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Description

This invention concerns a diesel fuel having a reduced tendency to form deposits in and around the combustion chambers of diesel engines.

Oxidation of fuel and incomplete combustion results in a phenomenon known as coking, that is the deposition of highly carbonaceous material in and around the combustion chambers of internal combustion engines. First, excessive deposits around the tip of fuel injectors in indirect injection diesel engines can impair engine performance leading to poor startability, power reduction, higher noise, higher fuel consumption, etc.. Second, deposits around the pistons can lead to ring sticking, bore polishing, etc. leading to power reduction, high oil consumption, high emissions, etc.. In recent years these problems have become important because of the increasing use of indirect injection diesel engines in passenger cars particularly those operating at high speeds.

It is therefore desirable to reduce deposits to acceptable levels which do not result in impaired performance. Many products are known to reduce injector deposits when added to the fuel, whilst claims have also been made on general combustion chamber cleanliness.

We have now found that the tendency of diesel fuels to form deposits in and around the combustion chambers of the indirect injection diesel engines may be significantly reduced by incorporating in the fuel a quaternary ammonium compound. There exist several patents dating back to the 1950's, 1960's and early 1970's (i.e. prior to the development of the high speed diesel engines) which propose the addition of quaternary ammonium compounds to distillate fuels for various functions although there is no suggestion that the addition of such compounds, will reduce the formation of deposits due to incomplete fuel combustion in and around combustion chambers.

Examples of such patents include US-A-3158647 which discloses the use of quaternary ammonium fatty acid, phenate, and naphthenate salts in the stabilisation of distillate fuel oils. This patent relates to the problem of sludge deposition in distillate fuel oil during storage at ambient temperatures and the problem of sludge deposits causing clogging of burner filters etc.. This patent does not concern the formation of deposits in and around the combustion chambers of diesel engines.

US-A-3008813 and US-A-3346353 concern a petroleum distillate fuel containing an ashless oil soluble polymeric dispersant stabilising additive and a dialkyl dimethyl ammonium chloride or a dialkyl dimethyl ammonium nitrite, respectively. These additives are adapted to prevent the formation of persistent haze and stable emulsions when the petroleum distillate fuel is contacted with water during handling and storage.

US-A-3397970 relates to a petroleum distillate oil containing a pour point depressing amount of a copolymer of ethylene and an olefinically unsaturated aliphatic ester monomer (for example vinyl acetate) said copolymer tending to promote the formation of water haze in said oil, and as an inhibitor of said haze a dimer of linoleic acid and quaternary ammonium salt selected from dicocyl dimethyl ammonium chloride and dicocyl dimethyl ammonium nitrite.

US-A-3493354 discloses a diesel fuel additive containing a major amount of an organic barium compound in combination with a minor amount of a quaternary ammonium salt. The additive promotes the combustion of the fuel, thereby reducing the proportion of unburned hydrocarbons and suspended soot particles in the exhaust gases of diesel engines. The quaternary ammonium salts serves to prevent the extraction of barium by water with which the additive or fuel containing the additive may come into contact.

GB-A-973826 and GB-A-1076497 relate to using quaternary ammonium compounds, particularly nitrates as distillate fuel stabilisers whereas GB-A-1432265 proposes their use as antistatic agents together with polysulphones.

It is one object of the present invention to reduce the levels of coking deposits formed in and around the combustion chambers of diesel engines to acceptable levels withour impairing performance.

The present invention is directed to the use in an indirect injection diesel engine for inhibiting coking, especially injector nozzle coking, of a diesel fuel composition containing a minor proportion by weight of a quaternary ammonium salt soluble therein.

The four residues connected to the quaternary nitrogen atom of the quaternary ammonium salt are essentially hydrocarbyl residues. These residues may be similar or dissimilar. They may be substituted with functional groups or have incorporated therein functional groups as parts of the hydrocarbyl chain.

Usually one or two of these residues contain at least 6 carbon atoms while the remaining residues contain less than 6 carbon atoms. It is preferred that one of the residues contains at least 8 carbon atoms while the remaining residues contain less than 6 carbon atoms.

Usually the hydrocarbyl residues are alkyl groups, alkenyl groups, aryl groups or alkaryl groups. Examples of alkyl groups containing less than 6 carbon atoms are methyl, ethyl, isopropyl, propyl and butyl groups. Examples of alkyl groups containing more than 6 carbon atoms are dodecyl (lauryl), tetradecyl (myristyl), hexadecyl (cetyl) and octadecyl (stearyl) groups. Examples of alkenyl groups containing more than 6 carbon atoms are dodecenyl, tetradecenyl, octadecenyl (oleyl), and octadecadienyl (linoleyl) groups. The residues containing more than 6 carbon atoms can be derived from natural fats and oils, for example coconut oil, soya bean oil, animal tallow and the like. In such instances these residues will consist essentially of mixed alkyl groups containing 8 to 22 carbon atoms.

As mentioned above, the hydrocarbyl residues may contain functional groups. Examples of functional groups which may be present in the residues are hydroxy, halide, ester, amide, ether, amine, and sulphide functions.

It is preferred that the anionic radical is a strong acid radical. Examples of strong acid radicals useful according to the invention are nitrate, sulphate, ethosulphate, sulphonate (both alkyl and alkylaryl), sulphurised phenate, carboxylate, and borate. It is also possible to employ mixtures of anionic radicals.

When the quaternary ammonium compound is a sulphonate it can be made from :

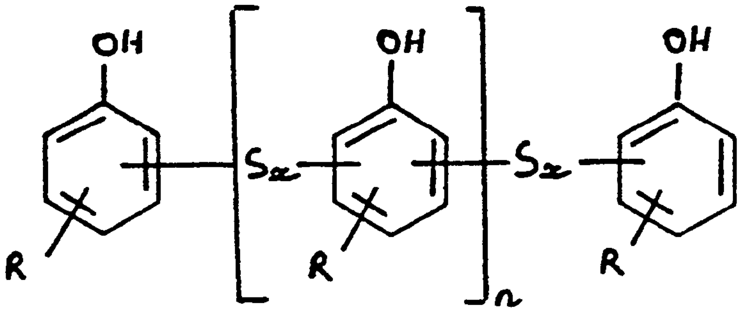
(1) Alkylbenzene-sulphonic acids or alkylnaphthalene-sulphonic acids examples of which include Benzene-sulphonic acids with straight-chain or branched single or multiple substituted alkyl radicals with 4-24 (preferably 8-20) carbon atoms in the aromatic nucleus, for example dodecylbenzene-sulphonic acid, dinonylbenzene-sulphonic acid, dodecylnaphthalenesulphonic acid etc.

(2) Alkane-sulphonic acids including Sulphonic acids possessing straight-chain or branched alkyl radicals usually with 10-30 carbon atoms, for example tetradecyl sulphonic acid etc.

(3) Alkene-sulphonic acids including Sulphonic acids which have straight-chain or branched alkenyl radicals usually with 15-30 carbon atoms, for example 2-eicosenyl sulphonic acid etc.

The sulphonic acids are typically obtained by sulphonation of alkyl substituted aromatic hydrocarbons, such as those obtained from the fractionation of petroleum by distillation and/or extraction, or by the alkylation of an aromatic hydrocarbon, for example, benzene, toluene, xylene, naphthalene, diphenyl. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to more than 30 carbon atoms, such as, for example, haloparaffins, olefins that may be obtained by dehydrogenation of paraffins, polyolefins, or, for example, polymers of ethylene, propylene, butene, etc. The alkaryl sulphonates usually contain from about 9 to about 20 or more carbon atoms, preferably from about 16 to about 50 carbon atoms per alkyl substituted aromatic moiety.

Quaternary ammonium sulphurised phenates are synthesised from sulphurised alkylphenols which have the general structure :



where R is an alkyl radical, n is an integer from 0 to 4 and x is an integer from 1 to 4. The average number of carbon atoms in all of the R groups is preferably at least about 9 in order to ensure adequate solubility in oil. The individual R groups may contain from 5 to 40, preferably 8 to 20 carbon atoms. Alkylation of phenol may be carried out with alkylating agents of the types used to alkylate aromatic hydrocarbons in the manufacture of alkaryl sulphonates. Sulphurisation may be by reaction of the alkyl phenol with sulphur chloride or by reaction with sulphur. In the latter case, the alkyl phenol is usually present as the metal salt, although other sulphurisation promoters may be used, such as amines.

Quaternary ammonium carboxylates are synthesised from :

(1) Monocarboxylic acids including
(a) Aliphatic monocarboxylic acids possessing saturated or unsaturated straight or branched chains usually with 0-6 carbon atoms, for example, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid.

(b) Aromatic monocarboxylic acids with single or multiple substituted hydrocarbon radicals possessing saturated or unsaturated straight or branched chains usually with 0-35 (preferably 0-24) carbon atoms in the aromatic nucleus, for example, benzoic acid, 0-toluic acid, m-toluic acid, p-toluic acid, p-octylbenzoic acid, p-nonylbenzoic acid, dibutylbenzoic acid, salicylic acid, methyl salicylic acid, ethyl salicylic acid, octylsalicylic acid, nonylsalicylic acid, dodecylsalicylic acid, tetradecylsalicylic acid, octadecylsalicylic acid etc.

(2) Polycarboxylic acids including

(a) Aliphatic polycarboxylic acids possessing saturated or unsaturated straight or branched chains usually with 0-80 (preferably 0-50) carbon atoms, for example oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, tricarballylic acid, polymeric fatty acids (dimeric acid, trimeric acid etc.), alkenyl succinic acids (such as polyisobutenylsuccinic acid), or the anhydrides of such polycarboxylic acids.

(b) Aromatic polycarboxylic acids with single or multiple substituted hydrocarbon radicals possessing saturated or unsaturated straight or branched chains usually with 0-35 (preferably 0-24) carbon atoms in the aromatic nucleus, for example phthalic acid, iso-phthalic acid, terephthalic acid, hemimellitic acid, trimellitic acid, trimeric acid, methyl phthalic acid, dodecylphthalic acid etc.

Preferred among the carboxylic acids are the simple monocarboxylic acids (such as formic acid and acetic acid), and the simple dicarboxylic acids (such as oxalic acid).

Many of the quaternary ammonium salts which may be employed according to the present invention are commercially available. It is preferred to use one of those readily available compounds. Alternatively the quaternary ammonium compounds can be synthesised in any suitable manner. Since the method of preparing the quaternary ammonium compounds is not part of the invention, the preparation of the compounds will not be described in detail. It should be noted, however, that we have two preferred methods for the synthesis of compounds such as quaternary ammonium sulphonates, sulphurised phenates and carboxylates.

In the first method a quaternary ammonium hydroxide is prepared by reacting a quaternary ammonium halide (for example the chloride) with an alkali metal hydroxide (for example sodium hydroxide) in an alcohol (for example methanol).

$$[R_4N]^{(+)}\ X^{(-)} + NaOH \longrightarrow [R_4N]^{(+)}\ OH^{(-)} + NaX$$

After removing the metal halide by filtration the solution of quaternary ammonium hydroxide is mixed with the acid HA where A is the desired anion in a suitable solvent and allowed to react :

$$[R_4N]^{(+)}\ OH^{(-)} + HA \longrightarrow [R_4N]^{(+)}\ A^{(-)} + H_2O$$

The rate of reaction may be increased by raising the reaction temperature above the ambient temperature. Once the reaction is complete the solvents and water are removed by distillation.

In the second method the organic acid HA is reacted with a metal oxide or hydroxide to form the metal salt:

$$HA + NaOH \longrightarrow NaA + H_2O$$

If the reaction is done in a suitable solvent (for example heptane or toluene) the water formed during the reaction may be removed by refluxing the solvent and using a Dean and Stark trap. Once all the water has been removed the solution of the metal salt is treated with a quaternary ammonium halide :

$$NaA + [R_4N]^{(+)}Cl^{(-)} \longrightarrow [R_4N]^{(+)}A^{(-)} + NaCl$$

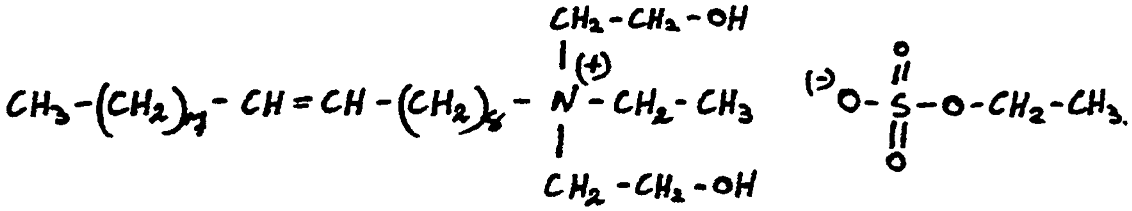
The metal halide is removed by filtration and the solvent is removed by distillation. Alternatively, the solvent can be removed by distillation and the metal halide filtered from the final product.

The amount of quaternary ammonium salt which is added to the diesel fuel is a minor proportion by weight preferably less than 1 wt.% and most preferably 0.000001 to 0.1 wt.% especially 2 to 200 ppm.

Other additive materials commonly used in diesel fuel may also be included in the diesel fuel compositions according to the present invention. Such other additive materials may comprise corrosion inhibitors, dyes and the like.

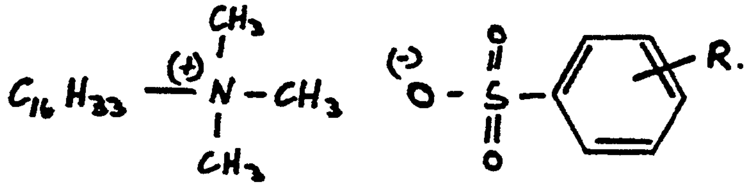
The effect of quaternary ammonium salts employed according to the present invention on the fouling of injector nozzles and combustion chamber and piston cleanliness of diesel engines is illustrated by the following specific examples in which the following compounds are employed :

Di(2-hydroxyethyl) ethyl octadecenyl ammonium etho-sulphate (compound A)

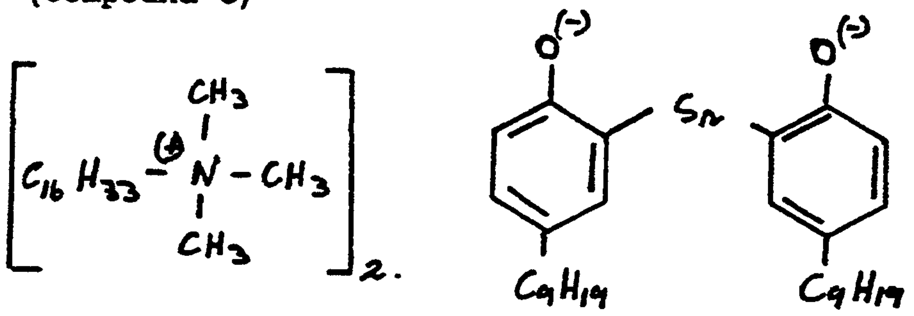


$$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-\overset{\overset{CH_2-CH_2-OH}{|\,(+)}}{\underset{\underset{CH_2-CH_2-OH}{|}}{N}}-CH_2-CH_3 \quad {}^{(-)}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-CH_2-CH_3.$$

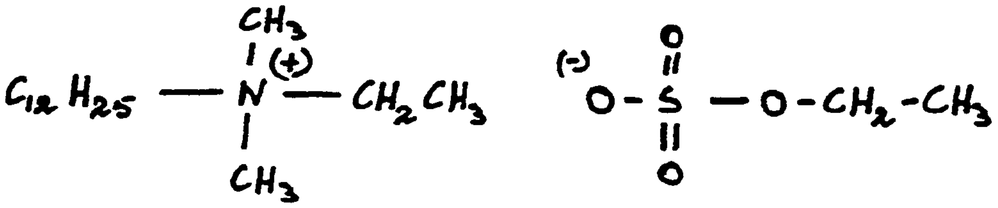
Cetyltrimethyl ammonium sulphonate (compound B)



Cetyltrimethyl ammonium nonylphenyl sulphide (compound C)

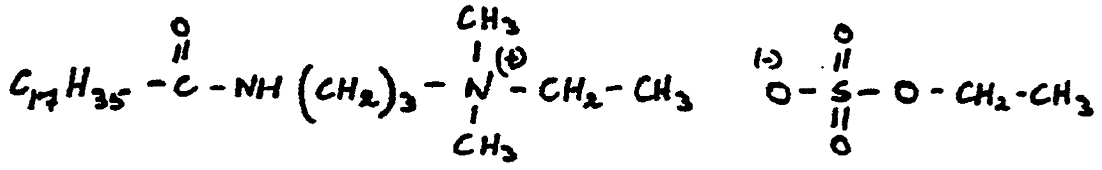


Dimethyl dodecyl ethyl ammonium etho-sulphate (compound D)



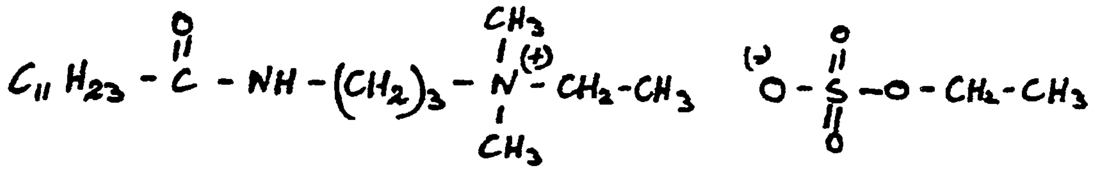
$$C_{12}H_{25}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}{}^{(+)}-CH_2CH_3 \quad {}^{(-)}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-CH_2-CH_3$$

Dimethyl ethyl (3-stearyl amino propyl) ammonium etho-sulphate (compound E)



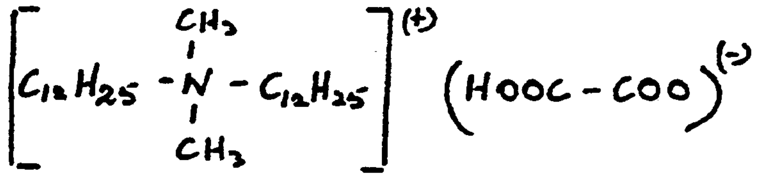
$$C_{17}H_{35}-\overset{O}{\overset{\|}{C}}-NH(CH_2)_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N^{(+)}}}}}-CH_2-CH_3 \quad {}^{(-)}O-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-O-CH_2-CH_3$$

Dimethyl ethyl (3-lauryl amino propyl) ammonium etho-sulphate (Compound F)



$$C_{11}H_{23}-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N^{(+)}}}}}-CH_2-CH_3 \quad {}^{(-)}O-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-O-CH_2-CH_3$$

Dicocodimethyl ammonium formate (Compound G)
Dicocodimethyl ammonium borate (Compound H)
Dicocodimethyl ammonium nonyl phenyl sulphide (Compound I)
Dicocdimethyl ammonium oxalate (Compound J)



$$\left[C_{12}H_{25}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{N}}}}-C_{12}H_{25}\right]^{(+)}(HOOC-COO)^{(-)}$$

Example 1

The effectiveness of quaternary ammonium salt additives on the coking of injector nozzles in diesel engines was determined using a Fiat Ritmo engine having the following specification.

Number of Cylinders	4 in line
Speed	4500 rpm
Maximum Power	42.66 kw
Bore	83 mm
Stroke	79.2 mm
Displacement	1.714 litres
Compression Ratio	20.5 : 1

Oil Volume	5.0 litres

In the tests the engine is run for 60 twenty minute cycles to simulate the urban driving cycle. Each cycle consists of four 5 minute periods as follows :

(a)	1000 rpm	idle	0 BHP	0 Load
(b)	3000 rpm	65% potential speed	27 BHP	40-45% Max Load
(c)	1600 rpm	35% potential speed	7.2 BHP	35-40% Max Load
(d)	4200 rpm	90% potential speed	42 BHP	70-8-% Max Load

Before and after the engine test the injectors were rated according to the test method of ISO 4010. This test works on the principle of a vacuum being maintained across the injector at a specific needle lift. In order to maintain this vacuum at the desired level the air-flow into the injector may vary. This air-flow into the injector is recorded. The air-flow into the injector becomes less as the injectors become coked. The results are recorded as the difference between clean and dirty, i.e. before and after tests air-flow. The formula used is as follows :

$$\text{Percent Air Flow Loss} = \frac{\text{Before Test} - \text{After Test}}{\text{Before Test}} \times 100$$

In this and the following examples the results presented are the averages of four results at one specific setting of the injectors (0.1 mm lift).

The diesel fuel used in Example 1 was a diesel fuel obtained from Italy. The compound according to the present invention tested in this diesel fuel was Compound A. A comparative test has been carried out using a typical product already being sold for injector nozzle cleanliness application (commercial product). This is an additive of the type described in the UK Patent Application No. 85-30907. It is a mixture of a phenol compound and a cyclic amide derived from a dicarboxylic acid or anhydride.

The results obtained are shown in Table I, attached.

Example 2

The effectiveness of quaternary ammonium salts according to the invention on the coking of injector nozzles in diesel engines was determined using a Fiat Regata engine having the following specification.

Number of Cylinders	4 in line
Speed	4600 rpm
Maximum Power	48.00 kw
Bore	82.60 mm
Stroke	90.00 mm
Displacement	1.92 litres
Compression Ratio	21 : 1
Oil Volume	5.7 litres

In the test the engine was run for 60 twenty-minute cycles to simulate the urban driving cycle.
The total duration of 20 hours represents 1,600 km (1,000 miles) of city driving conditions.
Each cycle consisted of four five minute periods as follows :

(a)	1100 rpm	idle	0 BHP	0 Load
(b)	3120 rpm	65% potential speed	21.1 BHP	40-45% Max Load
(c)	1680 rpm	35% potential speed	9.4 BHP	35-40% Max Load
(d)	4320 rpm	90% potential speed	45.4 BHP	70-80% Max Load

Further test conditions were as follows :

Manifold Air Temperature	26± 2°C
Coolant Outlet	92± 2°C
Coolant Temperature difference	5-6°C
Oil Temperature at 3000 rpm	110± 2°C
Fuel Temperature	48± 2°C
Exhaust Temperature at 300 rpm	300°C

Various compounds according to the present invention were tested in a UK commercial diesel fuel and the results obtained are presented in Table II.

Example 3

The tests in this example have been carried out as described for Example 2. Again, a UK commercial diesel fuel has been employed. A comparative result obtained with the commercial additive product mentioned in Example 1 is included in the attached Table III.

The compounds according to the present invention tested in this example are set out in Table 3.

TABLE 1

ANTI-COKING PERFORMANCE IN FIAT RITMO ENGINE TEST

Fuel		%FLOW LOSS
Base	Italian diesel	71.0
Base + 40	ppm of commercial product	44.7
Base	37.5 ppm of compound A	10.0

TABLE II

Fuel	% Flow Reduction
Base UK commercial diesel	65-70 (in repeat tests)
Base + 25 ppm of compound B	48.3
Base + 25 ppm of compound C	46.9
Base + 37.5 ppm of compound G	27.0
Base + 37.5 ppm of compound H	26.8
Base + 37.5 ppm of compound I	8.1
Base + 37.5 ppm of compound J	5.0

TABLE III

Fuel	%Flow Reduction
Base UK Commercial Diesel	72
Base + 40 ppm of commercial product	70
Base + 50 ppm of compound D	22.7
Base + 100 ppm of compound D	15.4
Base + 50 ppm of compound E	20.5

Claims

1. Use in an indirect injection diesel engine for inhibiting coking, especially injector nozzle coking, of a diesel fuel composition containing a minor proportion by weight of a quaternary ammonium salt soluble therein.

2. Use according to claim 1 wherein the four residues connected to the quaternary nitrogen atom of said salt are independently selected from hydrocarbyl residues which optionally contain at least one functional group as a substituent or as a member of the hydrocarbon chain.

3. Use according to claim 2 wherein one or two of said residues contain at least 6 carbon atoms while the remaining residues contain less than 6 carbon atoms.

4. Use according to claim 3 wherein one of said residues contains at least 8 carbon atoms while the remaining residues contain less than 6 carbon atoms.

5. Use according to claim 2, 3 or 4 wherein said hydrocarbyl residues are selected from alkyl groups, alkenyl groups, aryl groups or alkaryl groups.

6. Use according to claim 2, 3, 4 or 5 wherein said functional group is selected from hydroxy, halide, carboxy, amide, ether, amine, and sulphide.

7. Use according to any of the preceding claims wherein the anionic radical of the quaternary ammonium salt is a strong acid radical.

8. Use according to claim 7 wherein the anionic radical is nitrate, sulphate, ethosulphate, sulphonate (both

alkyl and alkylaryl), sulphurised phenate, carboxylate and borate, or any combination thereof.

9. Use according to any of the preceding claims wherein the composition comprises from 0.000001 to 0.1 weight percent of said quaternary ammonium salt.

10. Use according to claim 1 wherein the quaternary ammonium salt comprises one or more of the following:
di(2-hydroxyethyl) ethyl octadecenyl ammonium etho-sulphate
cetyltrimethyl ammonium sulphonate
cetyltrimethyl ammonium nonylphenyl sulphide
dimethyl dodecyl ethyl ammonium etho-sulphate
dimethyl ethyl (3-stearyl amino propyl) ammonium etho-sulphate
dimethyl ethyl (3-lauryl amino propyl) ammonium etho-sulphate
dicocodimethyl ammonium formate
dicocodimethyl ammonium borate
dicocodimethyl ammonium nonyl phenyl sulphide
dicocodimethyl ammonium oxalate.

Patentansprüche

1. Verwendung einer Dieselbrennstoffzusammensetzung, die eine kleinere Gewichtsmenge eines darin löslichen quaternären Ammoniumsalzes enthält, in einem Dieselmotor mit indirekter Einspritzung zum Inhibieren von Kohleablagerung, insbesondere von Kohleablagerung an Einspritzdüsen.

2. Verwendung nach Anspruch 1, bei der die vier mit dem quaternären Stickstoffatom dea Salzes verbundenen Reste unabhängig voneinander ausgewählt sind aus Kohlenwasserstoffresten, die gegebenenfalls mindestens eine funktionelle Gruppe als Substituent oder als Glied der Kohlenwasserstoffkette enthalten.

3. Verwendung nach Anspruch 2, bei der einer oder zwei der Reste mindestens 6 Kohlenstoffatome enthalten, während die übrigen Reste weniger als 6 Kohlenstoffatome enthalten.

4. Verwendung nach Anspruch 3, bei der einer der Reste mindestens 8 Kohlenstoffatome enthält, während die übrigen Reste weniger als 6 Kohlenstoffatome enthalten.

5. Verwendung nach Anspruch 2, 3 oder 4, bei der die Kohlenwasserstoffreste ausgewählt sind aus Alkylgruppen, Alkenylgruppen, Arylgruppen oder Alkarylgruppen.

6. Verwendung nach Anspruch 2, 3, 4 oder 5, bei der die funktionelle Gruppe ausgewählt ist aus Hydroxy, Halogenid, Carboxy, Amid, Ether, Amin und Sulfid.

7. Verwendung nach einem der vorhergehenden Ansprüche, bei der der anionische Rest des quaternären Ammoniumsalzes ein stark saurer Rest ist.

8. Verwendung nach Anspruch 7, bei der der anionische Rest Nitrat, Sulfat, Ethylsulfat, Sulfonat (sowohl Alkyl- als auch Alkylaryl-), sulfurisiertes Phenolat, Carboxylat und Borat oder eine Kombination derselben ist.

9. Verwendung nach einer der vorhergehenden Ansprüche, bei der die Zusammensetzung 0,000001 bis 0,1 Gew.% des quaternären Ammoniumsalzes umfaßt.

10. Verwendung nach Anspruch 1, bei der das quaternäre Ammoniumsalz eine oder mehrere der folgenden Verbindungen umfaßt:
Di(2-hydroxyethyl)ethyloctadecenylammoniumethylsulfat,
Cetyltrimethylammoniumsulfonat,
Cetyltrimethylammoniumnonylphenylsulfid,
Dimethyldodecylethylammoniumethylsulfat,
Dimethylethyl(3-stearylaminopropyl)ammoniumethylsulfat,
Dimethylethyl(3-laurylaminopropyl)ammoniumethylsulfat,
Dikokosdimethylammoniumformiat,
Dikokosdimethylammoniumborat,
Dikokosdimethylammoniumnonylphenylsulfid,
Dikokosdimethylammoniumoxalat.

Revendications

1. Utilisation, dans un moteur Diesel à injection indirecte pour inhiber le calaminage, notamment le calaminage de l'injecteur, d'une composition de carburant Diesel contenant une proportion secondaire en poids d'un sel d'ammonium quaternaire qui y est soluble.

2. Utilisation suivant la revendication 1, dans laquelle les quatre résidus attachés à l'atome d'azote qua-

ternaire dudit sel sont choisis indépendamment entre des résidus hydrocarbyle qui contiennent facultativement au moins un groupe fonctionnel comme substituant ou comme membre de la chaîne hydrocarbonée.

3. Utilisation suivant la revendication 2, dans laquelle un ou deux desdits résidus contiennent au moins 6 atomes de carbone tandis que les résidus restants contiennent moins de 6 atomes de carbone.

4. Utilisation suivant la revendication 3, dans laquelle l'un des résidus contient au moins 8 atomes de carbone tandis que les résidus restants contiennent moins de 6 atomes de carbone.

5. Utilisation suivant la revendication 2, 3 ou 4, dans laquelle lesdits résidus hydrocarbyle sont choisis entre des groupes alkyle, des groupes alcényle, des groupes aryle ou des groupes alkaryle.

6. Utilisation suivant la revendication 2, 3, 4 ou 5, dans laquelle ledit groupe fonctionnel est choisi entre des fonctions hydroxy, halogénure, carboxy, amide, éther, amine et sulfure.

7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le radical anionique du sel d'ammonium quaternaire est un radical d'acide fort.

8. Utilisation suivant la revendication 7, dans laquelle le radical anionique est un radical nitrate, sulfate, éthosulfate, sulfonate (de type alkyle et alkylaryle), phénate sulfuré, carboxylate et borate ou n'importe laquelle de leurs associations.

9. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la composition comprend 0,000001 à 0,1 pour cent en poids dudit sel d'ammonium quaternaire.

10. Utilisation suivant la revendication 1, dans laquelle le sel d'ammonium quaternaire comprend un ou plusieurs des sels suivants :
éthosulfate de di(2-hydroxyéthyl)éthyloctadécénylammonium
sulfonate de cétyltriméthylammonium
nonylphénylsulfure de cétyltriméthylammonium
éthosulfate de diméthyldodécyléthylammonium
éthosulfate de diméthyléthyl(3-stéarylaminopropyl)ammonium
éthosulfate de diméthyléthyl(3-laurylaminopropyl)ammonium
formiate de dicoprahdiméthylammonium
borate de dicoprahdiméthylammonium
nonylphénylsulfure de dicoprahdiméthylammonium
oxalate de dicoprahdiméthylammonium.