United States Patent Office 3,029,136 Patented Apr. 10, 1962

3,029,136
STABILIZED DISTILLATE FUEL OILS

Earl E. Myers, Cheswick, Pa., assignor to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

No Drawing. Filed Oct. 5, 1955, Ser. No. 538,799
10 Claims. (Cl. 44—66)

This invention relates to stabilized distillate fuel oils. More particularly, the invention is concerned with the stabilization of blended distillate fuel oils that tend to deposit sludge by incorporation therein of small amounts of the herein disclosed quaternary ammonium salt addition agents.

Uncompounded distillate fuel oil compositions are often troublesome with regard to sludge deposition during storage at normal atmospheric temperatures. Sludge deposits in distillate fuel oils are objectionable in that such deposits can cause clogging of burner filters, screens, nozzles, etc. and thereby lead to improper functioning of the combustion apparatus in which the fuel oil is consumed.

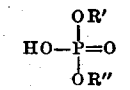
Although sludge deposition sometimes occurs in straight run distillate fuel oils, which oils contain mostly relatively stable paraffinic components, sludge deposition in these oils is normally considered to result from the presence of minor amounts of components that are not normally present and which impart instability to the otherwise stable oil, e.g., impurities added to and/or incompletely removed from the oil during refining, rather than from the inherent instability of the hydrocarbon components of the oil. The problem of sludge formation in such oils is considered essentially one involving oxidation and the formation of insoluble oxygenated products.

Catalytically cracked fuel oil distillates, on the other hand, are rich in olefinic, aromatic and mixed olefinic-aromatic compounds. Sludging in such oils, when such occurs, is considered to involve primarily condensation and/or polymerization type reactions which result in the formation of insoluble reaction products of relatively high molecular weight.

Sludge deposition in blends of straight run and catalytically cracked fuel oil distillates is an entirely distinct problem from that for either component oil. While the sludge formed in such blended fuel oils very probably contains some sludge of the type formed in each component oil, the sludge formed in blended fuel oils is consistently greatly in excess of the amount that can be accounted for from the known sludging tendencies of the individual component oils, thus indicating the existence of a special problem.

We have found that sludge deposition in blended distillate fuel oils can be substantially diminished by incorporation therein of small amounts of the addition agents disclosed herein. The addition agents whose use is included by this invention are oil-soluble quaternary ammonium salts having two of the covalent N-bonds attached to aliphatic hydrocarbon radicals containing 8 to 22 carbon atoms, and having the remaining covalent N-bonds attached to saturated aliphatic hydrocarbon radicals containing 1 to 4 carbon atoms, and having the ionic N-bond attached to an anionic, salt-forming radical derived from a material selected from the group consisting of (*a*) oil-soluble organic monocarboxylic acids, (*b*) oil-soluble monohydric phenols having attached to the aromatic nucleus at least one hydrocarbon substituent containing at least 4 carbon atoms, and having not more than one substituent in the ortho position that contains more than one carbon atom, and (*c*) oil-soluble

acid esters of o-phosphoric acid having the general formula:



where R′ is an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms and R″ is a member selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms. The present invention includes distillate fuel oil compositions containing said salts.

In what way the quaternary ammonium salts described herein function to improve the characteristics of distillate fuel oils is not clear, and accordingly the invention is not limited to any theory of operation. It would appear that they function as solubilizing agents for the sludge. However, in instances where other additive agents, considered to function similarly as the quaternary ammonium salts described herein, have been incorporated in blended distillate fuel oils in which some sludge has already formed, it has been noted that although the formation of additional sludge is inhibited, the already-formed sludge does not become dissolved. Nevertheless, in such instances it appears that although the already-formed sludge does not disappear, its characteristics are changed so as to prevent its deposition on burner screens, filters, or other burner parts.

The salts whose use is included by this invention can be prepared in any suitable manner. For example, these salts can be prepared by reacting a suitable quaternary ammonium halide with silver hydroxide in a solvent and at conditions such as to form a silver halide precipitate, and a quaternary ammonium hydroxide. The latter can then be neutralized with a salt-forming, oil-soluble acidic material of the class included by this invention to form a quaternary ammonium salt of the desired type. However, I prefer to form the quaternary ammonium salts disclosed herein by reacting a suitable quaternary ammonium halide with an alkali metal hydroxide, e.g., potassium hydroxide, in alcoholic solution, thus forming a precipitate of an alkali metal halide and an alcoholic solution of a quaternary ammonium hydroxide. After separation of the alcoholic quaternary ammonium hydroxide from any excess, or unreacted, alkali metal hydroxide, the quaternary ammonium salt can be formed by neutralizing the quaternary ammonium hydroxide with the desired oil-soluble salt-forming acidic material of the class included by this invention.

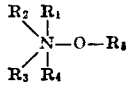
According to a preferred technique, any unreacted alkali metal hydroxide is separated from the alcoholic quaternary ammonium hydroxide by a procedure involving first, distilling the alcoholic solution containing quaternary ammonium hydroxide and unreacted alkali metal hydroxide, under reduced pressure sufficiently low to permit distillation of the alcohol at a temperature below the decomposition point of the quaternary ammonium compound, e.g., 150° F. or below, until a major portion of the alcohol has been removed. The alcohol removed by distillation is then replaced with an approximately equal volume of a non-polar solvent which is capable of forming an azeotropic mixture with alcohol and/or water, e.g., benzene. The addition of the non-polar solvent to the concentrated alcohol solution causes precipitation of excess alkali metal hydroxide. The thus precipitated alkali metal hydroxide can be removed by filtration. Since it is preferred to effect the neutralization of the quaternary ammonium hydroxide in a solvent other than alcohol, the above-described distillation, solvent addition and filtration can be repeated as many times as are necessary to remove not only excess alkali

metal hydroxide but also substantially all of the alcoholic solvent.

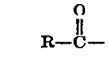
The reaction involving the liberation of the quaternary ammonium hydroxide from the corresponding halide takes place spontaneously at room temperature, and because of the formation of an insoluble reaction product, the reaction proceeds substantially to completion. Although equimolar proportions of the quaternary ammonium halide and the alkali metal hydroxide can be used, it is generally preferred to employ at least a small excess of the alkali metal hydroxide.

The quaternary ammonium hydroxides formed by reaction of the quaternary ammonium halide with an alkali metal hydroxide are strong bases, comparable to alkali metal bases, and they react spontaneously at room temperature with about equimolar proportions of oil-soluble, salt-forming acidic materials of the class included by the invention, to form the desired substantially neutral quaternary ammonium salts.

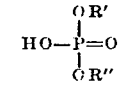
Quaternary ammonium salts whose use is included by this invention can be graphically represented by the generic formula:



where R_1 and R_2 are similar or dissimilar aliphatic hydrocarbon radicals containing 8 to 22 carbon atoms, R_3 and R_4 are similar or dissimilar saturated aliphatic hydrocarbon radicals containing 1 to 4 carbon atoms, N is nitrogen, O is oxygen and where R_5 is (*a*) the acyl residue



of an oil-soluble organic monocarboxylic acid, C representing carbon and R representing a hydrocarbon radical of a size and configuration such as to impart oil-solubility to the parent acid, (*b*) a substituted phenyl radical that has attached to the aromatic nucleus at least one hydrocarbon substituent containing at least 4, and preferably 4 to 15, carbon atoms and that has not more than one substituent in the ortho position containing more than one carbon atom, or (*c*) the phosphoryl residue of an oil-soluble acid ester of o-phosphoric acid having the general formula:



where R′ is an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms and R″ is selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms, O representing oxygen, H representing hydrogen, and P representing phosphorus.

In the foregoing formulae, R, R_1, R_2, R_3, R_4 and R′ and R″ can be straight or branched chain radicals, and R, R_1, R_2, R_3 and R_4 can be substituted with substituents that do not adversely affect the oil-solubility of the ultimate salts and that do not react preferentially with oil-soluble acidic materials of the class included by the invention. For example, these substituents may contain halogen, nitrogen, phosphorus, oxygen and sulfur. Examples of substituents containing such elements are hydroxy, mercapto, chloro, bromo and like substituents.

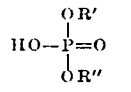
Referring to the various N-substituents in greater detail the two long chain aliphatic hydrocarbon substituents are important as regards the performance characteristics of the class of salts described herein, the latter being considered distinctly superior fuel oil sludge inhibitors as compared with similar salts containing other N-substituents or a lesser number of long chain N-substituents. Thus, the herein described salts are particularly outstanding as regards water separation and susceptibility to water-leaching. The long chain aliphatic hydrocarbon

substituents can be, for example, alkyl, alkenyl or alkadienyl radicals containing 8 to 22 carbon atoms. Quaternary ammonium salts wherein the two long chain aliphatic hydrocarbon N-substituents are alkyl groups containing 12 to 18 carbon atoms are considered especially effective fuel oil addition agents. Examples of preferred long chain aliphatic hydrocarbon N-substituents are dodecyl (lauryl), tetradecyl (myristyl), hexadecyl, and octadecyl (stearyl) radicals. Examples of other suitable long chain aliphatic hydrocarbon N-substituents are octyl, dodecenyl, tetradecenyl, octadecenyl (oleyl), and octadecadienyl (linoleyl) radicals.

If desired, the two long chain aliphatic hydrocarbon N-substituents containing 8 to 22 carbon atoms can be derived from natural fats and oils, for example coconut oil, soybean oil, animal tallow and the like. In such instances the long chain aliphatic hydrocarbon N-substituents will consist essentially of mixed alkyl groups containing 8 to 22 carbon atoms.

The two short chain aliphatic hydrocarbon N-substituents can be any lower alkyl group. Although methyl and ethyl groups are preferred for the reason that they tend to minimize any hindrance to the addition of the long chain substituents to the nitrogen atom, isopropyl, propyl, and butyl groups can be present.

The nature of the ionic N-substituents of the salts described herein is also important as regards the performance characteristics of these salts as sludge inhibitors in distillate fuel oils. Thus, it has been found that good results are obtained with quaternary ammonium salts having quaternary ammonium groups of the nature described above and whose ionic N-substituents are salt-forming radicals derived from materials selected from the group consisting of (*a*) oil-soluble organic monocarboxylic acids, (*b*) oil-soluble monohydric phenols having attached to the aromatic nucleus at least one hydrocarbon substituent containing at least 4 carbon atoms, and having not more than one substituent in the ortho position that contains more than one carbon atom, and (*c*) oil-soluble acid esters of o-phosphoric acid having the general formula:



where R′ is an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms and R″ is a member selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms.

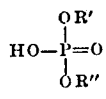
Oil-soluble organic monocarboxylic acids suitable for the purposes of this invention will normally contain 7 to 30 carbon atoms. Quaternary ammonium salts wherein the anionic substituent is a salt-forming radical derived from petroleum naphthenic acids form a preferred class of additives. As is known, such naphthenic acids are mixed alicyclic monocarboxylic acids recovered by alkali washing of petroleum distillates such as kerosene, naphtha, gas oil and lubricating distillates. The acids derived from these distillates are mixtures of alicyclic monocarboxylic acids containing about 7 to 30 carbon atoms per molecule, which mixtures have average molecular weights ranging from about 200 to about 450. Within the general class of petroleum naphthenic acids, the higher molecular weight acids derived from higher boiling distillates and containing 14 to 30 carbon atoms per molecule and having molecular weights of about 250 to 450 are considered to form especially effective quaternary ammonium salts for the purposes of this invention. Examples of other monocarboxylic acids that can be used to form quaternary ammonium salts whose use is included by this invention are oil-soluble, synthetic naphthenic acids such as cyclohexylacetic, cyclohexylpropionic, and cyclohexylstearic acids, and oil-soluble saturated or unsaturated fatty acids, such as caprylic, lauric, myristic, palmitic, stearic, oleic and linoleic acids. Mixtures of long chain fatty acids such as those derived from the saponification of natural

fats and oils also can be used to form quaternary ammonium salts within the scope of this invention. Examples of such mixed fatty acids are coconut, soya and tallow fatty acids. In such instances, the acids will consist essentially of mixtures of oil-soluble straight chain monocarboxylic acids containing 8 to 22 carbon atoms.

As previously indicated, phenols that form salts useful for the purposes of this invention are oil-soluble monohydric phenols having attached to the aromatic nucleus at least one hydrocarbon substituent containing at least 4 carbon atoms and having not more than one substituent in the ortho position that contains more than one carbon atom. The hydrocarbon substituent or substituents can be straight or branched chain and saturated or unsaturated. The hydrocarbon substituent or substituents, or the aromatic nucleus itself may contain substituent atoms, e.g., halogen, oxygen, phosphorus, nitrogen or sulfur, or substituent groups, e.g., nitro, amino, aryl, keto, or mercapto groups which do not affect the oil-solubility of the phenol and which do not react preferentially with the quaternary ammonium hydroxide. Phenols of the class described possess advantageous solubility and salt-forming characteristics.

Oil-soluble, monohydric phenols containing one aliphatic hydrocarbon substituent, having 4 to 15 carbon atoms, in the meta or para position to the hydroxyl group are considered to form especially effective quaternary ammonium salts for the purposes of this invention. For example, outstanding results have been obtained with quaternary ammonium salts of p-tert-octylphenol. Examples of other phenols that form suitable quaternary ammonium salts are p-tert-butylphenol, p-tert-amylphenol, p-sec-amylphenol, o-sec-amylphenol, o-tert-amylphenol, p-nonylphenol, cardanol, which consists essentially (approx. 90%) of a mixture of C_{15} straight chain meta-substituted phenols with different degrees of unsaturation in the side chains, hydrocarbanol, i.e., m-pentadecylphenol, 2,6-dimethyl-4-tert-butylphenol, 2-tert-amyl-4-methylphenol, 3-methyl - 6-tert-butylphenol, 2-methyl-4,6-di-tert-butylphenol, and 2,4-di-tert-butylphenol.

As also indicated above, oil-soluble acid esters of o-phosphoric acid that form salts whose use is included by this invention are those having the general formula:



wherein R′ is an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms and R″ is a member selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms. Acid esters of o-phosphoric acid that form a preferred class of quaternary ammonium salts according to this invention are those wherein R′ is an aliphatic hydrocarbon radical containing 8 to 18, and preferably 8 to 12, carbon atoms and wherein R″ is an aliphatic hydrocarbon radical containing 2 to 8 carbon atoms. Specific examples of acid esters of o-phosphoric acid capable of forming preferred quaternary ammonium salts according to this invention are diisooctyl acid o-phosphate, isoamyl octyl acid o-phosphate, ethyl lauryl acid o-phosphate, and ethyl oleyl acid o-phosphate. Other acid esters of o-phosphoric acid that form quaternary ammonium salts suitable for the purposes of this invention are dilauryl acid o-phosphate, dioleyl acid o-phosphate, dimyristyl acid o-phosphate, dipalmityl acid o-phosphate, octyl di-acid o-phosphate, lauryl di-acid o-phosphate, and oleyl di-acid o-phosphate.

Specific examples of preferred quaternary ammonium salts included by this invention are didodecyldimethylammonium naphthenate, dioctadecyldimethylammonium naphthenate, di-(hydrogenated tallow alkyl-)dimethylammonium naphthenate, dicocoalkyldimethylammonium oleate, didodecyldimethylammonium oleate, dicocoalkyldimethylammonium naphthenate, di-(hydrogenated tallow alkyl-)dimethylammonium p-tert-octylphenate, the chief component of which is dioctadecyldimethylammonium p-tert-octylphenate, dioctadecyldimethylammonium diisooctyl o-phosphate, bis-(dioctadecyldimethylammonium) isooctyl o-phosphate, dilauryl dimethylammonium ethyl oleyl o-phosphate, dicocoalkyldimethylammonium ethyl oleyl o-phosphate and the mixed neutral di-(hydrogenated tallow alkyl-)dimethylammonium salts of isooctyl and diisoctyl o-phosphoric acids. Examples of other salts included by the invention are the dioctyldimethylammonium, the didodecyldiethylammonium, the dihexadecyldipropylammonium, and the dioctadecenyldimethylammonium salts of naphthenic, oleic, stearic, caprylic, cyclohexylstearic acids, p-tert-amylphenol, p-sec-amylphenol, o-sec-amylphenol, o-tert-amylphenol, p-nonylphenol, cardanol, m-pentadecylphenol, 2,6-dimethyl-4-tert-butylphenol, 2-tert-amyl-4-methylphenol, 3-methyl-6-tert-butylphenol, 2-methyl-4,6-di-tert-butylphenol, 2,4-di-tert-butylphenol, diisooctyl o-phosphoric acid, isooctyl o-phosphoric acid, dilauryl o-phosphoric acid, dimyristyl o-phosphoric acid, dioleyl o-phosphoric acid, octyl o-phosphoric acid, and ethyl lauryl o-phosphoric acid.

The preparation of quaternary ammonium salts whose use is included by this invention is illustrated by the following specific examples.

Example I

An alcoholic solution of a quaternary ammonium halide was prepared by dissolving about 1380 grams of Arquad 2HT in approximately 2 liters of absolute ethanol, the mixture being warmed to provide a reasonably clear solution, and this solution was then reacted as indicated below. Arquad 2HT is manufactured by Armour & Company, Chicago, Illinois, and consists essentially of a 75 weight percent solution of di-hydrogenated tallow alkyl-) dimethylammonium chloride in isopropyl alcohol. The "hydrogenated tallow alkyl" radical consists essentially of a mixture of $C_{16}H_{33}$ and $C_{18}H_{37}$ radicals, with the latter predominating. The average molecular weight of the di-(hydrogenated tallow alkyl-)dimethylammonium chloride is about 570. An alcoholic solution of potassium hydroxide was then prepared by dissolving about 150 grams of potassium hydroxide in about 1600 ml. of absolute ethanol. Approximately 1200 ml. of the alcoholic potassium hydroxide were added slowly to the alcoholic Arquad 2HT solution with stirring over a period of about 10 to 15 minutes. A precipitate of potassium chloride was formed immediately. Precipitated potassium chloride was separated from the mixture by filtration, and the remaining 400 ml. of alcoholic potassium hydroxide were then slowly added to the filtrate with stirring over a period of about 10 to 15 minutes. Further precipitation of potassium chloride was observed. The mixture was again filtered to remove precipitated potassium chloride and the filtrate was distilled under reduced pressure to remove about 75 percent of the alcohol solvent. Heat was applied to the stillpot through the medium of a water bath which was kept well below the boiling point, at an estimated temperature of not greater than about 150° F. The reduction in pressure was achieved by the use of the laboratory vacuum line, which varies typically between about 25 and about 75 mm. Hg. The alcohol thus removed from the mixture was replaced with approximately an equal volume of benzene. The addition of benzene to the concentrated alcoholic solution caused precipitation of unreacted potassium hydroxide. After filtering the benzene:alcohol:di(hydrogenated tallow alkyl-)dimethylammonium hydroxide solution to remove precipitated potassium hydroxide, the mixture was again distilled as described above to remove approximately 75 percent of the solvent. The distilled solvent was again replaced with an approximately equal volume of benzene, and the mixture was again filtered. Approximately 3450 ml. of a benzene solution of di-(hydrogenated tallow alkyl-)dimethylammonium hydroxide were obtained.

Approximately 2100 ml. of the foregoing solution were used to neutralize 200 ml. of a petroleum naphthenic acid cut boiling from about 145° to about 185° C. at 3 mm. Hg, having a neutralization value of 213, and having an average molecular weight of about 381. The neutralization point was determined by the use of a litmus paper indicator. To the quaternary ammonium salt solution was then added a solvent-treated. Mid-Continent lubricating oil having a viscosity of about 450 Saybolt Universal seconds at 100° F. and an ASTM union color of about 3, in an amount sufficient to provide an ultimate, approximately 1:1 by weight solution of mineral lubricating oil and the quaternary ammonium salt. The thus obtained mixture was then distilled under vacuum as described above to remove benzene and water, and the remaining product was filtered. This product consisted essentially of an approximately 50 percent solution of di-(hydrogenated tallow alkyl-)dimethylammonium naphthenate in a mineral lubricating oil. The principal component of the active portion of the solution was dioctadecyldimethylammonium naphthenate.

The 50 percent mineral oil solution produced in accordance with the above-described procedure had the following analysis:

Neutralization value	—7.12
Oxide ash	0.10
Percent nitrogen	1.14

Example II

Another addition agent according to this invention is obtained by first, dissolving about 587 grams of Arquad 2C in approximately 1 liter of absolute ethanol, with warming to obtain a fairly clear solution, and then reacting this mixture as indicated in detail below. Arquad 2C is manufactured by Armour & Company and consists essentially of 75 weight percent dicocoalkyldimethylammonium chloride in isopropyl alcohol. The dicocoalkyldimethylammonium chloride has an average molecular weight of about 440. The "cocoalkyl" radical is a mixture of alkyl radicals derived from coconut oil fatty acids, the predominant component of the mixed alkyl radicals being the lauryl radical, the balance of said mixed alkyl radicals being made up of smaller amounts of C_8, C_{10}, C_{14}, C_{16} and C_{18} n-alkyl radicals. An alcoholic solution of potassium hydroxide is prepared by dissolving about 75 grams of potassium hydroxide in about 800 ml. of absolute ethanol, and this solution is added slowly to the Arquad 2C solution with stirring, until no additional precipitation of potassium chloride is observed. The mixture is filtered to separate potassium chloride, and the filtrate is distilled under vacuum as described in Example I to remove about 75 percent of the alcoholic solvent. The volume of distilled alcohol is replaced with benzene, and the mixture is filtered to remove precipitated potassium hydroxide. The filtrate is again distilled under vacuum as described above to remove about 75 percent of the solvent, and the removed volume of solvent is again replaced with an equal volume of benzene. The mixture is again filtered to remove any precipitated potassium hydroxide. The filtrate comprises a benzene solution of dicocoalkyldimethylammonium hydroxide. This mixture is then neutralized using approximately 278 grams (the calculated stoichiometric quantity) of a commercial oleic acid (Emersol 233 LL Elaine, Emery Industries, Inc.) having an iodine value of 88±2, a free fatty acid content, calculated as oleic acid, of 101%±1%, and a saponification value of 203±2. The neutralized mixture is then diluted with about 682 grams of the lubricating oil diluent described in Example I. The benzene and water of neutralization are then distilled off at reduced pressure following the procedure described above. The remaining product is an approximately 50 percent mineral oil solution of dicocoalkyldimethylammonium oleate, the predominant component of the active portion of the solution being dilauryldimethylammonium oleate.

Example III

An alcoholic solution of a quaternary ammonium hydroxide was prepared by a procedure including first, dissolving about 690 grams of Arquad 2HT in approximately 1 liter of absolute ethanol, the mixture being warmed to provide a reasonably clear solution, and then reacting the solution as indicated below. An alcoholic solution of potassium hydroxide was then prepared by dissolving about 75 grams of potassium hydroxide in about 800 ml. of absolute ethanol. Approximately 400 ml. of the alcoholic potassium hydroxide were added slowly to the alcoholic Arquad 2HT solution with stirring over a period of about 10 to 15 minutes. A precipitate of potassium chloride was formed immediately. Precipitated potassium chloride was separated from the mixture by filtration, and the remaining 200 ml. of alcoholic potassium hydroxide were then slowly added to the filtrate with stirring over a period of about 10 to 15 minutes. Further precipitation of potassium chloride was observed. The mixture was again filtered to remove precipitated potassium chloride and the filtrate was distilled under reduced pressure to remove about 75 percent of the alcoholic solvent. Heat was applied to the stillpot through the medium of a water bath which was kept well below the boiling point, at an estimated temperature of not greater than about 150° F. The reduction in pressure was achieved by the use of the laboratory vacuum line which varies typically between about 25 and about 75 mm. Hg. The alcohol thus removed from the mixture was replaced with approximately an equal volume of benzene. The addition of the benzene to the concentrated alcoholic solution caused precipitation of unreacted potassium hydroxide. After filtering the benzene:alcohol:di-(hydrogenated tallow alkyl-)dimethylammonium hydroxide solution to remove precipitated potassium hydroxide, the mixture was again distilled as described above to remove approximately 75 percent of the solvent. The distilled solvent was again replaced with an approximately equal volume of benzene and the mixture was again filtered. Approximately 1650 ml. of a benzene solution of di-(hydrogenated tallow alkyl-) dimethylammonium hydroxide were obtained.

Approximately 488 ml. of the foregoing solution were neutralized with about 50 grams, the calculated stoichiometric quantity, of a commercial (Rohm and Haas) p-tert-octylphenol having a hydroxyl number of 270, a 90 percent boiling point of 278°–308° C. at 760 mm. Hg, and a specific gravity (fused) of 0.941. To the quaternary ammonium salt solution was then added about 187 grams of a solvent-treated, Mid-Continent lubricating oil having a viscosity of about 450 Saybolt Universal seconds at 100° F. and an ASTM union color of about 3. The thus obtained mixture was then distilled under vacuum as described above to remove benzene and water of neutralization, and the remaining product was filtered. This product consisted essentially of an approximately 50 percent mineral oil solution of di-(hydrogenated tallow alkyl-)dimethylammonium p-tert-octylphenate. Dioctadecyldimethylammonium p-tert-octylphenate was the chief component of the active portion of the solution.

The 50 percent mineral oil solution produced in accordance with the above-described procedure had the following analysis:

Neutralization value	—35.1
Oxide ash	0.09
Percent nitrogen	0.95

Example IV

A benzene solution of dicocoalkyldimethylammonium hydroxide is prepared from Arquad 2C using the same quantities, materials and procedure described in Example II. This mixture is then neutralized using 164.2 grams, the calculated stoichiometric quantity, of a commercial p-tert-amylphenol, having a melting point within the range 81°–91° C., a boiling point within the range

250°–260° C., a flash point (open cup) of about 230° F., and a phenol coefficient of about 50–55. The neutralized mixture is then diluted with about 551 grams of the lubricating diluent described in Example I. The benzene and water of neutralization are then distilled off at reduced pressure, following the procedure described above. The remaining product is an approximately 50 percent mineral oil solution of dicocoalkyldimethylammonium p-tert-amylphenate, the principal component of the active portion of this solution being dilauryldimethylammonium p-tert-amylphenate.

Example V

Approximately 522 ml. of a benzene solution of di-(hydrogenated tallow alkyl-)dimethylammonium hydroxide, prepared as indicated in Example III, were used to neutralize approximately 41 grams of a commercial mixture of diisooctyl acid o-phosphate and isooctyl di-acid o-phosphate. The mixed acid esters of orthophosphoric acid used in this example were manufactured by the Victor Chemical Company and consisted essentially of the components named in approximately 1:1 mol proportions. The mixture of acids has an average molecular weight of about 266, a phosphorus content, calculated as P_2O_5, of 27.0 percent, a specific gravity at 25° C./4° C. of 1.020, a refractive index at 25° C. of 1.4428 and a decomposition point of about 215° to 220° C. A temperature rise of approximately 10° C. was noted during the neutralization procedure. The neutralization point was determined by the use of a litmus paper indicator. To the quaternary ammonium salt solution was then added about 187 grams of a solvent-treated, Mid-Continent lubricating oil having a viscosity of about 450 Saybolt Universal seconds at 100° F. and an ASTM union color of about 3. The thus obtained mixture was then distilled under vacuum as described above to remove benzene and water of neutralization, and the remaining product was filtered. This product consisted essentially of an approximately 50 percent solution of mixed neutral di-(hydrogenated tallow alkyl-)dimethylammonium salts of isooctyl and diisooctyl o-phosphoric acids. The neutral dioctadecyldimethylammonium salts of the mixed acid o-phosphates, i.e., dioctadecyldimethylammonium diisooctyl o-phosphate and bis-(dioctadecyldimethylammonium)isooctyl o-phosphate, were the predominant components of the active portion of the solution.

The 50 percent mineral oil solution produced in accordance with the above-described procedure had the following analysis:

Neutralization value	−13.11
Oxide ash	0.95
Percent nitrogen	0.94

Although the foregoing mixture of quaternary ammonium diisooctyl o-phosphates and bis-(quaternary ammonium)isooctyl o-phosphates is entirely suitable for the purposes of this invention, these two types of salts can be prepared and employed separately in fuel oils, if desired. This can best be accomplished by separating the isooctyl di-acid o-phosphate from the diisooctyl acid o-phosphate before neutralization with the quaternary ammonium hydroxide. Separation of the acid o-phosphates can be achieved, for example, by neutralizing the mixed acids with lime and by then extracting the neutralized mixture with a mineral oil solvent, e.g., a light lubricating oil. The extract will contain calcium diisooctyl o-phosphate, and the undissolved portion will contain calcium isooctyl o-phosphate. The respective acid o-phosphates can be regenerated from the thus separated salts by acidification with a mineral acid, e.g., hydrochloric acid, and by effecting separation of the acidified mixture on the basis of the preferential water-solubility of the excess mineral acid and the calcium salt thereof, and on the basis of the preferential solubility in organic solvents of the acid o-phosphates.

Example VI

A benzene solution of dicocoalkyldimethylammonium hydroxide is prepared from Arquad 2C using the same quantities, materials and procedure described in Example II. This mixture is then neutralized using approximately 376 grams (one combining mol) of a commercial ethyl oleyl acid o-phosphate manufactured by Victor Chemical Company and having a molecular weight of about 376, a phosphorus content, calculated as P_2O_5, of 19.1 percent, a specific gravity of 0.966, a refractive index at 25° C. of 1.4530 and a decomposition point of about 170° to 175° C. The neutralization point is determined by the use of litmus paper. The neutralized mixture is then diluted with about 880 grams of the lubricating oil diluent described in Example I. The benzene and water of neutralization are then distilled off at reduced pressure following the procedure described above. The remaining product is an approximately 50 percent mineral oil solution of dicocoalkyldimethylammonium ethyl oleyl o-phosphate, the principal component of the active portion being dilauryldimethylammonium ethyl oleyl o-phosphate.

The foregoing specific examples are illustrative of the salts whose use is included by this invention and the preparation thereof. Other quaternary ammonium salts whose use is included by the invention can be similarly prepared by substituting, in equivalent proportions, other suitable quaternary ammonium halides of the class herein indicated and other herein disclosed oil-soluble organic monocarboxylic acids, oil-soluble hydrocarbon-substituted monohydric phenols, and oil-soluble acid esters of o-phosphoric acid, for the corresponding reactants referred to in the foregoing embodiments.

The quaternary ammonium salts disclosed herein are useful when incorporated in blended distillate fuel oils in amounts sufficient to inhibit sludge deposition therefrom. The quaternary ammonium salts disclosed herein are especially useful in mixtures of straight run and catalytically cracked fuel oil distillates wherein the ratio of straight run to catalytically cracked components is between about 9:1 and about 1:9, and preferably between about 4:1 and about 1:4, since such mixtures exhibit especially severe sludge depositing tendencies. A reduction in the sludging tendencies of mixtures of straight run and catalytically cracked distillate fuel oils of the type described can usually be obtained by incorporation therein of as little as about 0.001 to about 0.005 percent by weight of the composition of the salts of this invention. Excellent reductions in the sludging tendencies of mixed catalytically cracked and straight run fuel oil distillates have been obtained by incorporation therein of amounts between about 0.005 and about 0.1 percent by weight of the composition of the salts of this invention. Although in some instances it can be advantageous to employ still larger amounts, e.g., up to about 1.0 percent by weight of the composition, of the salts of this invention, no additional advantage will ordinarily be obtained by the use of more than this amount. It will be understood that the optimum sludge-inhibiting concentration of the quaternary ammonium salt can vary to some extent with the character of individual fuel oils and with the character of individual quaternary ammonium salts.

The quaternary ammonium salts described herein can be incorporated in the blended distillate fuel oils in any suitable manner. For example, the desired quaternary ammonium salt can be added to either or both of the catalytically cracked or straight run oils prior to mixing of the two, or it may be added to the mixed oil. When a quaternary ammonium salt of this invention is incorporated in a mixed oil, it is unnecessary to do this immediately after mixing the oil, as the compounds are effective even after some sludge has formed. It will usually be preferable to add the compound prior to any sludge formation as this will normally produce the greatest reduction in sludge deposition. The quaternary ammonium

salts of this invention can be added to the blended fuel oils as such, but it is preferred to employ them in the form of concentrated solutions in an oil carrier. After addition, some circulation of the mixed oil is desirable to insure the early production of a uniform composition, but this is not absolutely necessary.

Specific examples of distillate fuel oils inhibited against sludge deposition by the quaternary ammonium salts of this invention are set forth below.

Example VII

A blended No. 2 fuel oil having severe sludging tendencies and consisting essentially of a 1:1:1 by volume mixture of a doctor sweetened West Texas straight run No. 2 fuel oil distillate, a South Louisiana straight run furnace oil boiling in the No. 2 range, and a fluid catalytically cracked light catalytic gas oil stock boiling in the No. 2 range was inhibited by incorporation therein of 0.02 weight percent of the 50 percent mineral oil solution of di-(hydrogenated tallow alkyl-)dimethylammonium naphthenate prepared according to Example I. The blended fuel oil used in this composition had the following characteristics.

Inspections:	
Gravity, ° API	33.5
Specific gravity	0.8576
Viscosity, SUS—	
70° F	37.9
100° F	34.5
Color, ASTM union	1½+
Pour point	−15
Flash point, open cup, ° F	168
Carbon residue on 10% bottoms, percent	0.38
Neutralization value	0.12
BS & W	Trace
Sulfur (lamp), percent	0.527
Bromine No	11.7
Olefins, percent	15.1
Aromatics, percent	21.9
Aniline point	129.0
Refractive index, n_D 20° C	1.4832
Ash oxide, percent	0.01
Distillation, ° F.—	
Initial	360
10%	416
50%	496
90%	580
End	630

Example VIII

Another fuel oil composition having reduced sludging tendencies is obtained by admixture of the uninhibited fuel oil blend of Example VII with 0.02 percent by weight of the composition of the mineral oil solution of dicocoalkyldimethylammonium oleate described in Example II.

Example IX

Another fuel oil composition having reduced sludging tendencies was obtained by admixture of the uninhibited fuel oil blend of Example VII with 0.02 percent by weight of the composition of the mineral oil solution of di-(hydrogenated tallow alkyl-)dimethylammonium p-tert-octylphenate described in Example III.

Example X

Another fuel oil composition having reduced sludging tendencies is obtained by admixture of the uninhibited fuel oil blend of Example VII with 0.02 percent by weight of the composition of the mineral oil solution of dicocoalkyldimethylammonium p-tert-amylphenate described in Example IV.

Example XI

Another fuel oil composition having reduced sludging tendencies was obtained by admixture of the uninhibited fuel oil blend of Example VII with 0.02 percent by weight of the composition of the mineral oil solution of mixed, substantially neutral di-(hydrogenated tallow alkyl-)dimethylammonium salts of isooctyl and diisooctyl o-phosphoric acids prepared according to Example V.

Example XII

Another fuel oil composition having reduced sludging tendencies is obtained by admixture of the uninhibited fuel oil blend of Example VII with 0.02 percent by weight of the composition of the mineral oil solution of di-cocoalkyldimethylammonium ethyl oleyl o-phosphate described in Example VI.

A "No. 2" oil is defined in "ASTM Standard on Petroleum Products and Lubricants," D396–48T. The "No. 2" indicates a distillate oil for general purpose domestic heating for use in burners not requiring a No. 1 fuel oil and having the following properties: flash point, ° F.—100 or legal (min.); pour point, ° F.—20 (max.); water and sediment, percent by volume—0.1 (max.); carbon residue, percent by weight—0.35 on 10% residuum; distillation temperature, ° F.—90% point, 675 (max.); viscosity, Saybolt Universal seconds at 100° F.—40 (max.); gravity, ° API—26 (min.); and max. sulfur content—1%.

The properties upon which the sludge inhibiting characteristics of the salts described herein depend appear to be shared by the entire class of salts disclosed herein. Accordingly, other suitable fuel oil compositions having reduced sludging tendencies can be obtained by substitution of other distillate fuel oils of the herein indicated kind and by substitution of other quaternary ammonium salts described herein, in the same or equivalent proportions, for the corresponding components in the foregoing specific embodiments. For example, good results can be obtained by incorporating into blended distillate fuel oils 0.02 weight percent, or more, of the dioctyldimethylammonium, the didodecyldiethylammonium, the dihexadecyldipropylammonium, and the dioctadecenyldimethylammonium salts of naphthenic, oleic, stearic, caprylic, and cyclohexylstearic acids, p-tert-amylphenol, p-sec-amylphenol, o-sec-amylphenol, o-tert-amylphenol, p-nonylphenol, cardanol, m-pentadecylphenol, 2,6-dimethyl-4-tert-butylphenol, 2-tert-amyl-4-methylphenol, 3-methyl-6-tert-butylphenol, 2-methyl-4,6-di-tert-butylphenol, 2,4-di-tert-butylphenol, diisooctyl o-phosphoric acid, isooctyl o-phosphoric acid, dilauryl o-phosphoric acid, dimyristyl o-phosphoric acid, dioleyl o-phosphoric acid, octyl o-phosphoric acid and ethyl lauryl o-phosphoric acid.

The usefulness of the herein disclosed quaternary ammonium salts as fuel oil sludge inhibitors has been demonstrated by means of a standard accelerated sludging test which is carried out by heating 600 gram samples of the fuel oil composition being tested for periods varying from 16 to 64 hours at 210° F. in loosely stoppered, one-quart clear glass bottles. Following each heating period each test sample is cooled to room temperature and filtered by suction through tared, medium porosity fritted glass Gooch-type crucibles. The sludge in each crucible is washed with heptane. Complete removal of the sludge adhering to the inside of the bottles is obtained by means of a rubber policeman and heptane. The respective crucibles are then dried in an oven maintained at 210° F. for 1 hour, cooled in a desiccator, and reweighed. The increase in weight is recorded as milligrams of sludge per 600 grams of oil. The effectiveness of an inhibitor can be judged by comparison of the sludge produced in inhibited and in uninhibited samples of the fuel oil.

Illustrative test results are presented below. In order to demonstrate more fully the unusual effectiveness of the herein disclosed quaternary ammonium salts, there are also presented in the table below the results obtained with blended fuel oil samples containing, respectively, the di-(hydrogenated tallow alkyl-)dimethyl-ammonium chloride of Example I, di-(hydrogenated tallow alkyl-)

dimethylammonium hydroxide, di-(hydrogenated tallow alkyl-)dimethylammonium sulfonate, and a widely accepted commercial fuel oil sludge inhibitor that is considered to consist essentially of a 50 percent solution in mineral oil of the neutral and/or basic barium salt of an alkylbenzene sulfonic acid wherein the $(CH_3):(CH_2)$ ratio in the alkyl portion of the material is about 1:16.

TABLE

Make-up: Percent by Wt.	1	2	3	4	5	6	7	8
Blended Fuel Oil of Example VII	100	99.98	99.98	99.98	99.99	99.99	99.98	99.96
Di-(hydrogenated tallow alkyl-)dimethylammonium Naphthenate of Example I (50% Mineral Oil Solution)		0.02						
Di-(hydrogenated tallow alkyl-)dimethylammonium Phenate of Example III (50% Mineral Oil Solution)			0.02					
Di-(hydrogenated tallow alkyl-)dimethylammonium Phosphate of Example V				0.02				
Di-(hydrogenated tallow alkyl-)dimethylammonium Chloride (75% Solution in Isopropanol)					0.01			
Di-(hydrogenated tallow alkyl-)dimethylammonium Hydroxide						0.01		
Di-(hydrogenated tallow alkyl-)dimethylammonium Salt of Oil-Soluble Alkylbenzene Sulfonic Acids (50% Mineral Oil Solution)							0.02	
Commercial Inhibitor (50% Mineral Oil Solution)								0.04
Inspections: Stability Test, 64 Hrs. at 210° F., Sludge: Mg./600 G	97	<1	1	1	57.6	57.3	17	74

The results shown in column 1 of the table indicate the sludging characteristics of an uninhibited, blended No. 2 fuel oil. The results presented in columns 2, 3 and 4 of the table show that a remarkable improvement in the sludge depositing characteristics of the fuel oil is obtained with quaternary ammonium salts of the kind included by this invention. The results presented in columns 5, 6, 7 and 8 of the table show the sludging properties of the fuel oil containing, respectively, the quaternary ammonium chloride, hydroxide, and sulfonate, and the commercial fuel oil sludge inhibitor previously referred to. Comparison of the various results indicates the outstanding qualities of the quaternary ammonium salts of this invention.

It is to be emphasized that the remarkable properties of the additives of this invention are attributable to the characteristics of both the covalent N-substituents and the ionic N-substituent. Thus, comparison of the results obtained for compositions 2, 3 and 4, with those obtained for compositions 5, 6 and 7 shows the importance of the nature of the ionic N-substituent.

Indicative of the importance of the character of the aliphatic hydrocarbon N-substituents of the quaternary ammonium salts whose use is included by the invention were the results of an experiment wherein 100 grams of a methanol solution containing 35 percent benzyltrimethylammonium hydroxide were neutralized with about 43.2 grams of p-tert-octylphenol to form benzyltrimethylammonium p-tert-octylphenate, a compound outside the scope of this invention. Approximately 78.2 grams of a solvent-treated lubricating oil, derived from a Mid-Continent crude and having a viscosity of about 450 S.U.S./100° F., were added to the mixture, and methanol and water were removed by distillation under vacuum. The product was a 50 percent mineral oil solution of benzyltrimethylammonium p-tert-octylphenate. On cooling, the mixture solidified. Additional lubricating oil was added to make a 10 percent mineral oil–90 percent phenate mixture, but the phenate failed to dissolve. Ten grams of the lubricating oil-phenate mixture were then added to 90 grams of benzene, but the phenate failed to dissolve. In view of its poor solubility, the benzyltrimethylammonium p-tert-octylphenate was unsuited for use as a fuel oil additive.

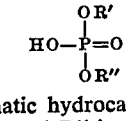
In addition to the sludging test indicated in the table the water separation properties of the various fuel oil compositions were determined according to Federal Specification VV–L–791d, Method FS 320.1.5 (modified), and were found to be relatively unimpaired for the fuel oil compositions of this invention.

If desired, the stable fuel oil compositions of this invention may contain, in addition to the additives disclosed herein, other improvement agents such as, for example, oxidation inhibitors, flash point control agents, corrosion inhibitors, anti-foam agents, ignition quality improvers, combustion improvers and other additives adapted to improve the oils in one or more respects.

It will be apparent to those skilled in the art that many modifications and variations of the herein disclosed invention may be resorted to without departing from the spirit thereof. Accordingly, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run distillate fuel oils tending to deposit sludge and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of a quaternary ammonium salt wherein two of the covalent N-bonds are attached to aliphatic hydrocarbon substituents containing 8 to 22 carbon atoms and the remaining covalent N-bonds are attached to saturated aliphatic hydrocarbon radicals containing 1 to 4 carbon atoms, and wherein the ionic N-bond is attached to an anionic salt-forming radical derived from a material selected from the group consisting of (*a*) oil-soluble organic monocarboxylic acids containing 7 to 30 carbon atoms per molecule, (*b*) oil-soluble monohydric phenols having attached to the aromatic nucleus one to three hydrocarbon substituents containing at least 4 carbon atoms, and having not more than one substituent in the ortho position that contains more than one carbon atom, and (*c*) oil-soluble acid esters of o-phosphoric acid having the general formula:



where R′ is an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms and R″ is a member selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms.

2. The fuel oil composition of claim 1 wherein said small amount is about 0.001 to about 1.0 percent by weight of the composition.

3. The fuel oil composition of claim 1 wherein said small amount is about 0.005 to about 0.1 percent by weight of the composition.

4. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight

run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of dioctadecyldimethylammonium naphthenate.

5. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of di-(hydrogenated tallow alkyl-)dimethylammonium naphthenate.

6. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of dioctadecyldimethylammonium p-tert-octylphenate.

7. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of di-(hydrogenated tallow alkyl-)dimethylammonium p-tert-octylphenate.

8. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of dioctadecyldimethylammonium diisooctyl o-phosphate.

9. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of bis-(dioctadecyldimethylammonium)isooctyl o-phosphate.

10. A fuel oil composition comprising a major proportion of a mixture of catalytically cracked and straight run fuel oil distillates tending to deposit sludge, and a small amount, sufficient to inhibit deposition of sludge from said mixture of oils, of the mixed neutral di-(hydrogenated tallow alkyl-)dimethylammonium salts of isooctyl and diisooctyl o-phosphoric acids.

References Cited in the file of this patent

UNITED STATES PATENTS

2,295,773	Chenicek	Sept. 15, 1942
2,344,886	Lieber	Mar. 21, 1944
2,422,658	Coleman et al.	June 24, 1947
2,487,189	Smith et al.	Nov. 8, 1949
2,487,190	Smith et al.	Nov. 8, 1949
2,516,913	Revukas	Aug. 1, 1950
2,541,816	Glarum et al.	Feb. 13, 1951
2,550,981	Eberz	May 1, 1951
2,563,506	Werntz	Aug. 7, 1951
2,590,815	Dosser et al.	Mar. 25, 1952
2,633,415	Chenicek	Mar. 31, 1953
2,743,294	Fakstorp	Apr. 24, 1956
2,819,954	Gebelein et al.	Jan. 14, 1958

FOREIGN PATENTS

356,717	Great Britain	Sept. 7, 1931