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EUROPEAN PATENT APPLICATION

21 Application number: **90302195.4**

51 Int. Cl.⁵: **C10L 1/22, C10L 1/24**

22 Date of filing: **01.03.90**

30 Priority: **02.03.89 GB 8904785**

43 Date of publication of application:
05.09.90 Bulletin 90/36

84 Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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54 **Fuel oil compositions.**

57 Sediment and colour formation in distillate fuels are reduced by the addition of a quaternary ammonium compound comprising a cation in which the ratio of carbon atoms to quaternary nitrogen atoms is not more than 10:1 and an anion which is derived from an acid which is a carboxylic acid, carboxylic acid anhydride, phenol, sulphurized phenol or sulphonic acid.

EP 0 385 778 A1

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
5 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,
10 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
15 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.

We have found that sediment and colour formation in distillate fuels which are stored at ambient temperatures for long periods may be reduced by the addition of certain quaternary ammonium compounds.
20

There are several patents which disclose the use of quaternary ammonium compounds in fuel oils. Most of these patents disclose the use of quaternary ammonium compounds in which the sum total of carbon atoms in the cation exceeds 10. U.S. Patents No. 3,008,813, 3,265,474, 3,397,970 and 3,346,353 all disclose the use of quaternary ammonium compounds containing the cation:

25 $[R_2NMe_2]^{(+)}$

where R is C_{12} to C_{14} , as agents for improving the water tolerance of hydrocarbon oils.

U.S. Patent No. 3,033,665 and U.S. Patent No. 3,158,647 both disclose the use of quaternary ammonium compounds containing the cation:

$[R_2NR'_2]^{(+)}$

30 where R is C_8 to C_{22} and R' is C_1 to C_4 , as additives for producing a non-stalling gasoline and as fuel oil stabilisers.

U.S. Patent No. 3,493,354 discloses the use of quaternary ammonium compounds containing the cation:
 $[R_4N]^{(+)}$

in which the sum total of carbon atoms is at least 12, as part of a package to prevent smoke.

35 U.K. Patent No. 973,826 discloses the use of quaternary ammonium nitrites containing the cation:

$[R_2NR'_2]^{(+)}$

where R is C_{12} to C_{22} and R' is C_1 to C_{10} , as a fuel additive to be used in conjunction with an amine.

U.K. Patent No. 1,078,497 discloses the use of quaternary ammonium compounds containing the cation:

$[R_2NR'_2]^{(+)}$

40 where R is C_6 to C_{22} and R' is C_1 to C_5 .

U.K. Patent No. 1,392,600 discloses the use as antiwear additives of quaternary ammonium phosphates in which the cation contains at least 10 (and preferably more) carbon atoms.

U.K. Patent No. 1,409,019 discloses the use of quaternary ammonium compounds containing the cation:

$[RN(CH_3)_3]^{(+)}$

45 where R is C_8 to C_{40} , as additives to improve the water tolerance of hydrocarbon liquids.

Three patents disclose the use of quaternary ammonium compounds in which the total number of cations atoms in the cation is less than 10. Two of the patents, U.K. Patents Nos. 1,199,015 and 1,221,647, disclose the use of quaternary ammonium phosphates and thiophosphates. However phosphorus "poisons" transition metal catalysts such as are commonly used as particulate traps in e.g. diesel engines. The third
50 patent, U.K. Patent No. 1,432,265, describes quaternary ammonium compounds to be used in combination with a sulphone polymer as an antistatic additive.

The present invention provides a fuel composition comprising a fuel oil obtained by the cracking of heavy oil and a quaternary ammonium compound which is soluble in the fuel and which comprises a hydrocarbyl cation in which the ratio of carbon atoms to quaternary nitrogen atoms is not more than 10:1 and an anion which is derived from an acid which is a carboxylic acid, carboxylic acid anhydride, a phenol,

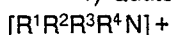
a sulphurized phenol or a sulphonic acid. The hydrocarbonyl group or groups optionally carries or carry a tertiary amino nitrogen atom or atoms but is or are otherwise unsubstituted.

Advantageously, the quaternary ammonium compound contains 1 to 4 quaternary nitrogen atoms, and not more than 10 carbon atoms.

5 The quaternary ammonium compounds are effective fuel stabilizers in the absence of any other additive. Furthermore, the quaternary ammonium compounds are more effective as fuel stabilizers than quaternary ammonium compounds in which the ratio of carbon atoms to quaternary nitrogen atoms in the cation exceeds 10.

Examples of suitable compounds are

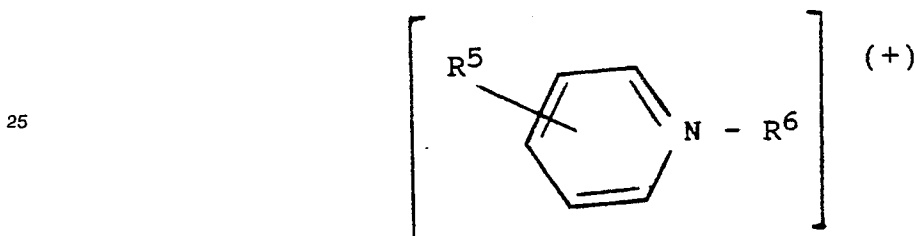
10 1) Quaternary ammonium compounds in which the structure of the cation is:



in which R^1 , R^2 , R^3 , R^4 are alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl or aralkyl groups such that the sum total of carbon atoms in the cation does not exceed 10.

15 Examples of such cations include tetramethylammonium, ethyltrimethylammonium, n-propyltrimethylammonium, iso-propyltrimethylammonium, n-butyltrimethylammonium, pentyltrimethylammonium, hexyltrimethylammonium, heptyltrimethylammonium, phenyltrimethylammonium, o-tolyltrimethylammonium, m-tolyltrimethylammonium, p-tolyltrimethylammonium, benzyltrimethylammonium, diethyldimethylammonium,

20 2) Quaternary ammonium compounds in which the structure of the cation is:

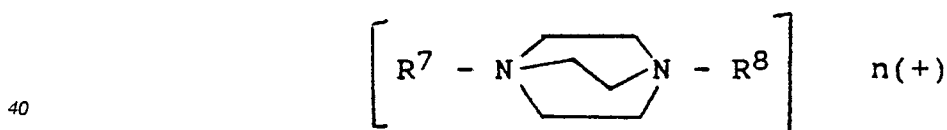


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- where R^5 and R^6 are alkyl, cycloalkyl, alkenyl, or cycloalkenyl and may be the same or different but are such that the total number of carbon atoms in the cation does not exceed 10.

35 Examples of such cations include methylpyridinium, ethylpyridinium, methyl-2-picolinium, methyl-3-picolinium and methyl-4-picolinium.

3) Quaternary ammonium compounds in which the structure of the cation is:

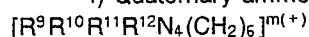


- where R^7 is alkyl, cycloalkyl, alkenyl, cycloalkenyl

45 - where R^8 is nothing, when $n = 1$, or alkyl, cycloalkyl, alkenyl or cycloalkenyl, when $n = 2$, such that the ratio of carbon atoms in the cation to quaternary nitrogen atoms does not exceed 10:1.

Examples of such cations are the cations in which $R^7 = \text{methyl}$, R^8 is absent, and $n = 1$, and in which $R^7 = R^8 = \text{methyl}$, and $n = 2$.

4) Quaternary ammonium compounds in which the structure of the cation is:

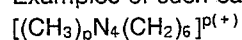


50 - where R^9 is alkyl, cycloalkyl, alkenyl, cycloalkenyl

- where R^{10} , R^{11} , R^{12} can be nothing, or alkyl, cycloalkyl, alkenyl, cycloalkenyl such that the ratio of carbon atoms in the cation to quaternary nitrogen atoms does not exceed 10:1.

- m is 1 to 4, the value of m being increased from unity by one for each of R^{10} , R^{11} , R^{12} , having a meaning other than zero.

55 Examples of such cations are:



where p is 1, 2, 3 or 4.

It will be understood that in compounds containing two or more quaternary nitrogen compounds the

linkages between them will also be hydrocarbyl groups, i.e., the cation consists of quaternary nitrogen, carbon and hydrogen atoms, optionally substituted by tertiary amino nitrogen atoms.

Cations in groups (3) and (4) when R^8 , or one or more of R^{10} , R^{11} , R^{12} , represent zero are examples of hydrocarbyl groups carrying tertiary amino nitrogen atoms.

5 The acid which is used to form the anion may be a carboxylic acid, carboxylic acid anhydride, phenol, sulphurized phenol or sulphonic acid.

The carboxylic acid may be e.g.:

i) An acid of the formula

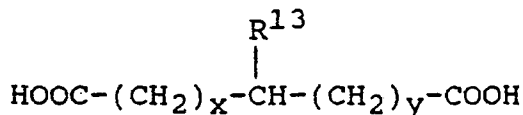
R^{13} -COOH

10 where R^{13} is hydrogen, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl, or aryl. Examples of such acids include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, palmitic acid, stearic acid, cyclohexanecarboxylic acid, 2-methylcyclohexanecarboxylic 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

$\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$

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



25

where x is zero or an integer, y is zero or an integer and x and y may be equal or different and R^{13} 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^{13} 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.

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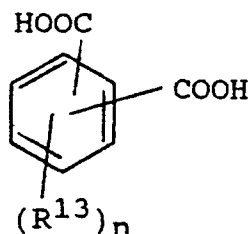
The dicarboxylic acids also include acids of the formula:

$\text{HOOC}-(\text{C}_r\text{H}_{2r-2})\text{COOH}$

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.

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



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where R^{13} is defined as in (i) and $n = 1, 2, 3$ or 4 and when $n > 1$ then the R^{13} 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.

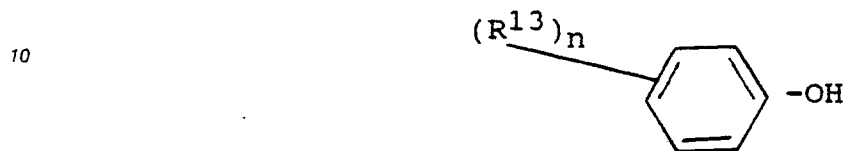
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The carboxylic acid anhydrides include the anhydrides that may be derived from the carboxylic acids described above. Also included are the anhydrides that may be derived from a mixture of any of the

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.

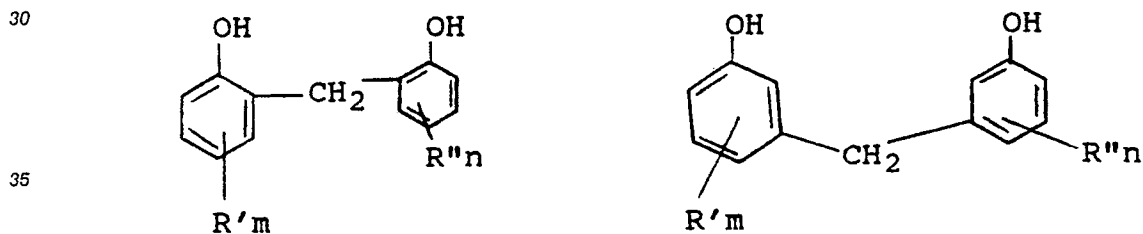
5 The phenols from which the anion of the quaternary ammonium compound may be derived are of many different types. Examples of suitable phenols include:

(i) Phenols of the formula:

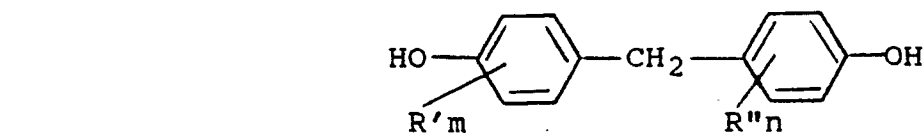


15 where $n = 1, 2, 3, 4$ or 5 , where R^{13} is defined above and when $n > 1$ then the substituents may be the same or different. The hydrocarbon group(s) may be bonded to the benzene ring by a keto or thio-keto group. Alternatively the hydrocarbon group(s) may be bonded through an oxygen, sulphur 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-n-butylphenol; 4-isobutylphenol; 4-sec-butylphenol; 4-t-butylphenol; 4-nonylphenol; 2-dodecylphenol; 4-dodecylphenol; 4-octadecylphenol; 2-cyclohexylphenol; 4-cyclohexylphenol; 2-allylphenol; 4-allylphenol; 2-hydroxydiphenyl; 4-hydroxydiphenyl; 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:



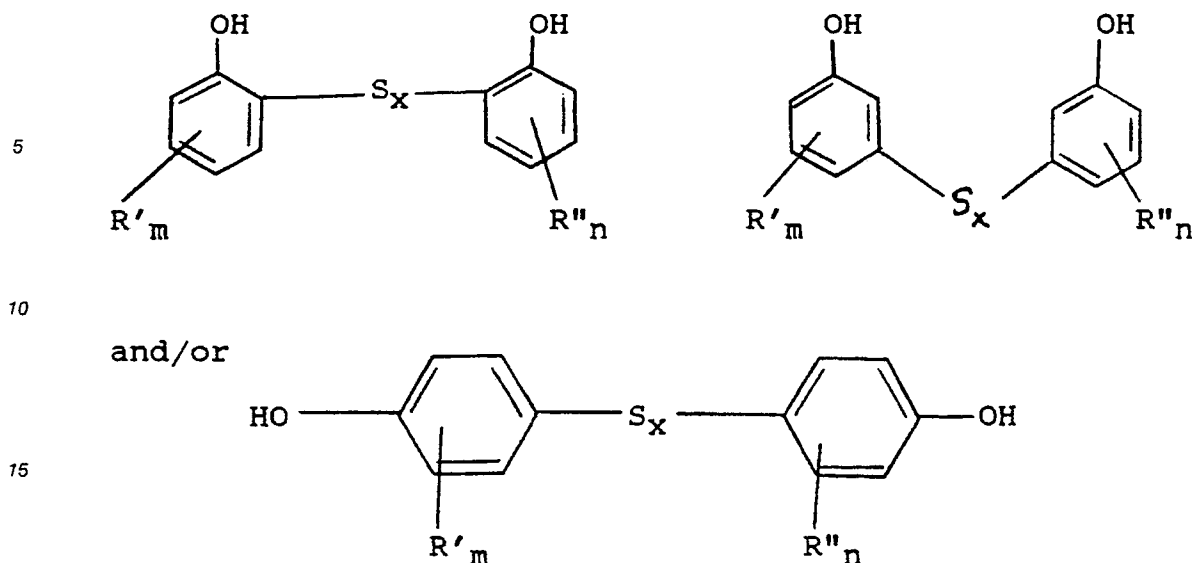
and/or



where R' and R'' which may be the same or different are as defined above for R^{13} and m and n are integers. Examples of such phenols include 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane; 5,5'-dihydroxy-2,2'-dimethyldiphenylmethane; 4,4'-dihydroxy-2,2'-dimethyl-dimethyldiphenylmethane; 2,2'-dihydroxy-5,5'-dinonyldiphenylmethane; 2,2'-dihydroxy-5,5'-didodecyldiphenylmethane and 2,2',4,4'-tetra-t-butyl-3,3'-dihydroxydiphenylmethane.

Also included are sulphurized phenols of the formula:

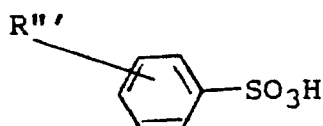
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where R' and R'' which may be the same or different are as defined above, and m and n are integers and x is 1, 2, 3 or 4. Examples of such phenols include:

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 1-200 carbon atoms per molecule although the preferred range is 1-80 atoms per molecule. Included in this description are aryl sulphonic acids of the formula:



where $n = 1, 2, 3, 4, 5$ and when $n > 1$ the substituents may be the same or different, and R''' may represent R^{13} as defined above.

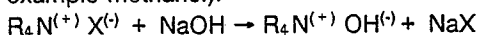
The hydrocarbon group(s) may be bonded to the benzene ring through a carbonyl group or the thio-keto group. Alternatively the hydrocarbon group(s) may be bonded to the benzene ring through a sulphur, oxygen or nitrogen atom. Thus examples of sulphonic acids that may be used include: benzene sulphonic 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; 4-*n*-butylbenzenesulphonic acid; 4-isobutylbenzenesulphonic acid; 4-*sec*-butylbenzenesulphonic acid; 4-*t*-butylbenzenesulphonic acid; 4-nonylbenzenesulphonic acid; 2-dodecylbenzenesulphonic acid; 4-dodecylbenzenesulphonic acid; 4-cyclohexylbenzenesulphonic acid; 2-cyclohexylbenzenesulphonic acid; 2-allylbenzenesulphonic acid; 2-phenylbenzenesulphonic acid; 4-(4-methylphenyl)benzenesulphonic acid; 4-methylmercaptobenzenesulphonic acid; 2-methoxybenzenesulphonic 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 R''' 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:
 $R-SO_3H$

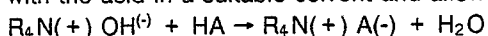
where R is alkyl, cycloalkyl, alkenyl or cycloalkenyl. Examples of such sulphonic acids that may be used include methylsulphonic acid; ethylsulphonic acid; n-propylsulphonic acid; n-butylsulphonic acid; isobutylsulphonic acid; sec-butylsulphonic acid; t-butylsulphonic; nonylsulphonic acid; dodecylsulphonic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

Some of the quaternary ammonium salts which may be employed according to the present invention are commercially available. It is preferred to use one of these compounds. Alternatively the quaternary ammonium compounds may be synthesized in any suitable manner. The quaternary ammonium compounds may be prepared by known processes. Two methods are preferred for the synthesis of compounds such as quaternary ammonium sulphonates, sulphurized phenates and carboxylates.

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



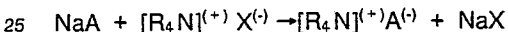
After removing the metal halide by filtration, the solution of quaternary ammonium hydroxide is mixed with the acid in a suitable solvent and allowed to react:



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

In the second method the organic acid is reacted with a metal oxide or hydroxide to form the metal salt: $HA + NaOH \rightarrow NaA + H_2O$

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:



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

Preferably the fuel composition comprises 5 to 1000 ppm, more preferably 10 to 500 ppm, and most preferably 20 to 200 ppm of quaternary ammonium compound based on parts of the fuel.

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. 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 present invention accordingly provides a fuel composition comprising a distillate fraction and a cracked fraction and a quaternary ammonium compound soluble in the composition, the quaternary ammonium compound having a cation in which the substituent on the or each quaternary nitrogen is a hydrocarbyl group optionally bearing a tertiary amino nitrogen atom, and in which cation the ratio of carbon atoms to quaternary nitrogen atoms is at most 10:1, the anion being derived from a carboxylic acid or anhydride, a phenol, a sulphurized phenol or a sulphonic acid. The invention also provides the use of such a quaternary ammonium compound in inhibiting sediment and color formation in a fuel oil composition, especially one containing a component obtained by the cracking of heavy oil.

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 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).

The present invention is illustrated by the following examples:

Example 1

Synthesis of Tetramethylammonium Dodecylphenate

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A solution of sodium hydroxide (10 g; 0.25 moles) in methanol (100 mls) was added slowly, under nitrogen, to a stirred solution of tetramethylammonium bromide (38.5 g; 0.25 moles) in methanol (200 mls). When the addition was complete the solution was stirred for a further 30 minutes.

10 The sodium bromide was filtered off and the solution of the tetramethylammonium hydroxide added directly to a solution of dodecylphenol (65.5 g; 0.25 moles) in toluene (200 mls). The reaction mixture was heated to reflux for 1 hour and then the solvents were removed by heating to 150 ° C under vacuum.

Stanco 150 (83.8 g), a mineral oil base stock (Exxon), was added to the product which was then filtered through Dicalite 4200 (diatomaceous earth).

15 TBN = 122 mg KOH/g

TABLE 1 Shows the effect of blending different amounts of a straight distillate with an unhydrofined catalytically cracked gas oil on sediment and colour in the AMS 77.061 accelerated stability test.

TABLE 2 Shows typical nitrogen and sulphur levels for straight run distillates and unhydrofined catalytically cracked gas oils.

20 TABLE 3 Shows the effect of doping a stable fuel with compounds containing nitrogen and sulphur.

TABLE 4 Shows AMS 77.061 test results on fuels treated with quaternary ammonium compounds in accordance with the present invention. From a comparison of the results for the treated fuels with the results for the untreated fuel, it is clear that the compounds of this invention give good control of colour and sediment.

25

TABLE 1

Fuel 3*	Fuel 4**	Sediment	
wt %	(*)	(mg/100 ml)	Δ Colour (a)
100	0	(0.14 $\pm$ 0.09)	$\approx$ 0.5, <0.5, <0.5
80	20	(0.61 $\pm$ 0.13)	$\approx$ 1.0, 1.0, 1.0, 1.0
60	40	(1.12 $\pm$ 0.10)	$\approx$ 1.0, $\approx$ 1.0, $\approx$ 1.0, $\approx$ 1
40	60	(1.80 $\pm$ 0.04)	$\sim$ 2.0, $\sim$ 2.0
20	80	(2.10 $\pm$ 0.10)	$\sim$ 2.0, $\sim$ 2.0
0	100	2.90	$\sim$ 6.0

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* Straight distillate

** Unhydrofined catalytically cracked gas oil (CCGO)

(a) Colour Change (ASTM D1500 test)

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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

TABLE 3

The 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	SA	Sediment	Colour	
(ppm) ^(a)	(ppm) ^(b)	(mg/100 ml)	Before	After
NIL	NIL	0.06, 0.10	< 0.5	< 1.0
NIL	50	0.02, 0.00	< 0.5	< 1.5
			< 0.5	< 1.5
50	NIL	0.76, 0.59	< 0.5	< 1.0
			< 0.5	< 1.0
50	50	1.06, 1.01	< 1.5	< 3.0
			< 1.5	< 3.0

(a) 2,5-dimethylpyrrole

(b) a commercially available alkyl-aryl sulphonic acid having a SAN of approximately 80 mg KOH/g of acid

TABLE 4

The Effect of Short Chain Quaternary Ammonium compounds in the AMS 77.061 Test			
CATION	ANION	SEDIMENT ^(a)	Δ COLOUR
NONE	NONE	(1.18 ± 0.20) ^(b)	≈1.0
(CH ₃) ₄ N	PIBSATE	(0.05 ± 0.06) ^(c)	≈1.0, ≈1.0
(CH ₃) ₄ N	DDP ^(d)	(0.16 ± 0.00) ^(c)	≈0.5, ≈0.5
(CH ₃) ₄ N	NPS ^(e)	(0.00 ± 0.00) ^(c)	≈0.5, ≈0.5

a) mgs/100 mls of fuel

b) (mean ± standard deviation) of 14 tests

c) (mean ± standard deviation) of 2 tests

d) dodecylphenol

e) nonylphenol sulphide

* Fuel is 80% straight distillate and 20% unhydrofined catalytically cracked gas oil

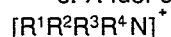
**Additive used at 100 ppm

Claims

1. A fuel composition comprising a fuel oil obtained by the cracking of heavy oil and a quaternary ammonium compound which is soluble in the fuel and which comprises a hydrocarbyl cation in which optionally the hydrocarbyl group carries or groups carry a tertiary amino nitrogen atom or atoms but is or are otherwise unsubstituted, and in which cation the ratio of carbon atoms to quaternary nitrogen atoms is not more than 10:1, and an anion which is derived from an acid which is a carboxylic acid, carboxylic acid anhydride, phenol, sulphurized phenol or sulphonic acid.

2. A composition according to claim 1, in which the cation of the quaternary ammonium compound contains from 1 to 4 quaternary nitrogen atoms.

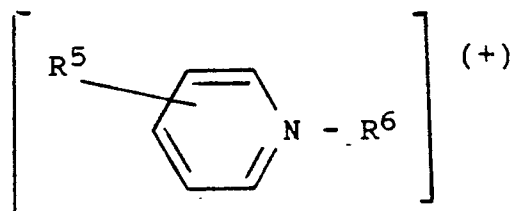
3. A fuel composition according to claim 1, in which the cation is of the formula:



in which R¹, R², R³, and R⁴, which may be the same or different, are each alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl or alkaryl such that the number of carbon atoms in the cation does not exceed 10.

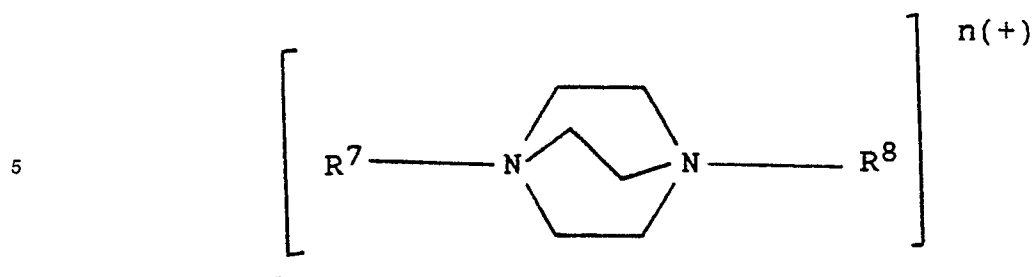
4. A composition according to claim 3, in which the cation is tetramethylammonium.

5. A composition according to claim 1, in which the cation is of the formula:



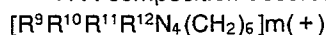
in which R⁵ and R⁶ which may be the same or different are each alkyl, cycloalkyl, alkenyl, or cycloalkenyl such that the number of carbon atoms in the cation does not exceed 10.

6. A composition according to claim 1, in which the cation is of the formula:



10 in which R^7 is alkyl, cycloalkyl, alkenyl or cycloalkenyl; R^8 is nothing in which case n is 1 or alkyl, cycloalkyl, alkenyl, or cycloalkenyl in which case n is 2, such that the ratio of carbon atoms to quaternary nitrogen atoms in the cation does not exceed 10.

7. A composition according to claim 1, in which the cation is of the formula:

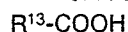


15 in which R^9 is alkyl, cycloalkyl, alkenyl or cycloalkenyl; R^{10} , R^{11} or R^{12} which may be the same or different are each nothing, alkyl, cycloalkyl, alkenyl or cycloalkenyl, such that the ratio of carbon atoms to quaternary nitrogen atoms in the cation does not exceed 10; and m is an integer of 1 to 4, the value of m increasing from unity by one for each of R^{10} , R^{11} , and R^{12} that represents a substituent.

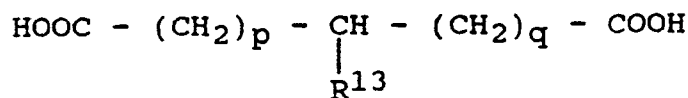
20 8. A composition according to claim 7, in which the cation is N-methylhexamethylenetetrammonium or N,N',N'',N'''-tetramethylhexamethylenetetrammonium.

9. A composition according to any one of the preceding claims in which the anion of the quaternary ammonium compound is derived from a carboxylic acid.

10. A composition according to claim 9, in which the carboxylic acid is of the formula:



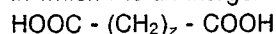
25 or



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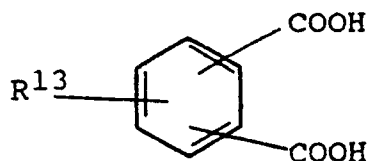
in which p and q which may be the same or different are each zero or an integer or $\text{HOOC} - (\text{C}_r\text{H}_{2r-2}) - \text{COOH}$

35 in which r is an integer of 2 or more or



in which z is zero or an integer of 1 or more or

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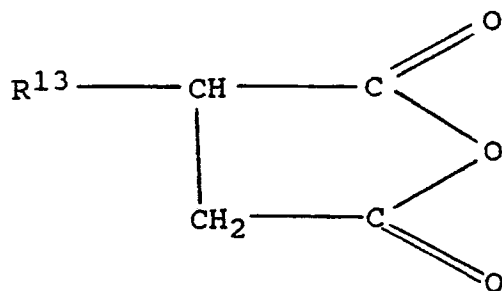
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in which R^{13} is hydrogen, alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkaryl or aralkyl.

11. A composition according to any one of claims 1 to 8, in which the anion of the quaternary ammonium compound is derived from a carboxylic acid anhydride, advantageously a carboxylic acid as defined in claim 10 or is a substituted succinic anhydride of the formula:

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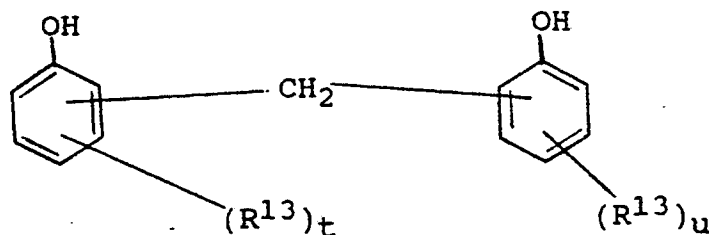


in which R^{13} is defined as in claim 10, or is a substituted anhydride with an optionally substituted polyisobutylene, in which the polyisobutylene advantageously has a molecular weight of between 500 to 2000 daltons.

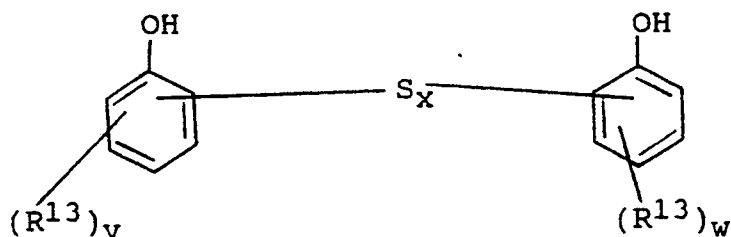
12. A composition according to any one of claims 1 to 8, in which the anion of the quaternary ammonium compound is derived from a phenol, advantageously one of the formula:



in which s is an integer from 0 to 5 and R^{13} is defined as in claim 10, and when s is greater than 1 each R^{13} may be the same or different, preferably nonylphenol or dodecylphenol; or of the formula:



in which t and u , which may be the same or different, are each an integer from 0 to 4; or of the formula:

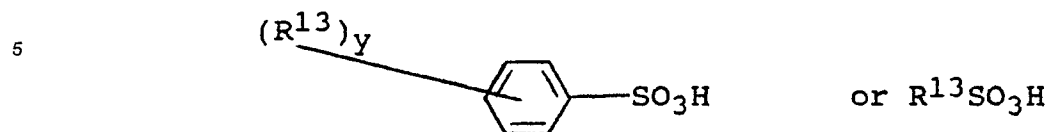


in which v and w , which may be the same or different, are each an integer from 0 to 4; R^{13} is as defined in claim 10, and for each t , u , v and w greater than 1, each R^{13} may be the same or different; and x is zero or an integer from 1 to 10.

13. A composition according to claim 12 in which:

- R^{13} is C_9
- v is 1 or 2
- w is 1 or 2
- x is 1 to 6 or in which
- R^{13} is C_{12}
- both v and w are 1
- x is 1 to 6.

14. A composition according to any one of claims 1 to 8, in which the anion of the quaternary ammonium compound is derived from a sulphonic acid, preferably one of the formula:



10 in which y is an integer from 0 to 5; R^{13} is as defined in claim 10, and when y is greater than 1 each R^{13} may be the same or different.

15. A composition as defined in any one of the preceding claims in which the fuel oil comprises a direct-distillation fraction and a cracked fraction, the cracked fraction comprising 5 to 97% by weight of the composition.

15 16. A composition as defined in any one of the preceding claims which comprises from 5 to 1000 ppm, advantageously 10 to 500 ppm, and preferably 20 to 200 ppm, of the quaternary ammonium compound.

17. Use of a quaternary ammonium compound as defined in any one of claims 1 to 14 as an inhibitor for sediment and colour formation in a fuel oil composition.

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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)
X	US-A-3 256 074 (ECKERT) * Whole document *	1,2,9, 10,11, 16	C 10 L 1/22 C 10 L 1/24
X	--- US-A-3 361 546 (RAYMOND et al.) * Whole document *	1-4,9, 10,16, 17	
A	---	5	
X	US-A-2 867 515 (ANDRESS) * Whole document *	1,2,9, 10,12, 15-17	
A	---	7,8	
X	DE-C-1 021 525 (SOCONY MOBIL OIL) * Whole document *	1,2,9, 10,12, 15-17	
X	--- US-A-2 633 415 (CHENICEK) * Whole document *	1-4,12, 15-17	
X	--- US-A-3 129 699 (MILLIKAN) * Whole document *	1,2,9, 10,14, 16	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	---	7,8	C 10 L
A	--- US-A-1 973 676 (VOORHEES) * Whole document *	1,6-8	
A	--- US-A-3 102 797 (UDELHOFEN) * Whole document *	1	
A	--- EP-A-0 293 192 (EXXON) * Pages 3,5 *	12,13	
	---	-/-	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-06-1990	Examiner DE LA MORINERIE B.M.S.B.
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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)
A	CH-A- 405 330 (SANDOZ) * Claims * ---	6-8	
A	US-A-2 900 788 (FELBERG et al.) * Whole document * -----	7,8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-06-1990	Examiner DE LA MORINERIE B.M.S.B.
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