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(54) **Fuel oil compositions.**

(57) Sediment and colour formation are reduced in a diesel or heating fuel by incorporating in the fuel a quaternary ammonium salt, the cation of which is the reaction product of a tertiary amine, an olefin oxide and water.

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Fuel Oil Compositions

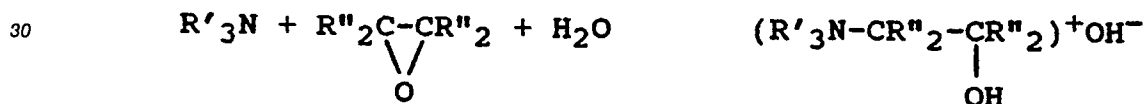
This invention relates to fuel oil compositions and more especially to fuel oil compositions containing cracked components which are stabilized against sediment formation and colour development during storage. Cracked components are frequently included to give higher yields of diesel fuel and heating oil.

However, when diesel and heating oils containing cracked components are stored at ambient or elevated temperatures in air they become discoloured and precipitate sludge or sediment.

It is clear that the problem of discoloration and sediment formation is exacerbated by the presence of cracked components in the fuel. This is demonstrated by the results in Table 1 which show the amount of sediment formed and the colour change when various fuel blends are tested in the AMS 77.061 accelerated stability test. Published research (see, for example, Offenbauer et. al, Industrial and Engineering Chemistry, 1957, Volume 49, page 1265, and the Proceedings of the 2nd International Conference on the Long Term Stability of Liquid Fuels, San Antonio, Texas, published October 1986) suggests that discoloration and sediment result from the oxidation of sulphur and nitrogen compounds present in the fuel. The analysis of cracked components is consistent with this. The results in Table 2 show that cracked components contain significantly larger quantities of nitrogen and sulphur than straight distillates. Also, the addition of nitrogen and sulphur compounds to a stable straight distillate causes an increase in both sediment and colour in the AMS 77.061 test (Table 3) with the worst result being obtained when both nitrogen and sulphur compounds are present in the fuel.

It has now been found that sediment and colour formation may be substantially reduced in diesel fuels or heating fuels, especially those containing cracked components, by the addition of certain quaternary ammonium compounds. According to this invention fuel compositions comprise a base fuel, which may contain cracked components, and a quaternary ammonium salt in which the cation is derivable from, and advantageously derived from, the reaction of a tertiary amine with an olefin oxide in the presence of excess water to yield a solution of a quaternary ammonium hydroxide, and the anion is derived from an organic acid, subject to the proviso that when the acid is an alkane monocarboxylic acid the alkane is a straight chain alkane.

The quaternary ammonium salts may be made in two stages: In the first stage a tertiary amine is reacted with an olefin oxide in the presence of excess water to yield a solution of a quaternary ammonium hydroxide, e.g.



in which each R' , which may be the same or different, is an organic group; and each R'' , which may be the same or different, is hydrogen or an organic group.

In the second stage the quaternary ammonium hydroxide is neutralized with an organic acid to form a quaternary ammonium salt, i.e.

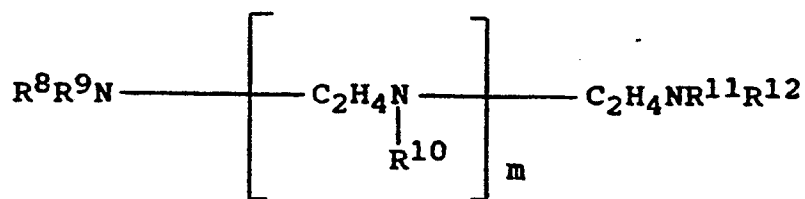


As examples of suitable tertiary amines there may be mentioned:

(i) amines of the formula $R^1R^2R^3N$ where R^1 , R^2 and R^3 which may be the same or different are each substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl. Each group R^1 , R^2 and R^3 preferably has 1 to 20 carbon atoms. Examples of this type of amine are trimethylamine; ethyl-dimethylamine; n-propyldimethylamine; triethanolamine; N,N-dimethylbenzylamine; N,N-dimethylcyclohexylamine; N,N-dimethylaniline; N,N-dimethyl-(4-methylcyclohexylamine) and N,N-dimethyl-p-toluidine.

(ii) diamines of the formula $R^4R^5N(CH_2)_nNR^6R^7$ where n is an integer of one or more, and R^4 , R^5 , R^6 and R^7 , which may be the same or different, are as defined above for R^1 . Thus, one may use N,N,N',N'-tetramethyl ethylenediamine.

(iii) fully alkylated alkylene polyamines of the formula:



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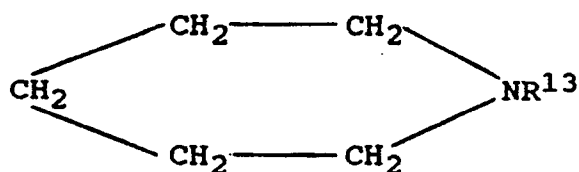
where m is an integer of one or more and R^8 , R^9 , R^{10} , R^{11} , and R^{12} , which may be the same or different, are as defined for R^1 above.

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(iv) pyridine and substituted pyridines e.g., α , β and gamma- picolines, quinoline and substituted quinolines and similar heterocyclic tertiary amines.

(v) N-substituted piperidines of the formula:

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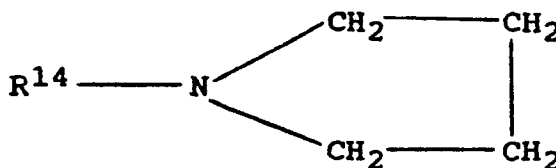


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where R^{13} is as defined for R^1 above.

(vi) N-substituted pyrrolidines of the formula:

25

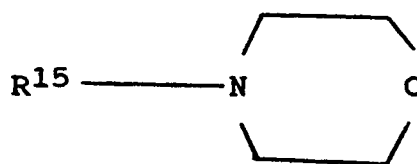


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where R^{14} is as defined for R^1 above.

(vii) N-substituted morpholines of the formula:

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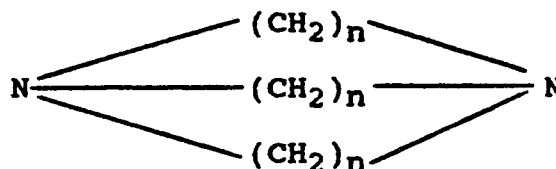


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where R^{15} is as defined for R^1 above.

(viii) amines of the formula:

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where n is an integer of two or more e.g. triethylene diamine.

(xi) hexamethylenetetramine $(CH_2)_6N_4$ (hexamine).

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The olefin oxides are preferably of the formula:



where R^{16} , R^{17} , R^{18} , and R^{19} which may be the same or different, are each hydrogen, or substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl. Specific examples are ethylene oxide, propylene oxide, but-1-ene oxide, but-2-ene oxide, oct-1-ene oxide and styrene oxide.

The organic acid which may be used in the second stage of the reaction and hence forms the anion in the quaternary ammonium salt may be, for example, a carboxylic acid, carboxylic acid anhydride, phenol, sulphurized phenol, or sulphonic acid, subject to the proviso that in the aspect of the invention which is a fuel oil composition, unlimited as to type, then when the acid is an alkane monocarboxylic acid the alkane is a straight chain alkane and, preferably, the acid is an alkane 1-carboxylic acid.

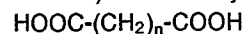
The carboxylic acid may be, for example:

i) An acid of the formula:

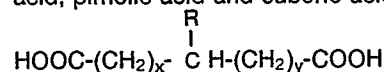


where R is hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group. Examples of such acids include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, palmitic acid, stearic acid, cyclohexanecarboxylic acid, 2-methylcyclohexane carboxylic acid, 4-methylcyclohexane carboxylic acid, oleic acid, linoleic acid, linolenic acid, cyclohex-2-eneoic acid, benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, salicylic acid, 2-hydroxy-4-methylbenzoic acid, 2-hydroxy-4-ethylsalicylic acid, p-hydroxybenzoic acid, 3,5-di-tert-butyl-4-hydroxybenzoic acid, o-aminobenzoic acid, p-aminobenzoic acid, o-methoxybenzoic acid and p-methoxybenzoic acid.

ii) A dicarboxylic acid of the formula

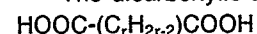


where n is zero or an integer, including e.g. oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid and suberic acid. Also included are acids of the formula



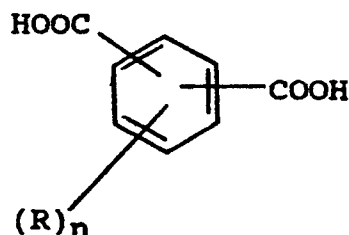
where x is zero or an integer, y is zero or an integer and x and y may be equal or different and R is defined as in (i). Examples of such acids include the alkyl or alkenyl succinic acids, 2-methylbutanedioic acid, 2-ethylpentanedioic acid, 2-n-dodecylbutanedioic acid, 2-n-dodecenylbutanedioic acid, 2-phenylbutanedioic acid, and 2-(p-methylphenyl)butanedioic acid. Also included are polysubstituted alkyl dicarboxylic acids wherein other R groups as described above may be substituted on the alkyl chain. These other groups may be substituted on the same carbon atom or different atoms. Such examples include 2,2-dimethylbutanedioic acid; 2,3-dimethylbutanedioic acid; 2,3,4-trimethylpentanedioic acid; 2,2,3-trimethylpentanedioic acid; and 2-ethyl-3-methylbutanedioic acid.

The dicarboxylic acids also include acids of the formula:



where r is an integer of 2 or more. Examples include maleic acid, fumaric acid, pent-2-enedioic acid, hex-2-enedioic acid; hex-3-enedioic acid, 5-methylhex-2-enedioic acid; 2,3-di-methylpent-2-enedioic acid; 2-methylbut-2-enedioic acid; 2-dodecylbut-2-enedioic acid; and 2-polyisobutylbut-2-enedioic acid.

The dicarboxylic acids also include aromatic dicarboxylic acids e.g. phthalic acid, isophthalic acid, terephthalic acid and substituted phthalic acids of the formula:



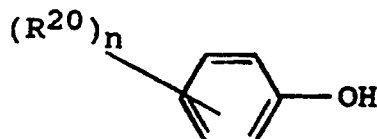
where R is defined as in (i) and $n = 1, 2, 3$ or 4 and when $n > 1$ then the R groups may be the same or different. Examples of such acids include 3-methylbenzene-1,2-dicarboxylic acid; 4-phenylbenzene-1,3-dicarboxylic acid; 2-(1-propenyl)benzene-1,4-dicarboxylic acid, and 3,4-dimethylbenzene-1,2-dicarboxylic acid.

acid.

The carboxylic acid anhydrides include the anhydrides that may be derived from the carboxylic acids described above. Also included are the anhydrides that may be derived from a mixture of any of the carboxylic acids described above. Specific examples include acetic anhydride, propionic anhydride, benzoic anhydride, maleic anhydride, succinic anhydride, dodecylsuccinic anhydride, dodecenylsuccinic anhydride, an optionally substituted polyisobutylenesuccinic anhydride, advantageously one having a molecular weight of between 500 and 2000 daltons, phthalic anhydride and 4-methylphthalic anhydride.

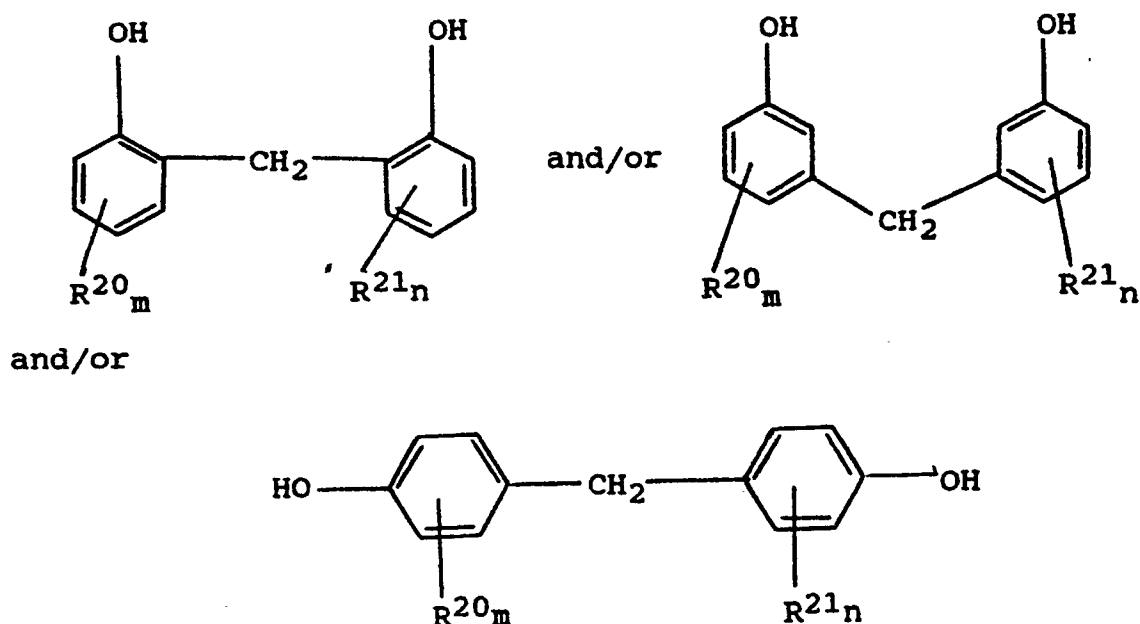
The phenols from which the anion of the quaternary ammonium compound may be derived are of many different types. Examples of suitable phenols include:

(i) Phenols of the formula:



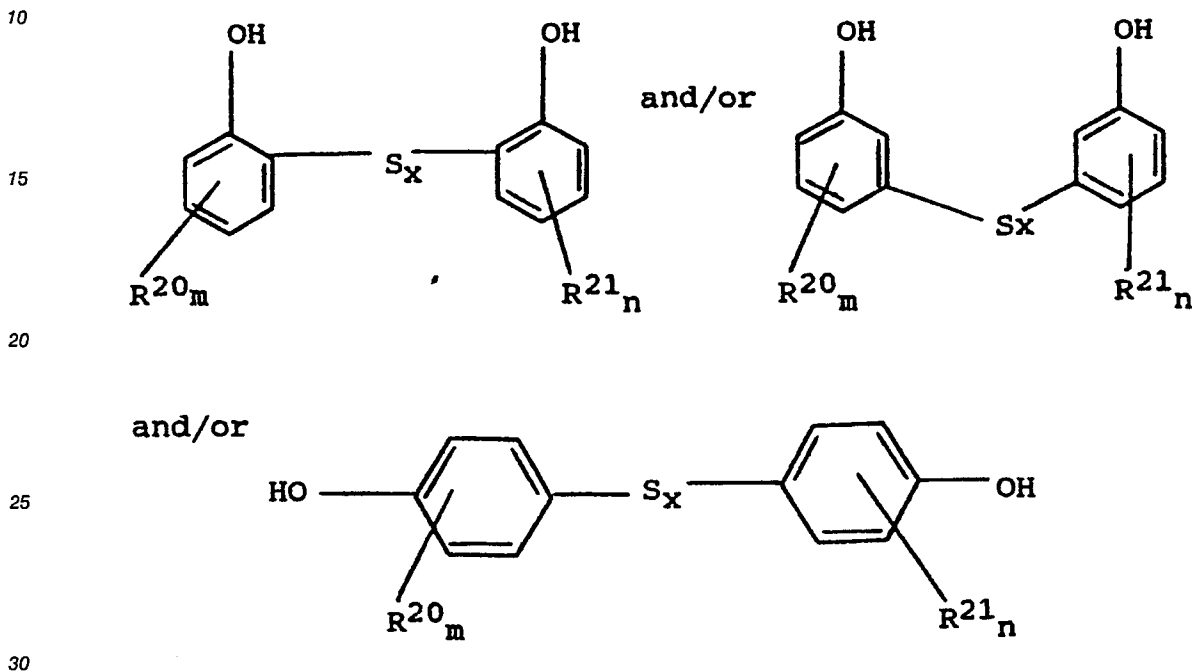
where $n = 1, 2, 3, 4$ or 5 , where R^{20} is defined below and when $n > 1$ then the substituents may be the same or different. R^{20} may be hydrogen, or a substituted or unsubstituted, alkyl, cycloalkyl, alkenyl, cycloalkenyl or aryl group. The hydrocarbon group(s) may be bonded to the benzene ring by a keto or thio-keto group. Alternatively the hydrocarbon group(s) may be bonded through an oxygen, sulphur or nitrogen atom. Examples of such phenols include o-cresol; m-cresol; p-cresol; 2,3-dimethylphenol; 2,4-dimethylphenol; 2,3,4-trimethylphenol; 3-ethyl-2,4-dimethylphenol; 2,3,4,5-tetramethylphenol; 4-ethyl-2,3,5,6-tetramethylphenol; 2-ethylphenol; 3-ethylphenol; 4-ethylphenol; 2-n-propylphenol; 2-isopropylphenol; 4-isopropylphenol; 4-n-butylphenol; 4-isobutylphenol; 4-secbutylphenol; 4-t-butylphenol; 4-nonylphenol; 2-dodecylphenol; 4-dodecylphenol; 4-octadecylphenol; 2-cyclohexylphenol; 4-cyclohexylphenol; 2-allylphenol; 4-allylphenol; 2-hydroxydiphenyl; 4-hydroxydiphenol; 4-methyl-4'-hydroxydiphenyl; o-methoxyphenol; p-methoxyphenol; p-phenoxyphenol; 2-hydroxydiphenylsulphide; 4-hydroxydiphenylsulphide; 4-hydroxyphenylmethylsulphide; and 4-hydroxyphenyldimethylamine. Also included are alkyl phenols where the alkyl group is obtained by polymerization of a low molecular weight olefin e.g. polypropylphenol or polyisobutylphenol.

Also included are phenols of the formula:



where R^{20} and R^{21} which may be the same or different are as defined above for R^{20} and m and n are integers and for each m or n greater than 1 each R^{20} or R^{21} may be the same or different. Examples of such phenols include 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane; 5,5'-dihydroxy-2,2'-dimethyldiphenylmethane; 4,4'-dihydroxy-2,2'-dimethyldiphenylmethane; 2,2'-dihydroxy-5,5'-dinonyldiphenylmethane; 2,2'-dihydroxy-5,5'-didodecyldiphenylmethane; 2,2',4,4'-tetra-*t*-butyl-3,3'-dihydroxy-5,5'-didodecyldiphenylmethane; and 2,2',4,4'-tetra-*t*-butyl-3,3'-dihydroxydiphenylmethane.

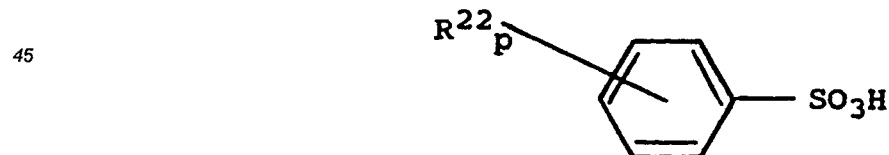
Also included are sulphurized phenols of the formula:



where R^{20} and R^{21} which may be the same or different are as defined above, and m and n are integers, for each m and n greater than 1 each R^{20} and R^{21} may be the same or different, and x is 1, 2, 3 or 4. Examples of such phenols include:

2,2'-dihydroxy-5,5'-dimethyldiphenylsulphide; 5,5'-dihydroxy-2,2'-di-*t*-butyldiphenyldisulphide; 4,4'-dihydroxy-3,3'-di-*t*-butyldiphenylsulphide; 2,2'-dihydroxy-5,5'-dinonyldiphenyldisulphide; 2,2'-dihydroxy-5,5'-didodecyldiphenyldisulphide; 2,2'-dihydroxy-5,5'-didodecyldiphenyltrisulphide; and 2,2'-dihydroxy-5,5'-didodecyldiphenyltetrasulphide.

The sulphonic acids from which the anion of the quaternary ammonium salt can be derived include alkyl and aryl sulphonic acids which have a total of 1 to 200 carbon atoms per molecule although the preferred range is 10-80 atoms per molecule. Included in this description are aryl sulphonic acids of the formula:

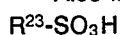


where $p = 1, 2, 3, 4, 5$ and when $p > 1$ the substituents may be the same or different, and R^{22} may represent R^{20} as defined above.

The hydrocarbon group(s) may be bonded to the benzene ring through a carbonyl group or a thio-keto group. Alternatively the hydrocarbon group(s) may be bonded to the benzene ring through a sulphur, oxygen or nitrogen atom. Thus examples of sulphonic acids that may be used include: benzene sulphonic acid; *o*-toluenesulphonic acid, *m*-toluenesulphonic acid; *p*-toluenesulphonic acid; 2,3-dimethylbenzenesulphonic acid; 2,4-dimethylbenzenesulphonic acid;

2,3,4-trimethylbenzenesulphonic acid;
 4-ethyl-2,3-dimethylbenzenesulphonic acid;
 4-ethylbenzenesulphonic acid;
 4-n-propylbenzenesulphonic acid;
 5 4-n-butylbenzenesulphonic acid;
 4-isobutylbenzenesulphonic acid;
 4-sec-butylbenzenesulphonic acid;
 4-t-butylbenzenesulphonic acid;
 4-nonylbenzenesulphonic acid;
 10 2-dodecylbenzenesulphonic acid; 4-dodecylbenzenesulphonic acid; 4-cyclohexylbenzenesulphonic acid;
 2-cyclohexylbenzenesulphonic acid;
 2-allylbenzenesulphonic acid;
 2-phenylbenzenesulphonic acid;
 4(4'-methylphenyl)benzenesulphonic acid;
 15 4-methylmercaptobenzenesulphonic acid; 2-methoxybenzene sulphonic acid; 4-phenoxybenzenesulphonic
 acid;
 4-methylaminobenzenesulphonic acid;
 2-dimethylaminobenzenesulphonic acid; and
 2-phenylaminobenzenesulphonic acid. Also included are sulphonic acids of the type listed above where R²²
 20 is derived from the polymerization of a low molecular weight olefin e.g. polypropylbenzenesulphonic acid
 and polyisobutylenebenzenesulphonic acid.

Also included are sulphonic acids of the formula:



where R²³ is substituted or unsubstituted alkyl, cycloalkyl, alkenyl or cycloalkenyl. Examples of such
 25 sulphonic acids that may be used include methylsulphonic acid; ethylsulphonic acid; n-propylsulphonic
 acid; n-butylsulphonic acid; isobutylsulphonic acid; sec-butylsulphonic acid; t-butylsulphonic; nonylsulphonic
 acid; dodecylsulphonic acid; polypropylsulphonic acid; polyisobutylsulphonic acid; cyclohexylsulphonic acid;
 and 4-methylcyclohexylsulphonic acid.

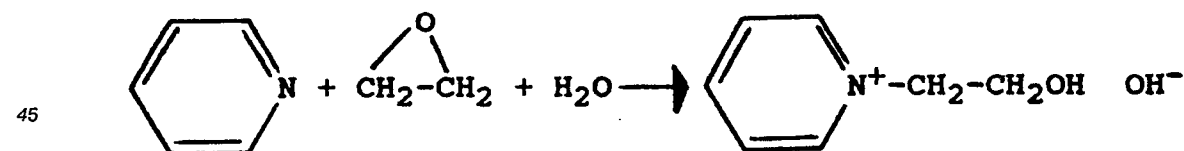
The quaternary ammonium salts may be made in two stages, the first stage of which comprises the
 30 reaction of a tertiary amine with an olefin oxide.

Generally 1 mole of the tertiary amine is treated with A moles of the olefin oxide (where A is the
 number of tertiary nitrogens in the amine molecule) in the presence of an excess of water over that required
 by the stoichiometry of the reaction.

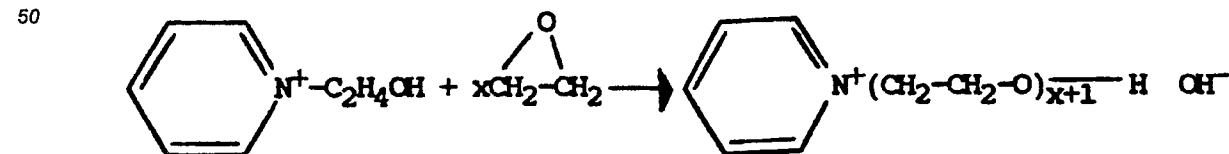
Thus pyridine (1 mole) is treated with an olefin oxide (1 mole) in water (>1 mole). Triethylenediamine (1
 35 mole) is treated with an olefin oxide (2 moles) in water (>2 mole). Hexamine (1 mole) is treated with an
 olefin oxide (4 moles) in water (>4 moles).

However, the olefin oxide may be used in excess if required, or desired, the excess olefin oxide then
 reacting with the quaternary ammonium hydroxide. One possible mechanism for this further reaction with
 olefin oxide is illustrated by the equations:

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As indicated above any quantity of water may be used as long as it represents an excess over that

required by the stoichiometry of the reaction.

The reaction may be carried out in the following ways:

(i) The amine is stirred with the olefin oxide in the reactor and the water added to the reaction mixture. The rate of addition of the water does not affect the quality of the final product but slow addition of water may be used to control an exothermic reaction.

(ii) The amine is mixed with the water in the reactor and the olefin oxide is added to the stirred reaction mixture. The olefin oxide may be added as:

(a) a gas either pure or diluted with an inert carrier (e.g., nitrogen)

(b) a liquid

(c) a solution in water

(d) a solution in a water miscible organic solvent (e.g., methyl or ethyl alcohol).

The rate of addition of the olefin oxide is not critical for the quality of the final product but a slow addition rate may be used to control an exothermic reaction.

(iii) The olefin oxide is mixed with the water in the reactor and the amine is added to the reaction mixture. The amine may be added as:

(a) a pure gas, liquid or solid

(b) a solution in water

(c) a solution in a water soluble organic solvent.

As with the olefin oxide and water addition, slow addition of the amine may be used to control an exothermic reaction.

To facilitate the reaction, the mixed reactants may be heated together at a given temperature while the third reactant is added at a rate sufficient to maintain a steady reaction. Alternatively the reactants may be heated in a pressure vessel but, when heating the reactants to promote the reaction, a temperature greater than 100°C should be avoided to prevent decomposition of the quaternary ammonium hydroxide.

The second stage of the reaction comprises neutralization of the quaternary ammonium hydroxide formed in the first stage with the organic acid.

Generally, sufficient acid is mixed with the solution obtained from the first stage to neutralize the quaternary ammonium hydroxide. However, an excess of acid may be used if required, as for example when only one carboxylic acid group of a polybasic acid is to be neutralized. The neutralization reaction may be carried out:

(i) In the absence of any solvent.

(ii) In the presence of an alcohol, e.g., methanol, ethanol, isopropanol, ethyl Cellosolve (a trademark), or ethylene glycol.

(iii) In the presence of any other polar organic solvent, e.g., acetone, methyl ethyl ketone, chloroform, carbon tetrachloride, or symtetrachloroethane.

(iv) In the presence of a hydrocarbon solvent, e.g., hexane, heptane, white spirit, benzene, toluene or xylene.

(v) In the presence of a mixture of any of the above solvents.

The neutralization reaction may be carried out at ambient temperature but generally an elevated temperature is used. When the reaction is completed the water and any solvents used may be removed by heating under vacuum. The product is generally diluted with mineral oil, diesel fuel, kerosene, or an inert hydrocarbon solvent to prevent the product being too viscous.

The fuel composition advantageously comprises a minor proportion by weight of the quaternary ammonium compound, preferably less than 1% by weight, more preferably from 0.000001 to 0.1%, especially 2 to 200 ppm.

The cracked component in the fuel oil which leads to the undesirable colour formation and sediment is generally obtained by cracking of heavy oil and may be fuel oil in which the main constituent is a fraction obtained from a residual oil.

Typical methods available for the thermal cracking are visbreaking and delayed coking. Alternatively the fuels may be obtained by catalytic cracking, the principal methods being moving-bed cracking and fluidized-bed cracking. After cracking, the distillate oil is extracted by normal or vacuum distillation, the boiling point of the distillate oil obtained usually being 60-500°C, and is a fraction called light-cycle oil, preferably corresponding to the boiling point range of light oil of 150-400°C. Compositions composed entirely of this fuel or fuels which are mixtures of the cracked fraction and normal distillates may be used in the present invention.

The proportion by weight of direct-distillation fraction and cracked fraction in a fuel oil composition which is a mixture can vary considerably, but is usually 1:0.03 - 1:2 and preferably 1:0.05 - 1:1. Typically the content of cracked fraction is usually 5-97%, and preferably 10-50%, based on the weight of the

composition.

The present invention accordingly also provides a fuel oil composition comprising a distillate fraction and a cracked fraction and a quaternary ammonium compound the cation of which is the reaction product of a tertiary amine, an olefin oxide, and water, the anion being derived from an organic acid. The invention also provides the use of such a compound in inhibiting sediment and colour formation in a fuel oil composition, especially one containing a component obtained by the cracking of heavy oil.

The fuel oil compositions of the present invention may contain other additives such as antioxidants, anticorrosion agents, fluidity improvers, agents absorbing ultraviolet radiation, detergents, dispersants and cetane improvers in small amounts (for example, usually less than 2% based on the weight of the composition).

Details and examples of the synthesis of the quaternary ammonium compounds have been given in British Specification No. 1,445,993, the disclosure of which is incorporated by reference herein. The products were tested in a fuel that was a blend of a stable distillate (Fuel A), containing 50 ppm nitrogen and 0.24% sulphur, and an unhydrofined catalytically cracked gas oil (Fuel B) with 695 ppm nitrogen and 1.11% sulphur. The present invention is illustrated by the following examples.

Table 1 shows the effect on sediment and colour in the AMS 77.061 test of blending different amounts of the straight distillate fuel with the unhydrofined catalytically cracked gas oil.

Table 2 shows the nitrogen and sulphur contents of various fuels.

Table 3 shows the effect on colour and sediment of doping the stable fuel (A) with compounds containing nitrogen and sulphur.

Table 4 shows the effect on sediment and colour in the AMS 77.061 test of adding 100 ppm of quaternary ammonium compounds to a fuel containing 20% of cracked components. Comparison of the results for the fuels treated with quaternary ammonium compounds with the results for the untreated fuel show that the compounds of this invention control sediment and colour.

Table 5 shows the long term storage characteristics of fuel to which has been added 100 ppm of quaternary ammonium compound. It can be seen that the sediment and colour of the treated fuel are much better in the long term than that of the untreated fuel.

Table 1

The Effect of Fuel Composition on Sediment and Colour in the AMS 77.061 Accelerated Stability Test			
Fuel A wt. %	Fuel B wt. %	Sediment mg/100 ml	Colour (a)
100	0	0.14 ± 0.09	≈0.5, <0.5, <0.5
80	20	0.61 ± 0.13	≈1.0, 1.0, 1.0
60	40	1.12 ± 0.10	≈1.0, ≈1.0, ≈1.0, ≈1.0
40	60	1.80 ± 0.04	≈2.0, ≈2.0
20	80	2.10 ± 0.10	≈2.0, ≈2.0
0	100	2.90	6.0

(a) Colour change (ASTM D1500 test)

Table 2

The Nitrogen and Sulphur Contents of Various Fuels		
Type of Fuel	Nitrogen (ppm)	Sulphur (%)
Unhydrofined CCGO	695	1.11
Unhydrofined CCGO	650	1.70
Straight distillate	50	0.24
Straight distillate	70	0.25
Straight distillate	97	0.23
Straight distillate	128	0.24
Straight distillate	179	1.44

Table 3

Effect of doping with dimethyl pyrrole (DMP) and a sulphonic acid (SA) on the stability of a straight distillate fuel in the AMS 77.061 test					
DMP ppm(a)	SA ppm(b)	Sediment (mg/100 ml)	Colour		C
			Before	After	
Nil	Nil	0.06,0.10	<0.5	<1.0	0.5
Nil	50	0.02,0.00	<0.5	<1.5	1.0
			<0.5	<1.5	1.0
50	Nil	0.76,0.59	<0.5	<1.0	0.5
			<0.5	<1.0	0.5
50	50	1.06,1.01	<1.5	<3.0	1.5
			<1.5	<3.0	1.5

(a) 2,5-dimethylpyrrole

(b) A commercially available alkyl-aryl sulphonic acid having a standard acid number of approximately 80 mg KOH/g of acid.

TABLE 4

The Effect of Quaternary Ammonium Phenate on Sediment and Colour in the AMS 77,061 Stability Test.				
AMINE	OLEFIN OXIDE	ACID	AMS 77.061 RESULTS	
			SEDIMENT (mg /100 ml)	COLOUR (ASTM D1500)
	UNTREATED FUEL		(1.18 + 0.20) ^(a)	~ 1.0
HEXAMINE	PROPYLENE OXIDE	DDP	(0.00 + 0.00) ^(b)	~ 0.5, ~ 0.5
HEXAMINE	PROPYLENE OXIDE	NPS	(0.00 + 0.00) ^(b)	~ 1.0, ~ 0.5
TRIETHYLENE DIAMINE	PROPYLENE OXIDE	DDP	(0.07 + 0.10) ^(b)	~ 1.0, ~ 0.5
TRIETHYLENE DIAMINE	PROPYLENE OXIDE	NPS	(0.00 + 0.00) ^(b)	~ 1.0, ~ 1.0
TRIETHANOLAMINE	PROPYLENE OXIDE	DDP	(0.12 + 0.02) ^(b)	~ 0.5, ~ 0.5

(a) (mean ± standard deviation) of 14 results

(b) (mean ± standard deviation) of 2 results

* Fuel is a blend of straight distillate (FUEL A ; 80 wt%) and catalytically cracked gas oil (FUEL B ; 20 wt%)

* Additive treat is 100 ppm

* DDP - is dodecylphenol

* NPS - is a sulphurized nonylphenol

TABLE 5LONG TERM STORAGE TESTS ON AMINE/PROPYLENE OXIDE/DDPS

ADDITIVE	0 DAYS	28 DAYS	56 DAYS	84 DAYS	112 DAYS
None	NIL/< 2.0	0.72/< 2.5	2.34/< 3.0	2.26/< 3.0	3.02/< 3.5
Hexamine/PO/DDP	NIL/< 2.0	0.034/< 2.0	0.68/< 2.0	0.50/< 2.0	0.48/< 2.5
Triethylamine/PO/DDP	NIL/< 2.0	0.62/< 2.5	0.72/< 1.5	0.94/< 2.5	1.00/< 3.5
Triethanolamine/PO/DDP	NIL/< 2.0	0.18/< 2.5	0.94/< 1.5	0.28/< 2.0	0.84/< 3.0

PO is propylene oxide

DDP is dodecylphenol

Fuel is Fuel A (80%) : stable fuel

Fuel H

80091/87 (20%) : unstable unhydrofined catalytically cracked fuel

* TESTS carried out at 40°C for 112 days

* Results shows : Sediment (mg/100g of fuel)/Colour ASTM D1500 test.

Claims

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1. A fuel oil composition comprising a diesel fuel oil or heating fuel oil and a quaternary ammonium salt the cation of which is the reaction product of a tertiary amine, an olefin oxide and water and the anion is derived from an organic acid, subject to the proviso that when the acid is an alkane monocarboxylic acid the alkane is a straight chain alkane.

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2. A composition according to claim 1 containing a cracked component derived from a heavy oil, the cracked component advantageously comprising 5 to 97%, preferably 5 to 50%, by weight of the composition.

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3. A composition according to claim 1 or claim 2, wherein the tertiary amine has the formula $R^1R^2R^3N$ where R^1 , R^2 and R^3 , which may be the same or different, are each independently a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group, each group advantageously having at most 20 carbon atoms.

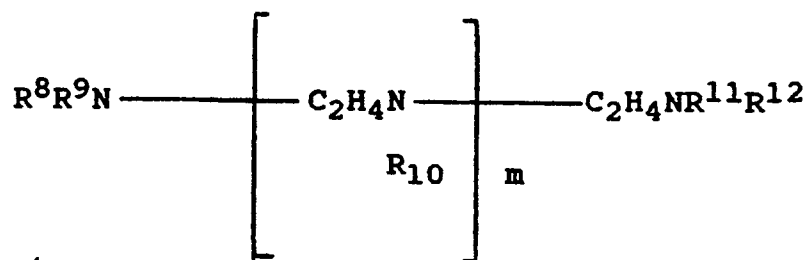
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4. A composition according to claim 1 or claim 2, wherein the tertiary amine is a diamine of the formula $R^4R^5N(CH_2)_nNR^6R^7$ where n is an integer of one or more and R^4 , R^5 , R^6 and R^7 , which may be the same or different, are each independently an unsubstituted or substituted alkyl, cycloalkyl, alkenyl, cycloalkenyl or aryl group.

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5. A composition according to any one of claims 1 to 4 wherein the tertiary amine is an alkylated alkylene polyamine of the formula:

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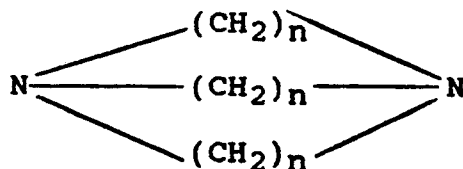
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where m is an integer of one or more and R^8 , R^9 , R^{10} , R^{11} and R^{12} , which may be the same or different, are each independently a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group.

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6. A composition according to claim 1 or claim 2, wherein the tertiary amine is pyridine or a substituted pyridine; an amine of the formula:

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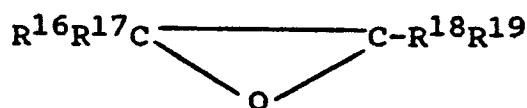


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where n is an integer of two or more, or is hexamethylene tetramine.

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7. A composition according to any one of the preceding claims wherein the olefin oxide has the formula:



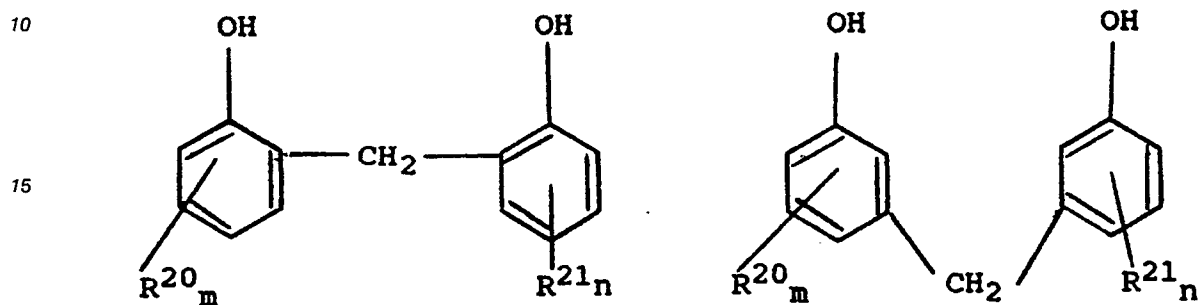
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where R^{16} , R^{17} , R^{18} and R^{19} , which may be the same or different, are each hydrogen or an unsubstituted or substituted alkyl, cycloalkyl, alkenyl, cycloalkenyl or aryl group.

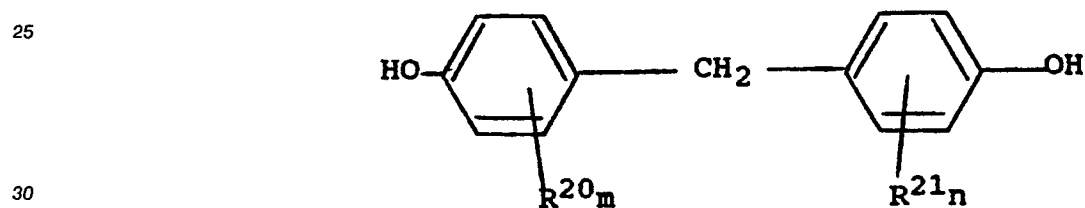
8. A composition according to any one of the preceding claims wherein the anion of the salt is derived from a carboxylic acid or a carboxylic acid anhydride, advantageously an alkyl or alkenyl succinic acid or an anhydride thereof.

9. A composition according to any one of claims 1 to 7, wherein the anion of the quaternary ammonium salt is derived from a phenol, advantageously a monoalkylphenol.

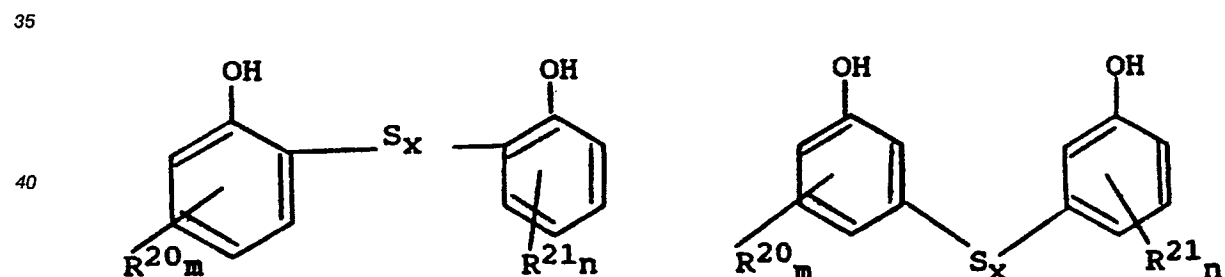
10. A composition according to any one of claims 1 to 7, wherein the anion of the salt is derived from a methylene bis-phenol of the formula:



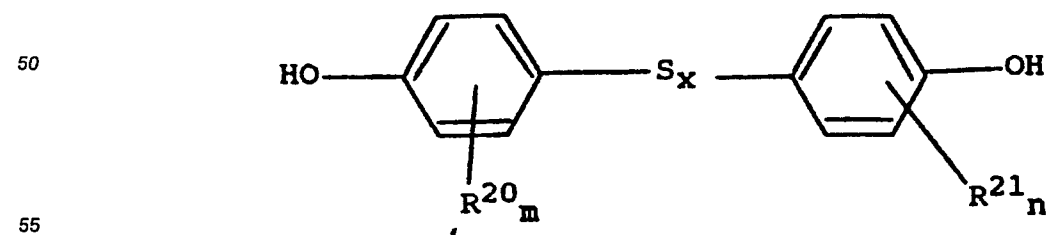
or



or a sulphurized phenol of the formula:



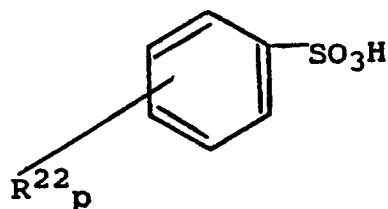
or



where R^{20} and R^{21} which may be the same or different are hydrogen, or a substituted or unsubstituted alkyl,

cycloalkyl, alkenyl, cycloalkenyl, or aryl group, m and n which may be the same or different are each zero or an integer from 1 to 4 and for each m or n greater than 1 each R^{20} or R^{21} may be the same or different, and x is 1, 2, 3 or 4.

11. A composition according to any one of claims 1 to 7, wherein the anion of the quaternary ammonium salt is derived from a sulphonic acid, advantageously one of the formula:



where R^{22} is hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group, p is an integer of 1 to 5 and when p is greater than 1 each R^{22} may be the same or different.

12. A composition according to any one of the preceding claims which comprises a major proportion by weight of the diesel or heating fuel oil and a minor proportion by weight of the quaternary ammonium salt.

13. A composition according to claim 12 which comprises 0.001 to 5.0% by weight of the quaternary ammonium salt.

14. Use of a quaternary ammonium salt the cation of which is the reaction product of a tertiary amine, an olefin oxide, and water, the anion being derived from an organic acid, to inhibit colour and sediment formation in a fuel oil.

15. The use as claimed in claim 14, wherein the fuel oil comprises a distillate fraction and a cracked fraction.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	US-A-3 962 104 (SWIETLIK et al.) * Whole document * ---	1-15	C 10 L 1/22 C 10 L 1/24
Y	US-A-3 419 366 (FARERI et al.) * Whole document * ---	1-15	
A	EP-A-0 293 192 (EXXON) * Pages 3-7 * ---	1-15	
A	FR-A-2 249 948 (LUBRIZOL) * Whole document * ---	1-15	
A	US-A-4 056 531 (MALEC) * Whole document * ---	1-15	
A	FR-A-1 301 479 (STANDARD OIL) * Whole document * ---	1-5,13-15	
A	US-A-3 527 804 (CYBA) * Whole document * ---	1-5,13-15	
A	EP-A-0 220 892 (MOBIL OIL) * Cl.; page 1 * -----	1-5,7,8,13-15	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C 10 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-07-1990	Examiner DE LA MORINERIE B.M.S.B.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			