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FUEL OIL COMPOSITION

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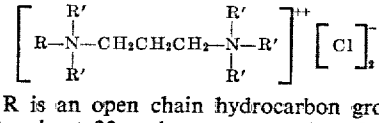
This invention relates to distillate fuel oil compositions containing multi-functional addition agents. More particularly, this invention relates to distillate fuel oil compositions containing addition agents capable of imparting dispersancy or detergency properties and oxidation stability to the distillate fuel oil compositions.

In the storage of distillate fuel oil compositions there exists a problem of oxidative deterioration of the fuel oil under storage conditions. The deterioration of distillate fuels through oxidation under conditions of storage manifests itself in the appearance of darker colors, sediment, gum or sludge, etc., in the oil. Sediment formation is often the most troublesome problem with which formulators of fuel oils are concerned because sediment formation normally may result in clogging of fuel system equipment such as filters, screens, nozzles, burners, etc., with sludge formed from sediment. The deterioration of fuel oils is much more prevalent where the fuel oil contains cracked materials and beacuse of recent tendencies to blend fuel oils by mixing virgin furnace oil fractions with cracked components, oxidative deterioration has become a problem associated with many commercial fuel oil blends. The oxidative deterioration problem has, therefore, attracted much study and as a result has been successfully lessened using addition agents known as "fuel oil stabilizers" which inhibit such deterioration.

In addition to fuel oil stabilizers, other addition agents may also be necessary, such as dispersants, to improve filterability of the fuel oil and thereby prevent clogging of fuel system equipment by sediment and sludge which has formed in the fuel oil.

Many addition agents which act as stabilizers have been proposed. However, because perfect protection of fuel oils against deterioration with resulting sludge and sediment formation has not been obtained using addition agents, i.e., because no stabilizer used gives perfect protection in all fuel oils, it is often necessary to use a dispersant in addition to the fuel oil stabilizer. Rather than use two different addition agents for the two functions, it is desirable to provide a "multi-function" addition agent which acts both as a fuel oil stabilizer and as a dispersant.

I have now discovered a new composition of matter useful as a multi-function addition agent in distillate fuel oil compositions as a combination dispersant and fuel oil stabilizer. The composition of this invention is an oil-soluble di-quaternary ammonium chloride having the following structural formula:



wherein R is an open chain hydrocarbon group having from 6 to about 22 carbon atoms and preferably from about 12 to about 18 carbon atoms and R′ is selected from the class consisting of alkyl groups having from 1 to 22 and more advantageously from 1 to 10 carbon atoms and aralkyl groups having from 7 to 22 and more advantageously from 7 to 10 carbon atoms. In the preferred chloride salts, R contains no more than two unsaturated linkages. R′ is preferably selected from methyl and benzyl.

In accordance herewith, the above di-quaternary ammonium chlorides are useable in small amounts in fuel

oil compositions containing a major amount of distillate fuel oil. Advantageously, the salts may be used in distillate fuel oils in amounts of from about 0.0001 to about 10 weight percent and preferably from about 0.0005 to about 0.05 weight percent.

The quaternary ammonium chloride salts of this invention can be prepared by reacting the corresponding hydrocarbon chlorides, i.e., R′ chloride (with R′ as defined above) with the corresponding N-alkyl propylene diamine (wherein the alkyl group is the R group of the above formula). Five moles of the hydrocarbon chloride are reacted with each mole of N-alkyl propylene diamine. The reaction is advantageously carried out in the presence of a suitable solvent such as butanol, isopropanol, etc. The reaction goes readily to completion and the solvent may be removed from the resulting product by evaporation.

The N-alkyl propylene diamine may be any such diamine wherein the alkyl group contains from 6 to about 22 carbon atoms and preferably from about 12 to about 18 carbon atoms. Thus, the N-hexyl, N-heptyl, N-octyl, N-octenyl, N-decyl, N-dodecyl, N-palmityl, N-hexadecyl, N-octadecyl, N-octadecenyl, N-octadecadienyl, N-eicosyl- N-docosyl, etc., propylene diamines may be used. The amines include the normal and branched chained N-alkyl propylene diamines, e.g., they include N-lauryl as well as 2-ethyl decyl propylene diamine and also include palmityl, myristyl, oleyl, linoleyl, linolenyl, stearyl, 2,3-dimethyl hexyl, etc., propylene diamines. Also included are the higher molecular weight N-alkyl propylene diamines wherein the alkyl group is derived from polymerized acids such as dimerized linoleic acid and the like. N-alkyl propylene diamines, useable in forming quaternary ammonium chloride salts for use herein, may be prepared by reactions well known to the art or may more conveniently be obtained commercially. Because of their commercial availability, the N-alkyl propylene diamines marketed by Armour and Company are particularly preferred. These N-alkyl propylene diamines are marketed under the names Duomeen T (wherein the alkyl groups are derived from tallow fatty acid and include alkyl groups in the C_{14} to C_{18} range, predominating in palmityl and stearyl groups), Duomeen C (wherein the alkyl groups are derived from coco fatty acid and include alkyl groups in the C_{12} to C_{18} range, predominating in lauryl, stearyl and palmityl groups), Duomeen S (wherein the alkyl groups are derived from commercial stearic acid and include alkyl groups in the C_{16} to C_{18} range, over about 90% of which are stearyl group), and Duomeen O (wherein the alkyl groups predominate in oleyl group).

The hydrocarbon chloride which is used to react with the tertiary amine is an alkyl chloride of from 1 to 22 carbon atoms or an aralkyl chloride of from 7 to 22 carbon atoms. The useable N-alkyl propylene diamines and hydrocarbon chlorides are well known to the art.

The following are examples of useable di-quaternary ammonium chlorides in accordance herewith:

N-hexyl N,N,N′,N′,N′-pentaphenylmethyl 1,3-propylene diammonium dichloride,

N-dodecyl N,N,N′,N′,N′-pentadecyl 1,3-propylene diammonium dichloride,

N-coco N,N,N′,N′,N′-pentamethyl 1,3-propylene diammonium dichloride,

N-tallow N,N,N′,N′,N′-pentamethyl 1,3-propylene diammonium dichloride,

N-stearyl N,N,N′,N′,N′-pentamethyl 1,3-propylene diammonium dichloride,

N-oleyl N,N,N′,N′,N′-pentamethyl 1,3-propylene diammonium dichloride,

N-lauryl N,N,N′,N′,N′-pentaphenylmethyl 1,3-propylene diammonium dichloride,

N-myristyl N,N,N',N',N'-pentaphenylmethyl 1,3-propylene diammonium dichloride,
N-tallow N,N,N',N',N'-pentaphenylmethyl 1,3-propylene diammonium dichloride,
N-coco N,N,N',N',N'-pentaphenylmethyl 1,3-propylene diammonium dichloride,
N-heneicosyl N,N,N',N',N'-pentaxylyl 1,3-propylene diammonium dichloride,
N-octadecyl N,N,N',N',N'-pentadodecyl 1,3-propylene diammonium dichloride,
N-myristyl N,N,N',N',N'-pentaeicosyl 1,3-propylene diammonium dichloride,
N-hexadecyl N,N,N',N',N'-pentaethyl 1,3-propylene diammonium dichloride,
N-tallow N,N,N',N',N'-pentacoco 1,3-propylene diammonium dichloride,
N-stearyl N,N,N',N',N'-pentalauryl 1,3-propylene diammonium dichloride,
N-hexadecadienyl N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride,
N-lauryl N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride,
N-octadecyl N,N,N',N',N'-penta 2-methyl pentyl 1,3-propylene diammonium dichloride,
N-octadecyl N,N,N',N',N'-pentaethyl 1,3-propylene diammonium dichloride,
N-octadecyl N,N,N',N',N'-penta 3-ethyl hexyl 1,3-propylene diammonium dichloride,
N-hexadecyl N,N,N',N',N'-pentaeicosyl 1,3-propylene diammonium dichloride,
N-octadecyl N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexahexyl 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexaoctyl 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexalauryl 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexacoco 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexatallow 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexastearyl 1,3-propylene diammonium dichloride,
N,N,N,N',N',N'-hexadocosyl 1,3-propylene diammonium dichloride, and
N,N,N,N',N',N'-hexadecyl 1,3-propylene diammonium dichloride.

In a typical preparation, N-coco N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride is prepared by reacting five moles of methyl chloride with one mole of N-coco, 1,3-propylene diamine in the presence of a benzene solvent at the reflux temperature of the solvent for about five hours in the presence of a small amount of water. The benzene solvent is evaporated leaving the desired product.

In another typical preparation, N-tallow N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride is prepared by reacting five moles of methyl chloride with one mole of N-tallow 1,3-propylene diamine in the presence of a benzene solvent and under benzene reflux conditions, as above, four or five hours. The solvent is removed by evaporation leaving the desired product. Other reflux solvents such as acetone, n-butanol, isopropanol, hexane, etc., may be used if desired in lieu of the benzene.

The quaternary ammonium chlorides described herein may be used in a distillate fuel oil, preferably a distillate heating oil, in a minor amount sufficient to stabilize the distillate oil and impart detergency properties to the fuel oil composition. The minor amount may advantageously be from about .0001 to about 10 weight percent and preferably from about .0005 to about .05 weight percent.

The distillate oil or distillate fuel oil is a hydrocarbon oil, such, for example, as a diesel fuel, a gasoline, a jet fuel, a heavy industrial residual fuel (e.g., Bunker C), a

furnace oil, a heater oil fraction, kerosene, a gas oil, or any other like light oil. Of course, any mixtures of distillate oils are also intended. The distillate fuel oil may be virgin or cracked petroleum distillate fuel oil. The distillate fuel oil may advantageously boil in the range of from about 200 to about 750° F., and preferably in the range of 350 to 650° F. The distillate fuel oil may contain or consist of cracked components, such, for example, as those derived from cycle oils or cycle oil cuts boiling heavier than gasoline, usually in the range of from about 450 to about 750° F. and may be derived by catalytic or thermal cracking. The addition agents of this invention are particularly effective against fuel oils containing cracked components. High-sulfur-containing and low-sulfur-containing oils such as diesel oils and the like may also be used. The distillate oil may, of course, contain other components such as addition agents used to perform particular functions, for example, pour point depressants, corrosion inhibitors, combustion improvers, etc.

The distillate fuel oil is preferably a hydrocarbon distillate heating oil in which the quaternary ammonium salts of this invention are used in accordance herewith. Such distillate heating oil is a distillate oil intended for use by burning to obtain heat, such as intended for furnace or heater fuel used as opposed to use in an internal combustion engine wherein the explosiveness of the fuel in a combustion chamber is important. Examples of such heating oils are a heavy industrial residual fuel (e.g., Bunker C), a heater oil fraction, a gas oil, a furnace oil, kerosene, or any other light oil intended for furnace or heater fuel use.

The following examples are illustrative of the addition agents of this invention as typically used in distillate fuel oil compositions.

EXAMPLES

In order to test the effectiveness of the above-defined quaternary ammonium chloride salts as addition agents in fuel oil compositions and more particularly as heating oil stabilizers and dispersants, examples of distillate oils containing salts as addition agents were prepared. Each example was prepared by mixing the indicated salt in the indicated amounts with the base distillate oil defined below.

Base oil—A 50–50 blend of light catalytic cycle oil and virgin gas oil.

Example 1—Base oil containing 0.005 weight percent of N-coco N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride.

Example 2—Base oil containing 0.005 weight percent of N-tallow N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride.

Example 3—Base oil containing 0.0025 weight percent of N-coco N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride.

Example 4—Base oil containing 0.0025 weight percent of N-tallow N,N,N',N',N'-pentamethyl 1,3-propylene diammonium dichloride.

A sample of the above base oil and each of the compositions of Examples 1 and 2 were aged in open containers in the dark at 200° F. for 20 hours. Another sample of the base oil and each of the compositions of Examples 3 and 4 were aged in the dark at 110° F. for 12 weeks. Samples of each aged base oil and example were then subjected to the tests below with the results reported at the end of each test procedure. The base oil samples are differentiated in the reported results by an indication of the aging temperature for each.

Sediment Test

One hundred mgs. of each aged sample was passed through a fritted glass crucible of fine porosity and the insolubles were collected on the crucible, washed with hexane and the crucible was then evaporated. Weights of insolubles collected from each sample were as follows:

Sample:	Mg. of insolubles
Base oil (200° F.)	3.5
Example 1	3.0
Example 2	3.5
Base oil (110° F.)	3.3
Example 3	1.7
Example 4	1.0

Soluble Gum Test

The filtrates from the above sediment test were each acid treated with 50 ml. hydrochloric acid and the resulting acid and oil mixture was sucked through a column of Celite whereby flocculated gum was deposited on the Celite. The Celite was washed with hexane and water to remove soluble materials and acid. The gum was then washed from the Celite with a mixture of aromatic solvent and the solvents were subsequently evaporated leaving soluble flocculated gum. Amounts of soluble gum recovered from each sample were as follows:

Sample:	Mg. of insolubles
Base oil (200° F.)	36.7
Example 1	9.0
Example 2	9.4
Base oil (110° F.)	32.2
Example 3	15.5
Example 4	15.0

Filterability Test

In this test, eight successive 50 ml. increments of each sample tested are poured through a one cm.^{2} area of 10 paper. The time in seconds for each increment was noted. Results were as follows:

Sample	Time in seconds, each increment							
	1st	2nd	3rd	4th	5th	6th	7th	8th
Base Oil (200° F.)			100+					
Example 1	24	29	32	35	37	40	44	50
Example 2	27	32	35	37	40	43	48	55
Base Oil (110° F.)	29	35	37	38	39	41	43	46
Example 3	27	30	32	32	32	33	33	36

Water Flocculation Test

The increments of filtrate from each of the above filterability tests for each sample were combined and the total filtrate from each sample was mixed with an equal amount (about 400 ml.) of water. Mixing was accomplished by vigorous shaking. The sample and water mixture was then allowed to settle for about 5 to 10 minutes until an interfacial rag appeared. Each mixture was then passed through a medium porosity fritted glass crucible. The appearance of the mat left in the crucible was noted and recorded as a measure of the sludge formed by contact with water. The results were as follows:

Sample:	Appearance
Base oil (200° F.)	Black.
Example 1	Light brown.
Example 2	Light brown.
Base oil (110° F.)	Black.
Example 3	Very light brown.

NPA Color Test

The following are the NPA colors for each of the aged samples:

Sample:	NPA color
Base oil (200° F.)	7+
Example 1	2½
Example 2	2½
Base oil (110° F.)	3½+
Example 3	3
Example 4	3

Sample:	Percent rusting
Base oil (200° F.)	50
Example 1	None
Example 2	15
Base oil (110° F.)	50
Example 3	None
Example 4	15

The results of the above test procedures demonstrate the efficiency of the quaternary ammonium salts of this invention as distillate oil stabilizers. With reference to the test results, the soluble gum test is a measure of the anti-oxidant properties of the various samples tested and indicates that the salts are effective anti-oxidation agents even in very small amounts. The sediment test results are a measure of the dispersant properties and anti-oxidant properties of the addition agents and the present agents were particularly good after 12 weeks of aging; the very small amounts of insolubles collected demonstrate excellent dispersant properties as well as anti-oxidant properties. The water flocculation test determines the sludge inhibiting tendencies of an additive and the above results demonstrate an improvement in appearance of the sample compared with the control base oil due to improved sludge inhibition. The filterability test is a measure of dispersant properties of the salts and the data show acceptably good filterability in comparison with the control. The NPA color test is well known and indicates the amount of color degradation of each sample due to the aging process. The NPA results show good color for the stabilized compositions and after accelerated aging at 200° F., the color was much better than the non-stabilized control. Good color is very important in formulating a commercial product since many purchasers have color specifications which must be met.

It is an advantage of this invention that fuel oil, and especially heating oil, addition agents are provided which stabilize distillate oils and impart dispersancy or detergency. The formation of sediment in distillate fuels containing cracked components is apparently the result of oxidation of hydrocarbons to free radicals and polymerization of the free radicals formed. Of course, this sediment can cause malfunctioning of burner equipment by plugging filters, screens and nozzles. The addition agents of this invention prevent burner failure by both reducing the formation of sediment and keeping any sediment formed well dispersed.

It is a further advantage of this invention that the addition agents provide retarded discoloration of fuel oils during aging. This is important in commercialization of a fuel oil composition since discoloration of a fuel oil during aging is undesirable and color specifications for the product must be met. It is still another advantage of this invention that sludge formation due to contact of a fuel oil with water is reduced, thereby reducing plugging of filters and nozzles. All of the above advantages may be attained by use of the hereindescribed addition agents.

The quaternary ammonium chloride salts of this invention may, for convenience, be prepared as addition agent concentrates. Accordingly, the salt is prepared in or dissolved in a suitable organic solvent therefor in amounts greater than 10% and preferably from about 25% to about 65%. The solvent in such concentrate may conveniently be present in amounts from about 35% to about 75%. The organic solvent preferably boils within the range of from about 100° F. to about 700° F. The preferred organic solvents are hydrocarbon solvents, for example, petroleum fractions such as naphtha, heater oil, mineral spirits and the like, because of their clean burning properties. The solvents selected should, of course, be selected with regard to possible beneficial or adverse effects they may have on the ultimate heating oil composition. Thus, the solvent should preferably burn without leaving a residue and should be non-corrosive with regard to metal, and especially ferrous metals. Other

desirable properties are obvious from the intended use of the solvent.

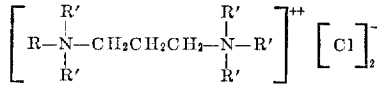
The defined di-quaternary ammonium chlorides may advantageously be used in combination with an N-alkyl propylene diamine such as those set out above. In such use from about 0.05 to about 10 parts by weight of the di-quaternary ammonium chloride may be used per part by weight of the diamine. The resulting combination is an excellent fuel oil stabilizer combination. The combination may further advantageously include a rust inhibitor such as a dimerized fatty acid, e.g., dimerized linoleic acid and/or a pour point depressant as an addition agent combination which is capable of imparting many desirable properties to a fuel oil by addition thereto.

All percentages given herein are percentages by weight unless otherwise indicated.

It is evident from the foregoing that I have provided distillate oil compositions containing defined di-quaternary ammonium salts as multipurpose addition agents effective in very small amounts.

I claim:

1. A fuel oil composition comprising a major amount of distillate fuel oil and from about 0.0001 to about 10 weight percent of a quaternary ammonium chloride having the structural formula:

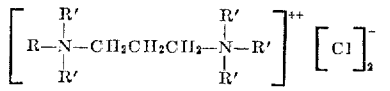


wherein R is an open-chain hydrocarbon group having from 6 to about 22 carbon atoms and R′ is a member selected from the class consisting of alkyl groups having from 1 to about 22 carbon atoms and aralkyl groups having from about 7 to about 22 carbon atoms.

2. The fuel oil composition of claim 1 wherein said distillate fuel oil is a heating oil.

3. The fuel oil composition of claim 1 wherein said fuel oil contains a cracked component.

4. A fuel oil composition comprising a major amount of a distillate heating oil and from about 0.0001 to about 10 weight percent of a quaternary ammonium chloride having the structural formula:



wherein R is an open-chain hydrocarbon group having from about 12 to about 18 carbon atoms and R′ is a member selected from the class consisting of alkyl groups having from 1 to 10 carbon atoms and aralkyl groups having from 7 to 10 carbon atoms.

5. The fuel oil composition of claim 4 wherein R′ is a methyl group.

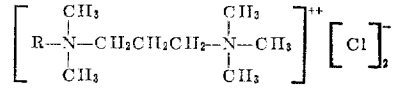
6. The fuel oil composition of claim 4 wherein R′ is a benzyl methyl group.

7. The fuel oil composition of claim 4 wherein said weight percent is from about 0.0005 to about 0.05 weight percent.

8. A fuel oil composition comprising a major amount of distillate fuel oil and from about 0.0001 to about 10 weight percent of N-tallow N,N,N′,N′,N′-pentamethyl 1,3-propylene diammonium dichloride.

9. A fuel oil composition comprising a major amount of distillate fuel oil and from about 0.0001 to about 10 weight percent of N-coco N,N,N′,N′,N′-pentamethyl 1,3-propylene diammonium dichloride.

10. A heating oil composition comprising a major amount of distillate heating oil and from about 0.0005 to about 0.05 weight percent of a quaternary ammonium chloride having the structural formula:



wherein R is an alkyl grup having from about 12 to about 18 carbon atoms.

11. The heating oil composition of claim 10 wherein R is an octadecyl group.

12. The heating oil composition of claim 10 wherein R is an octadecenyl group.

13. A fuel oil composition concentrate containing from about 25% to about 65% of the quaternary ammonium chloride defined in claim 1 and from about 35% to about 75% of a suitable solvent therefor, said concentrate being capable of dilution with a distillate fuel oil to a concentration of said chloride salt between about 0.0001 and 10 weight percent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,321,517	Rosen	June 8, 1943
2,617,806	Erickson	Nov. 11, 1952
2,861,874	O'Kelley et al.	Nov. 25, 1958
2,955,108	Omietanski	Oct. 4, 1960

FOREIGN PATENTS

789,620	Great Britain	July 23, 1958