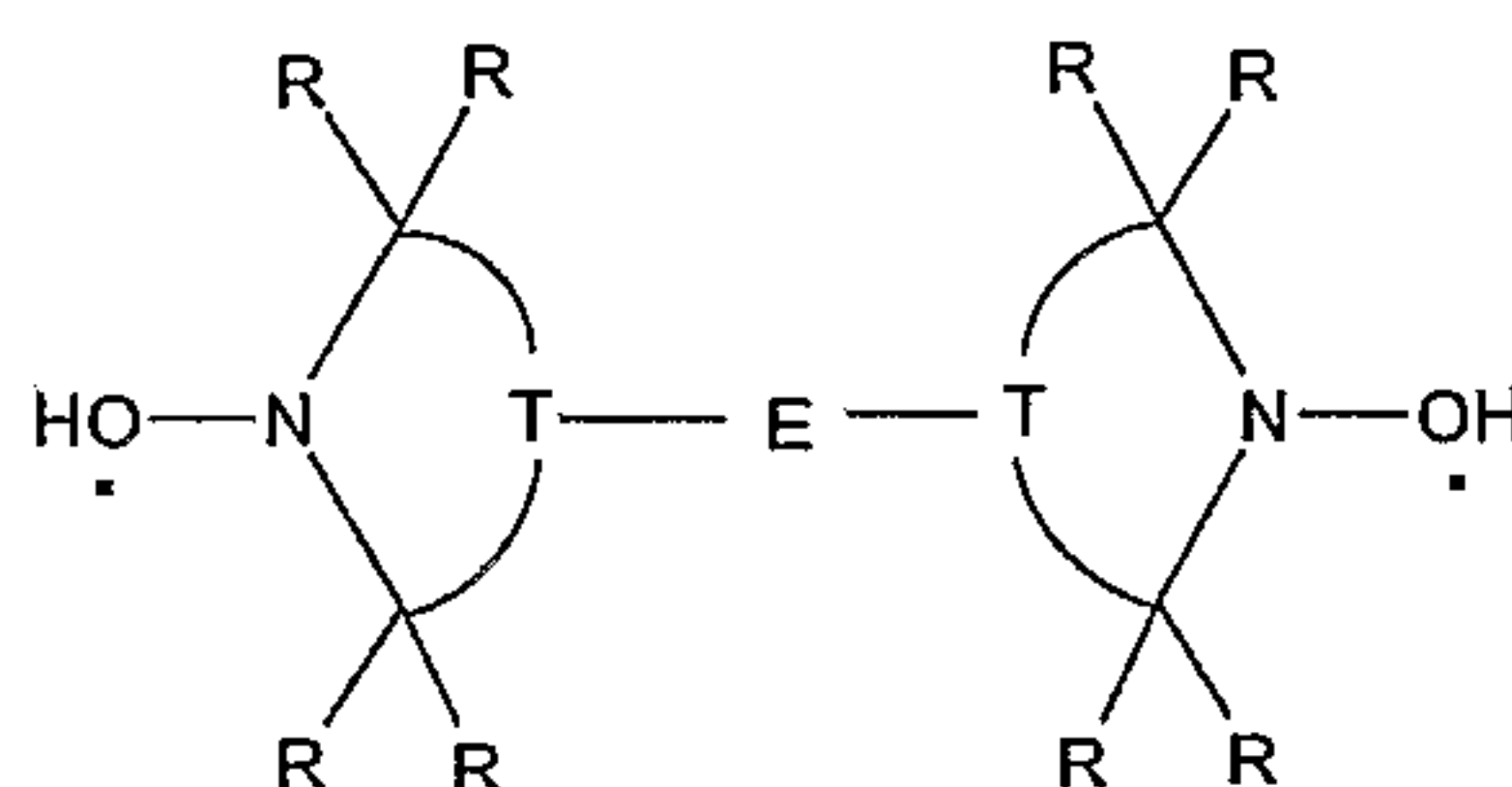


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or are compounds that contain one or more groups of the formula



or are of the formula



- 5 where each R is independently methyl or ethyl, T is a group required to complete a 5- or 6-membered ring and E is a linking group.
6. A composition according to claim 1, where the stable nitroxide compounds are selected from the group consisting of bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, 4-
 10 hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-ethoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-propoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-acetamido-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-t-butyl-benzoate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)n-butylmalonate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)phthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)isophthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)terephthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)hexahydroterephthalate, N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipamide, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)dodecylsuccinimide, 2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine, 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one), 2-oxyl-1,1,3,3-tetramethyl-2-isobenzazole, 1-oxyl-2,2,5,5-tetra-
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methylpyrrolidine, N,N-bis-(1,1,3,3-tetramethylbutyl)nitroxide, N,N-diphenylnitroxyl, a mixture of mono- and dialkylated tert-butyl/tert-octyl-N,N-diphenylnitroxyls and a mixture of mono- and dialkylated nonyl-N,N-diphenylnitroxyls.

- 5 7. A composition according to claim 6 where the stable nitroxide is bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate or 4-hydroxy-1-oxy-2,2,6,6-tetramethylpiperidine.
8. A process for improving the filterability and improving the cetane number of a Diesel fuel, which process comprises adding to a Diesel fuel with a cetane number less than or equal to 50,
- 10 b) An effective amount of at least one compound selected from the group consisting of the cetane improvers and
- c) i) An effective stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds or
- 15 ii) An effective synergistic stabilizing amount of at least one compound selected from the group consisting of the stable nitroxide compounds and at least one antioxidant compound selected from the group consisting of the aromatic amine antioxidants and the hindered phenolic antioxidants.